PHYSICAL CHEMISTRY

THIRD EDITION

ROBERT G. MORTIMER

Physical Chemistry

Third Edition

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Robert G. Mortimer
Professor Emeritus
Rhodes College
Memphis, Tennessee

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To my wife, Ann,
and to my late father, William E. Mortimer,
who was responsible for my taking my first chemistry course

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Preface

This is the third edition of a physical chemistry textbook designed for a two-semester undergraduate physical chemistry course. The physical chemistry course is often the first opportunity that a student has to synthesize descriptive, theoretical, and mathematical knowledge about chemistry into a coherent whole. To facilitate this synthesis, the book is constructed about the idea of defining a system, studying the states in which it might be found, and analyzing the processes by which it can change its state.

The book is divided into four parts. The first part focuses on the macroscopic properties of physical systems. It begins with the descriptive study of gases and liquids, and proceeds to the study of thermodynamics, which is a comprehensive macroscopic theory of the behavior of material systems. The second part focuses on dynamics, including gas kinetic theory, transport processes, and chemical reaction kinetics. The third part presents quantum mechanics and spectroscopy. The fourth part presents the relationship between molecular and macroscopic properties of systems through the study of statistical mechanics. This theory is applied to the structure of condensed phases. The book is designed so that the first three parts can be studied in any order, while the fourth part is designed to be a capstone in which the other parts are integrated into a cohesive whole.

In addition to the standard tables of integrals and numerical values of various properties, the book contains several appendices that expand on discussions in the body of the text, such as more detailed discussions of perturbation theory, group theory, and several mathematical topics. Each chapter begins with a statement of the principal facts and ideas that are presented in the chapter. There is a summary at the end of each chapter to assist in synthesizing the material of each chapter into a coherent whole. There are also marginal notes throughout the chapters that present biographical information and some comments. Each chapter contains examples that illustrate various kinds of calculations, as well as exercises placed within the chapter. Both these exercises and the problems at the end of each section are designed to provide practice in applying techniques and insights obtained through study of the chapter.

Answers to all of the numerical exercises and to the odd-numbered numerical problems are placed in Appendix K. A solutions manual, with complete solutions to all exercises and all odd-numbered problems, is available from the publisher. An instructor's manual with solutions to the even-numbered problems is available on-line to instructors. The instructor can choose whether to allow students to have access to the solutions manual, but can assign even-numbered problems when he or she wants the students to work problems without access to solutions.

The author encourages students and instructors to comment on any part of the book; please send comments and suggestions to the author's attention.

Robert G. Mortimer
2769 Mercury St.
Bartlett, TN 38134, USA

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It has been my pleasure to have studied with many dedicated and proficient teachers, and I acknowledge their influence, example, and inspiration. I am also grateful for the privilege of working with students, whose efforts to understand the workings of the physical universe make teaching the most desirable of all professions.

I have benefited from the expert advice of many reviewers. These include:

Jonas Goldsmith	Bryn Mawr College
Jason D. Hofstein	Sienna College
Daniel Lawson	University of Michigan–Dearborn
Jennifer Mihalick	University of Wisconsin–Oshkosh
Cynthia M. Woodbridge	Hillsdale College

and the reviewers of the previous editions. All of these reviewers gave sound advice, and some of them went beyond the call of duty in searching out errors and unclarities and in suggesting remedies. The errors that remain are my responsibility, not theirs.

I wish to thank the editorial staff of Elsevier/Academic Press for their guidance and help during a rather long and complicated project, and also wish to thank Erica Ellison, who was a valuable consultant. I thank my wife, Ann, for her patience, love, and support during this project.

1

Thermodynamics and the Macroscopic Description of Physical Systems

1

The Behavior of Gases and Liquids

PRINCIPAL FACTS AND IDEAS

1. The principal goal of physical chemistry is to understand the properties and behavior of material systems and to apply this understanding in useful ways.
2. The state of a system is specified by giving the values of a certain number of independent variables (state variables).
3. In an equilibrium one-phase fluid system of one substance, three macroscopic variables such as temperature, volume, and amount of substance can be independent variables and can be used to specify the macroscopic equilibrium state of the system. At least one of the variables used to specify the state of the system must be proportional to the size of the system (be extensive). Other macroscopic variables are mathematical functions of the independent variables.
4. The intensive state, which includes only intensive variables (variables that are independent of the size of the system), is specified by only two variables in the case of an equilibrium one-phase fluid system of one substance.
5. Nonideal gases and liquids are described mathematically by various equations of state.
6. The coexistence of phases can be described mathematically.
7. The liquid–gas coexistence curve terminates at the critical point, beyond which there is no distinction between liquid and gas phases.
8. The law of corresponding states asserts that in terms of reduced variables, all substances obey the same equation of state.

1.1 Introduction

This book is a textbook for a standard two-semester physical chemistry course at the undergraduate level. Physical chemistry involves both physics and chemistry. Physics has been defined as the study of the properties of matter that are shared by all substances, whereas chemistry has been defined as the study of the properties of individual substances. Chemistry grew out of the ancient occult art of alchemy, which involved among other things the attempted transmutation of cheaper materials into gold. Chemistry began as a completely experimental science. Substances were named and studied without reference to their molecular structures. Sulfuric acid was called "oil of vitriol," and chemists memorized the fact that when copper was treated with oil of vitriol a solution of "blue vitriol" (now known as copper(II) sulfate) resulted. In the late 18th century, Lavoisier established the law of conservation of mass in chemical reactions, and Proust established the law of definite proportion. In order to explain these laws, Dalton proposed his atomic theory in 1803, as well as announcing the law of multiple proportions. With this theory, chemistry could evolve into a molecular science, with properties of substances tied to their molecular structures.

Antoine Laurent Lavoisier, 1743–1794, was a great French chemist who was called the "father of modern chemistry" because of his discovery of the law of conservation of mass. He was beheaded during the French Revolution because of his involvement in his father-in-law's firm, which was employed by the royal government to collect taxes. It is said that he arranged with a friend to observe his head to see how long he could blink his eyes after his head was severed. He blinked for 15 seconds.

Joseph Proust, 1754–1826, was a French chemist who was the first to isolate sugar from grapes.

John Dalton, 1766–1844, was an English schoolmaster and chemist. After he became a famous chemist, he continued to teach at what we would now call the elementary school level.

Systems

We call any object that we wish to study our *system*. A large system containing many atoms or molecules is called a *macroscopic system*, and a system consisting of a single atom or molecule is called a *microscopic system*. We consider two principal types of properties of systems. *Macroscopic properties* such as temperature and pressure apply only to a macroscopic system and are properties of the whole system. They can be observed and studied without reference to the molecular nature of matter. *Microscopic properties* such as kinetic energy and momentum are mechanical in nature. They apply to either macroscopic or microscopic systems.

The study of macroscopic properties involves thermodynamics, which is the major topic of this volume, along with gas kinetic theory, transport processes, and reaction kinetics. Quantum mechanics, spectroscopy, and statistical mechanics are molecular topics and are discussed in Parts 3 and 4 of this textbook.

Mathematics in Physical Chemistry

Galileo Galilei, 1564–1642, was a great Italian mathematician and physicist. He refuted the assertion of Aristotle that a heavier object should fall faster than a lighter one and is said to have dropped two balls of different masses from the leaning tower of Pisa to demonstrate that they fell at the same rate. He supported the hypothesis of Copernicus that the earth revolves around the sun and was convicted of heresy in 1633 by the Roman Catholic Church for this belief. He spent the rest of his life under house arrest.

The study of any physical chemistry topics requires mathematics. Galileo once wrote, "The book of nature is written in the language of mathematics." We will use mathematics in two different ways. First, we will use it to describe the behavior of systems without explaining the origin of the behavior. Second, we will use it to develop theories that explain why certain behaviors occur. This chapter is an example of the first usage, and the next chapter is an example of the second usage.

Much of the mathematical education that physical chemistry students have received has focused on mathematical theory rather than on practical applications. A student who was unable to apply an elementary calculus technique once said to the author, "I know that was in the calculus course, but nobody told me that I would ever have to use it." Mathematical theory is not always important in physical chemistry, but you need to be able to apply mathematical methods. There are several books that cover the application of mathematics to problems in physical chemistry.[1]

Arithmetic is the principal branch of *numerical mathematics*. It involves carrying out operations such as addition, subtraction, multiplication, and division on actual numbers. Geometry, algebra, and calculus are parts of *symbolic mathematics*, in which symbols that represent numerical quantities and operations are manipulated without doing the numerical operations. Both kinds of mathematics are applied in physical chemistry.

Mathematical Functions

A mathematical function involves two kinds of variables: An *independent variable* is one to which we can assign a value. A *mathematical function* is a rule that delivers the value of a *dependent variable* when values are assigned to the independent variable or variables. A function can be represented by a formula, a graph, a table, a mathematical series, and so on. Consider the *ideal gas law*:

$$PV = nRT \tag{1.1-1}$$

In this equation P represents the pressure of the gas, V represents its volume, n represents the amount of substance in moles, T represents the absolute temperature, and R stands for the *ideal gas constant*. The ideal gas law does a good but not perfect job of representing the equilibrium behavior of real gases under ordinary conditions. It is more nearly obeyed if the pressure of the gas is made smaller. A gas that is at a sufficiently low pressure that it obeys the ideal gas law to an adequate approximation is called a *dilute gas*. An *ideal gas* is defined to obey this equation for all pressures and temperatures. An ideal gas does not exist in the real world, and we call it a *model system*. A model system is an imaginary system designed to resemble some real system. A model system is useful only if its behavior mimics that of a real system to a useful degree and if it can be more easily analyzed than the real system.

We can solve the ideal gas law for V by symbolically dividing by P:

$$V = \frac{nRT}{P} \tag{1.1-2}$$

The right-hand side of Eq. (1.1-2) is a formula that represents a mathematical function. The variables T, P, and n are independent variables, and V is the dependent variable. If you have the numerical values of T, P, and n, you can now carry out the indicated arithmetic operations to find the value of V. We can also solve Eq. (1.1-1) for P by symbolically dividing by V:

$$P = \frac{nRT}{V} \tag{1.1-3}$$

We have now reassigned V to be one of the independent variables and P to be the dependent variable. This illustrates a general fact: *If you have an equation containing*

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[1] Robert G. Mortimer, *Mathematics for Physical Chemistry*, 3rd ed., Academic Press, San Diego, CA, U.S.A., 2005; James R. Barrante, *Applied Mathematics for Physical Chemistry*, 3rd ed., Pearson Prentice Hall, Upper Saddle River, NJ, 2004; Donald A. McQuarrie, *Mathematical Methods for Scientists and Engineers*, University Science Books, 2003.

several variables, you can manipulate the equation symbolically to turn any one of them into the dependent variable.

The ideal gas law might not be accurate enough for some gases under some conditions. If so, we can find some other function that will give the value of the pressure to greater accuracy. It is an experimental fact that the pressure of a gas or liquid of one substance at equilibrium is given by a function that depends on only three independent variables. We represent such a function by

$$P = P(T, V, n) \tag{1.1-4}$$

A mathematician would write $P = f(T, V, n)$ for the functional relation in Eq. (1.1-4), using the letter P for the variable and the letter f for the function. Chemists have too many variables to use two letters for each variable, so we use the same letter for the variable and the function. A functional relation that relates P, V, T, and n for a gas or a liquid at equilibrium is called an *equation of state* and is said to represent the *volumetric behavior* of the gas or liquid. We will introduce several equations of state later in this chapter.

EXAMPLE 1.1

Assume that the volume of a liquid is a linearly decreasing function of P, is a linearly increasing function of T, and is proportional to n. Write a formula expressing this functional relationship.

Solution

Let V_0 represent the volume at some reference temperature T_0, some reference pressure P_0, and some reference amount of substance n_0.

$$V = V_0 \frac{n}{n_0} [1 - k(P - P_0) + a(T - T_0)] = nV_{m0} [1 - k(P - P_0) + a(T - T_0)]$$

where k and a are constants and where V_m represents the molar volume, equal to V/n, and V_{m0} represents V_0/n_0.

A two-dimensional graph can represent a function of one independent variable. You plot the value of the independent variable on the horizontal axis and represent the value of the dependent variable by the height of a curve in the graph. To make a two-dimensional graph that represents the ideal gas law, we must keep two of the three independent variables fixed. Figure 1.1a shows a set of graphical curves that represent the dependence of P on V for an ideal gas for $n = 1.000$ mol and for several fixed values of T.

A three-dimensional graph can represent a function of two independent variables. Figure 1.1b shows a perspective view of a graphical surface in three dimensions that represents the dependence of P on V and T for an ideal gas with a fixed value of n (1.000 mol). Just as the height of a curve in Figure 1.1a gives the value of P for a particular value of V, the height of the surface in Figure 1.1b gives the value of P for a particular value of T and a particular value of V. Such graphs are not very useful for numerical purposes, but help in visualizing the general behavior of a function of two independent variables.

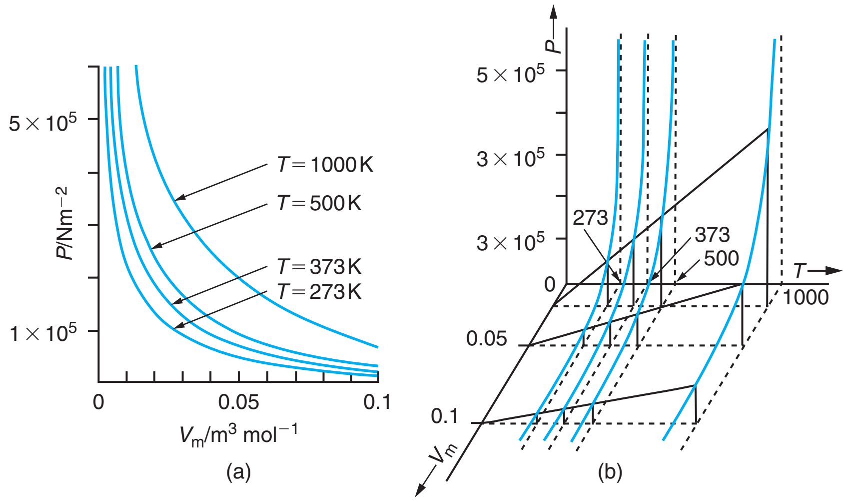

Figure 1.1 (a) The pressure of an ideal gas as a function of V at constant n and various constant values of T. (b) The pressure of an ideal gas as a function of V and T at constant n.

A function can also be represented by a table of values. For a function of one independent variable, a set of values of the independent variable is placed in one column. The value of the dependent variable corresponding to each value of the independent variable is placed in another column on the same line. A mathematician would say that we have a set of ordered pairs of numbers. Prior to the advent of electronic calculators, such tables were used to represent logarithms and trigonometric functions. Such a table provides values only for a finite number of values of the independent variable, but interpolation between these values can be used to obtain other values.

Units of Measurement

The values of most physical variables consist of two parts, a number and a unit of measurement. Various units of measurement exist. For example, the same distance could be expressed as 1.000 mile, 1609 meters, 1.609 kilometer, 5280 feet, 63360 inches, 1760 yards, 106.7 rods, 8.000 furlongs, and so on. A given mass could be expressed as 1.000 kilogram, 1000 grams, 2.205 pounds, 0.1575 stone, 195.3 ounces, and so on. There are sets of units that are consistent with each other. For example, pounds are used with feet, kilograms are used with meters, and grams are used with centimeters. Here is an important fact: *To carry out any numerical calculation correctly you must express all variables with consistent units*. If any quantities are expressed in inconsistent units, you will almost certainly get the wrong answer. In September 1999, a space probe optimistically named the "Mars Climate Orbiter" crashed into the surface of Mars instead of orbiting that planet. The problem turned out to be that some engineers had used "English" units such as feet and pounds, while physicists working on the same project had used metric units such as meters and kilograms. Their failure to convert units correctly caused the loss of a space vehicle that cost many millions of U.S. dollars. In another instance, when a Canadian airline converted from English units to metric units, a ground crew that was accustomed to English units incorrectly calculated how much fuel in kilograms to put into an airliner for a certain flight. The airplane ran out of fuel before reaching its destination. Fortunately, the pilot was able to glide to a former military air field and make a “deadstick” landing on an unused runway. Some people who were having a picnic on the runway were fortunately able to get out of the way in time. There was even a movie made about this incident.

The official set of units that physicists and chemists use is the *International System of Units*, or *SI units.* The letters SI stand for *Systeme Internationale*, the French name for the set of units. In this system there are seven *base units*. The unit of length is the *meter* (m). The unit of mass is the *kilogram* (kg). The unit of time is the *second* (s). The unit of temperature is the *kelvin* (K). The unit of electric current is the *ampere* (A). The unit of luminous intensity is the *candela* (cd). The unit for the amount of a substance is the *mole* (mol). The SI units are called *MKS* (meter-kilogram-second) units. Prior to 1961, most chemists and some physicists used *cgs* (centimeter-gram-second) units, but we now use SI units to avoid confusion.

The newton is named for Sir Isaac Newton, 1642–1727, the great English mathematician and physicist who invented classical mechanics and who was one of the inventors of calculus.

The pascal is named for Blaise Pascal, 1623–1662, a famous French philosopher, theologian, and mathematician.

In addition to the seven base units, there are a number of *derived units*. The *newton* (N) is the SI unit of force:

$$\boxed{1\ \mathrm{N} = 1\ \mathrm{kg\,m\,s^{-2}} \quad \text{(definition)}} \tag{1.1-5}$$

The *pascal* (Pa) is the SI unit of pressure (force per unit area):

$$\boxed{1\ \mathrm{Pa} = 1\ \mathrm{N\,m^{-2}} = 1\ \mathrm{kg\ m^{-1}\ s^{-2}} \quad \text{(definition)}} \tag{1.1-6}$$

We have enclosed these defining equations in boxes, and will enclose the most important equations in boxes throughout the rest of the book.

The joule is named for James Prescott Joule, 1818–1889, a great English physicist who pioneered in the thermodynamic study of work, heat, and energy in a laboratory that he constructed in his family’s brewery.

A force exerted through a distance is equivalent to an amount of work, which is a form of energy. The SI unit of energy is the *joule* (J):

$$\boxed{1\ \mathrm{J} = 1\ \mathrm{N\ m} = 1\ \mathrm{kg\ m^2\ s^{-2}} \quad \text{(definition)}} \tag{1.1-7}$$

Multiples and submultiples of *SI* units are indicated by prefixes, such as “milli” for 1/1000, “centi” for 1/100, “deci” for 1/10, “kilo” for 1000, and so on. These prefixes are listed inside the cover of this book. We do not use double prefixes such as millikilogram for the gram or microkilogram for the milligram.

We will also use some non-SI units. The *calorie* (cal), which was originally defined as the amount of heat required to raise the temperature of 1 gram of water by 1°C, is now defined by:

$$\boxed{1\ \mathrm{cal} = 4.184\ \mathrm{J} \quad \text{(exactly, by definition)}} \tag{1.1-8}$$

We will use several non-SI units of pressure; the *atmosphere* (atm), the *torr*, and the *bar*.

$$\boxed{1\ \mathrm{atm} = 101325\ \mathrm{Pa} \quad \text{(exactly, by definition)}} \tag{1.1-9}$$

$$\boxed{760\ \mathrm{torr} = 1\ \mathrm{atm} \quad \text{(exactly, by definition)}} \tag{1.1-10}$$

$$\boxed{1\ \mathrm{bar} = 100000\ \mathrm{Pa} \quad \text{(exactly, by definition)}} \tag{1.1-11}$$

The angstrom (Å, equal to 10^{-10} m or 10^{-8} cm) has been a favorite unit of length among chemists, because it is roughly equal to a typical atomic radius. Picometers are nearly as convenient, with 100 pm equal to 1 Å. Chemists are also reluctant to abandon the *liter* (L), which is the same as 0.001 $\mathrm{m^3}$ or 1 $\mathrm{dm^3}$ (cubic decimeter).

The Mole and Avogadro’s Constant

Lorenzo Romano Amadeo Carlo Avogadro, 1776–1856, was an Italian lawyer and professor of natural philosophy. He was the first to postulate that equal volumes of gases under the same conditions contained the same number of molecules.

The *formula unit* of a substance is the smallest amount of a substance that retains the identity of that substance. It can be an atom, a molecule, or an electrically neutral set of ions. A *mole* of any substance is an amount with the same number of formula units as the number of atoms contained in exactly 0.012 kg of the ^{12}C (carbon-12) isotope. The *atomic mass unit* (amu or u) is defined such that one atom of ^{12}C has a mass of exactly 12 amu. Therefore the mass of a mole of any substance expressed in grams is numerically equal to the mass of a formula unit expressed in atomic mass units.

The number of formula units, N, in a sample of any substance is proportional to the *amount of substance* measured in moles, denoted by n:

$$N = N_{\mathrm{Av}}n \tag{1.1-12}$$

Josef Loschmidt, 1821–1895, was an Austrian chemist who made various contributions, including being the first to propose using two line segments to represent a double bond and three line segments to represent a triple bond.

The proportionality constant N_{Av} is called *Avogadro’s constant* in some countries and *Loschmidt’s constant* in others. It is known from experiment to have the value

$$N_{\mathrm{Av}} = 6.02214 \times 10^{23}\ \mathrm{mol}^{-1} \tag{1.1-13}$$

The ideal gas equation can be written in terms of the number of molecules, N:

$$V = \frac{nRT}{P} = \frac{nN_{\mathrm{Av}}k_{\mathrm{B}}T}{P} = \frac{Nk_{\mathrm{B}}T}{p} \tag{1.1-14}$$

Boltzmann’s constant is named for Ludwig Boltzmann, 1844–1906, an Austrian physicist who was one of the inventors of gas kinetic theory and statistical mechanics.

The *ideal gas constant* R is known from experiment to have the value 8.3145 J K^{-1} mol^{-1}. In common non-SI units, it is equal to 0.082058 L atm K^{-1} mol^{-1}. The constant k_{B} is called *Boltzmann’s constant*:

$$k_{\mathrm{B}} = \frac{R}{N_{\mathrm{Av}}} = \frac{8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}}{6.02214 \times 10^{23}\ \mathrm{mol}^{-1}} = 1.3807 \times 10^{-23}\ \mathrm{J\ K^{-1}} \tag{1.1-15}$$

Problem Solving Techniques

If you have a home repair or automotive repair to do, the work will go better if you have the necessary tools at hand when you start the job. The same thing is true for physical chemistry problems. You should analyze the problem and make sure that you know what formulas and techniques are needed and make sure that you have them at hand. Think of your supply of formulas and techniques as your tools, and try to keep your toolbox organized.

One of the most important things in problem solving is that you must use consistent units in any numerical calculation. The conversion to consistent units is conveniently done by the *factor-label method*, which is a straightforward use of proportionality factors. It is illustrated in the following example, and you can review this method in almost any general chemistry textbook.

EXAMPLE 1.2

Find the pressure in Pa and in atm of 20.00 g of neon gas (assumed to be ideal) at a temperature of 0.00°C and a volume of 22.400 L.

Solution

The Celsius temperature differs from the absolute temperature by 273.15 K, but the Celsius degree is the same size as the kelvin.

$$T = 273.15\ \mathrm{K} + 0.00^\circ\mathrm{C} = 273.15\ \mathrm{K}$$

We convert amount of gas to moles and the volume to m^3 using the factor-label method:

$$n = (20.00\ \mathrm{g})\left(\frac{1\ \mathrm{mol}}{20.179\ \mathrm{g}}\right) = 0.9911\ \mathrm{mol}$$
$$V = (22.400\ \mathrm{L})\left(\frac{1\ \mathrm{m}^3}{1000\ \mathrm{L}}\right) = 0.022400\ \mathrm{m}^3$$

We now carry out the numerical calculation:

$$\begin{aligned} P &= \frac{nRT}{V} = \frac{(0.9911\ \mathrm{mol})\left(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}\right)(273.15\ \mathrm{K})}{\left(0.022400\ \mathrm{m}^3\right)} \\ &= 1.005 \times 10^5\ \mathrm{J\ m^{-3}} = 1.005 \times 10^5\ \mathrm{N\ m^{-2}} = 1.005 \times 10^5\ \mathrm{Pa} \end{aligned}$$

You can see how the symbolic formula is used as a template for setting up the numerical calculation. The unit conversions can also be included in a single calculation:

$$\begin{aligned} P &= \frac{(20.00\ \mathrm{g})\left(8.314\ \mathrm{J\ K^{-1}\ mol^{-1}}\right)(273.15\ \mathrm{K})}{(22.400\ \mathrm{L})}\left(\frac{1\ \mathrm{mol}}{20.179\ \mathrm{g}}\right)\left(\frac{1000\ \mathrm{L}}{1\ \mathrm{m}^3}\right) \\ &= 1.005 \times 10^5\ \mathrm{J\ m^{-3}} = 1.005 \times 10^5\ \mathrm{N\ m^2} = 1.005 \times 10^5\ \mathrm{Pa} \end{aligned}$$

The pressure can be expressed in atmospheres by another conversion:

$$P = (1.005 \times 10^5\ \mathrm{Pa})\left(\frac{1\ \mathrm{atm}}{101325\ \mathrm{Pa}}\right) = 0.9919\ \mathrm{atm}$$

A calculator displayed 100,486.28725 Pa for the pressure in the previous example. The answer was then rounded to four digits to display only *significant digits*. In carrying out operations with a calculator, it is advisable to carry insignificant digits in intermediate steps in order to avoid round-off error and then to round off insignificant digits in the final answer. You can review significant digits in any elementary chemistry textbook. The main idea is that if the calculation produces digits that are probably incorrect, they are insignificant digits and should be rounded away. An important rule is that in a set of multiplications and divisions, the result generally has as many significant digits as the factor or divisor with the fewest significant digits.

Another important technique in problem solving is to figure out roughly how large your answer should be and what its units should be. For example, the author had a student under time pressure in an examination come up with an answer of roughly 10^{30} cm for a molecular dimension. A moment's thought should have revealed that this distance is greater than the size of the known universe and cannot be correct. Many common mistakes produce an answer that either has the wrong units or is obviously too large or too small, and you can spot these errors if you look for them. You should always write the units on every factor or divisor when setting up a numerical calculation so that you will be more likely to spot an error in units.

EXAMPLE 1.3

The speed of sound in dry air at a density of $1.293\,\text{g L}^{-1}$ and a temperature of 0°C is $331.45\ \text{m s}^{-1}$. Convert this speed to miles per hour.

Solution

$$(331.45\ \text{m s}^{-1})\left(\frac{1\ \text{in}}{0.0254\ \text{m}}\right)\left(\frac{1\ \text{ft}}{12\ \text{in}}\right)\left(\frac{1\ \text{mile}}{5280\ \text{ft}}\right)\left(\frac{3600\ \text{s}}{1\ \text{hour}}\right) = 741.43\ \text{miles hour}^{-1}$$

Note that the conversion ratios do not limit the number of significant digits because they are defined to be exact values.

Exercise 1.1

a. Express the value of the ideal gas constant in $\text{cm}^3\ \text{bar K}^{-1}\ \text{mol}^{-1}$. Report only significant digits.

b. Find the volume of 2.000 mol of helium (assume ideal) at a temperature of 298.15 K and a pressure of 0.500 atm.

c. Find the pressure of a sample of 2.000 mol of helium (assume ideal) at a volume of 20.00 L and a temperature of 500.0 K. Express your answer in terms of Pa, bar, atm, and torr.

PROBLEMS

Section 1.1: Introduction

1.1 Express the speed of light in furlongs per fortnight. A furlong is 1/8 mile, and a fortnight is 14 days.

1.2 In the "cgs" system, lengths are measured in centimeters, masses are measured in grams, and time is measured in seconds. The cgs unit of energy is the erg and the cgs unit of force is the dyne.

a. Find the conversion factor between ergs and joules.

b. Find the conversion factor between dynes and newtons.

c. Find the acceleration due to gravity at the earth's surface in cgs units.

1.3 In one English system of units, lengths are measured in feet, masses are measured in pounds, abbreviated lb (1 lb = 0.4536 kg), and time is measured in seconds. The absolute temperature scale is the Rankine scale, such that 1.8° R corresponds to 1°C and to 1 K.

a. Find the acceleration due to gravity at the earth's surface in English units.

b. If the pound is a unit of mass, then the unit of force is called the poundal. Calculate the value of the ideal gas constant in ft poundals $(°\text{R})^{-1}\ \text{mol}^{-1}$.

c. In another English system of units, the pound is a unit of force, equal to the gravitational force at the earth's surface, and the unit of mass is the slug. Find the acceleration due to gravity at the earth's surface in this set of units.

1.4 A light-year is the distance traveled by light in one year.

a. Express the light-year in meters and in kilometers.

b. Express the light-year in miles.

c. If the size of the known universe is estimated to be 20 billion light-years (2×10^{10} light-years) estimate the size of the known universe in miles.

d. If the closest star other than the sun is at a distance of 4 light-years, express this distance in kilometers and in miles.

e. The mean distance of the earth from the sun is 149,599,000 km. Express this distance in light-years.

1.5 The parsec is a distance used in astronomy, defined to be a distance from the sun such that "the heliocentric parallax is 1 second of arc." This means that the direction of observation of an object from the sun differs from the direction of observation from the earth by one second of arc.

a. Find the value of 1 parsec in kilometers. Do this by constructing a right triangle with one side equal to 1 parsec and the other side equal to 1.49599×10^8 km, the distance from the earth to the sun. Make the angle opposite the short side equal to 1 second of arc.

b. Find the value of 1 parsec in light-years.

c. Express the distance from the earth to the sun in parsec.

1.6 Making rough estimates of quantities is sometimes a useful skill.

a. Estimate the number of grains of sand on all of the beaches of all continents on the earth, excluding islands. Do this by making suitable estimates of: (1) the average width of a beach; (2) the average depth of sand on a beach; (3) the length of the coastlines of all of the continents; (4) the average size of a grain of sand.

b. Express your estimate in terms of moles of grains of sand, where a mole of grains of sand is 6.02214×10^{23} grains of sand.

1.7 Estimate the number of piano tuners in Chicago (or any other large city of your choice). Do this by estimating: (1) the number of houses, apartments, and other buildings in the city; (2) the fraction of buildings containing a piano; (3) the average frequency of tuning; (4) how many pianos a piano tuner can tune in 1 week.

1.8 Estimate the volume of the oceans of the earth in liters. Use the fact that the oceans cover about 71% of the earth's area and estimate the average depth of the oceans. The greatest depth of the ocean is about 7 miles, slightly greater than the altitude of the highest mountain on the earth.

1.9 Find the volume of CO_2 gas produced from 100.0 g of $CaCO_3$ if the CO_2 is at a pressure of 746 torr and a temperature of 301.0 K. Assume the gas to be ideal.

1.10 According to Dalton's law of partial pressures, the pressure of a mixture of ideal gases is the sum of the partial pressures of the gases. The partial pressure of a gas is defined to be the pressure that would be exerted if that gas were alone in the volume occupied by the gas mixture.

a. A sample of oxygen gas is collected over water at 25°C at a total pressure of 748.5 torr, with a partial pressure of water vapor equal to 23.8 torr. If the volume of the collected gas is equal to 454 mL, find the mass of the oxygen. Assume the gas to be ideal.

b. If the oxygen were produced by the decomposition of $KClO_3$, find the mass of $KClO_3$.

1.11 The relative humidity is defined as the ratio of the partial pressure of water vapor to the pressure of water vapor at equilibrium with the liquid at the same temperature. The equilibrium pressure of water vapor at 25°C is 23.756 torr. If the relative humidity is 49%, estimate the amount of water vapor in moles contained in a room that is 8.0 m by 8.0 m and 3.0 m in height. Calculate the mass of the water.

1.12 Assume that the atmosphere is at equilibrium at 25°C with a relative humidity of 100% and assume that the barometric pressure at sea level is 1.00 atm. Estimate the total rainfall depth that could occur if all of this moisture is removed from the air above a certain area of the earth.

1.2 Systems and States in Physical Chemistry

Figure 1.2 depicts a typical macroscopic system, a sample of a single gaseous substance that is contained in a cylinder with a movable piston. The cylinder is immersed in a constant-temperature bath that can regulate the temperature of the system. The volume of the system can be adjusted by moving the piston. There is a valve between the cylinder and a hose that leads to the atmosphere or to a tank of gas. When the valve is closed so that no matter can pass into or out of the system, the system is called a *closed system*. When the valve is open so that matter can be added to or removed from the system, it is called an *open system*. If the system were insulated from the rest of the universe so that no heat could pass into or out of the system, it would be called an *adiabatic system* and any process that it undergoes would be called an *adiabatic*

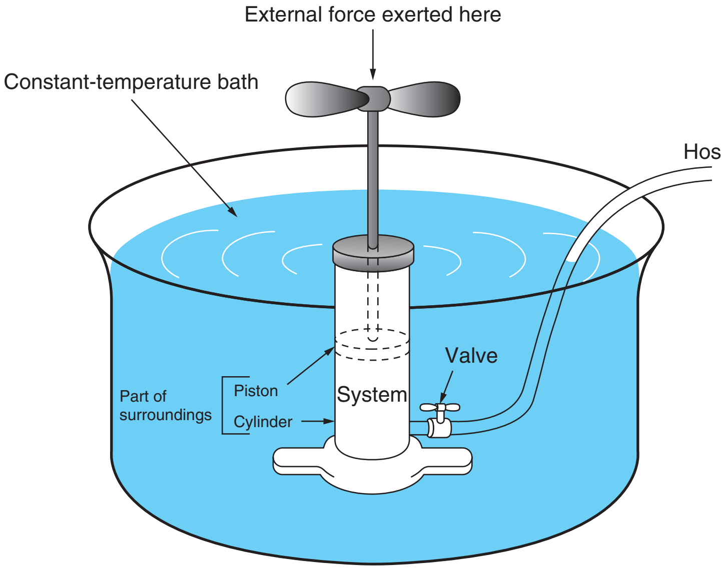

Figure 1.2 A Typical Fluid System Contained in a Cylinder with Variable Volume.

process. If the system were completely separated from the rest of the universe so that no heat, work, or matter could be transferred to or from the system, it would be called an *isolated system*.

The portion of the universe that is outside of the system is called the *surroundings*. We must specify exactly what parts of the universe are included in the system. In this case we define the system to consist only of the gas. The cylinder, piston, and constant-temperature bath are parts of the surroundings.

The State of a System

Specifying the *state of a system* means describing the condition of the system by giving the values of a sufficient set of numerical variables. We have already asserted that for an equilibrium one-phase liquid or gaseous system of one substance, the pressure is a function of three independent variables. We now assert as an experimental fact *that for any equilibrium one-phase fluid system (gas or liquid system) of one substance, there are only three macroscopic independent variables, at least one of which must be proportional to the size of the system.* All other equilibrium macroscopic variables are dependent variables, with values given as functions of the independent variables. We say that *three independent variables specify the equilibrium macroscopic state of a gas or liquid of one substance.* We can generally choose which three independent variables to use so long as one is proportional to the size of the system. For fluid system of one substance, we could choose T, V, and n to specify the equilibrium state. We could also choose T, P, and n, or we could choose T, P, and V.

All other equilibrium macroscopic variables must be dependent variables that are functions of the variables chosen to specify the state of the system. We call both the independent variables and the dependent variables *state functions* or *state variables*. There are two principal classes of macroscopic variables. *Extensive variables* are proportional to the size of the system if P and T are constant, whereas *intensive variables* are independent of the size of the system if P and T are constant. For example, V, n, and m

(the mass of the system) are extensive variables, whereas P and T are intensive variables. The quotient of two extensive variables is an intensive variable. The *density* ρ is defined as m/V, and the *molar volume* V_{m} is defined to equal V/n. These are intensive variables. One test to determine whether a variable is extensive or intensive is to imagine combining two identical systems, keeping P and T fixed. Any variable that has twice the value for the combined system as for one of the original systems is extensive, and any variable that has the same value is intensive. In later chapters we will define a number of extensive thermodynamic variables, such as the internal energy U, the enthalpy H, the entropy S, and the Gibbs energy G.

We are sometimes faced with systems that are not at equilibrium, and the description of their states is more complicated. However, there are some nonequilibrium states that we can treat as though they were equilibrium states. For example, if liquid water at atmospheric pressure is carefully cooled below 0°C in a smooth container it can remain in the liquid form for a relatively long time. The water is said to be in a *metastable state*. At ordinary pressures, carbon in the form of diamond is in a metastable state, because it spontaneously tends to convert to graphite (although very slowly).

Differential Calculus and State Variables

Because a dependent variable depends on one or more independent variables, a change in an independent variable produces a corresponding change in the dependent variable. If f is a differentiable function of a single independent variable x,

$$f = f(x) \tag{1.2-1}$$

then an infinitesimal change in x given by dx (the *differential* of x) produces a change in f given by

$$df = \frac{df}{dx}dx \tag{1.2-2}$$

where df/dx represents the *derivative* of f with respect to x and where df represents the *differential* of the dependent variable f. The derivative df/dx gives the rate of change of f with respect to x and is defined by

$$\frac{df}{dx} = \lim_{h\to 0}\frac{f(x+h) - f(x)}{h} \tag{1.2-3}$$

if the limit exists. If the derivative exists, the function is said to be *differentiable*. There are standard formulas for the derivatives of many functions. For example, if $f = a\ \sin(bx)$, where a and b represent constants, then

$$\frac{df}{dx} = ab\ \cos(x) \tag{1.2-4}$$

If a function depends on several independent variables, each independent variable makes a contribution like that in Eq. (1.2-2). If f is a differentiable function of x, y, and z, and if infinitesimal changes dx, dy, and dz are imposed, then the differential df is given by

$$df = \left(\frac{\partial f}{\partial x}\right)_{y,z} dx + \left(\frac{\partial f}{\partial y}\right)_{x,z} dy + \left(\frac{\partial f}{\partial z}\right)_{x,y} dz \tag{1.2-5}$$

where $(\partial f/\partial x)_{y,z}$, $(\partial f/\partial y)_{x,z}$, and $(\partial f/\partial z)_{x,y}$ are *partial derivatives*. If the function is represented by a formula, a partial derivative with respect to one independent variable is obtained by the ordinary procedures of differentiation, treating the other independent variables as though they were constants. The independent variables that are held constant are usually specified by subscripts.

We assume that our macroscopic equilibrium state functions are differentiable except possibly at isolated points. For an equilibrium gas or liquid system of one phase and one substance, we can write

$$dV = \left(\frac{\partial V}{\partial T}\right)_{P,n} dT + \left(\frac{\partial V}{\partial P}\right)_{T,n} dP + \left(\frac{\partial V}{\partial n}\right)_{T,P} dn \tag{1.2-6}$$

This equation represents the value of an infinitesimal change in volume that is produced when we impose arbitrary infinitesimal changes dT, dP, and dn on the system, making sure that the system is at equilibrium after we make the changes. For an ideal gas

$$dV = \frac{nR}{P}dT - \frac{nRT}{P^2}dP + \frac{RT}{P}dn \quad \text{(ideal gas)} \tag{1.2-7}$$

A *mathematical identity* is an equation that is valid for all values of the variables contained in the equation. There are several useful identities involving partial derivatives. Some of these are stated in Appendix B. An important identity is the *cycle rule*, which involves three variables such that each can be expressed as a differentiable function of the other two:

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -1 \quad \text{(cycle rule)} \tag{1.2-8}$$

If there is a fourth variable, it is held fixed in all three of the partial derivatives. Some people are surprised by the occurrence of the negative sign in this equation. See Appendix B for further discussion.

EXAMPLE 1.4

Take $z = xy$ and show that the three partial derivatives conform to the cycle rule.

Solution

$$\left(\frac{\partial z}{\partial x}\right)_y = y$$

$$\left(\frac{\partial x}{\partial y}\right)_z = -\frac{z}{y^2}$$

$$\left(\frac{\partial y}{\partial z}\right)_x = \frac{1}{x}$$

$$\left(\frac{\partial z}{\partial x}\right)_y \left(\frac{\partial x}{\partial y}\right)_z \left(\frac{\partial y}{\partial z}\right)_x = -y\frac{z}{y^2}\frac{1}{x} = -\frac{z}{xy} = -1$$

Exercise 1.2

Take $z = ax\ln(y/b)$, where a and b are constants.

a. Find the partial derivatives $(\partial z/\partial x)_y$, $(\partial x/\partial y)_z$, and $(\partial y/\partial z)_x$.

b. Show that the derivatives of part a conform to the cycle rule.

A *second partial derivative* is a partial derivative of a partial derivative. Both derivatives can be with respect to the same variable:

$$\left(\frac{\partial^2 f}{\partial x^2}\right)_y = \left(\frac{\partial}{\partial x}\left(\frac{\partial f}{\partial x}\right)_y\right)_y \tag{1.2-9}$$

The following is called a *mixed second partial derivative*:

$$\frac{\partial^2 f}{\partial y \partial x} = \left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x \tag{1.2-10}$$

The reciprocity relation is named for its discoverer, Leonhard Euler, 1707–1783, a great Swiss mathematician who spent most of his career in St. Petersburg, Russia, and who is considered by some to be the father of mathematical analysis. The base of natural logarithms is denoted by e after his initial.

Euler's reciprocity relation states that the two mixed second partial derivatives of a differentiable function must be equal to each other:

$$\boxed{\frac{\partial^2 f}{\partial y \partial x} = \frac{\partial^2 f}{\partial x \partial y}} \tag{1.2-11}$$

Exercise 1.3

Show that the three pairs of mixed partial derivatives that can be obtained from the derivatives in Eq. (1.2-7) conform to Euler's reciprocity relation.

Processes

A process is an occurrence that changes the state of a system. Every macroscopic process has a *driving force* that causes it to proceed. For example, a temperature difference is the driving force that causes a flow of heat. A larger value of the driving force corresponds to a larger rate of the process. A zero rate must correspond to zero value of the driving force. A *reversible process* is one that can at any time be reversed in direction by an infinitesimal change in the driving force. The driving force of a reversible process must be infinitesimal in magnitude since it must reverse its sign with an infinitesimal change. A reversible process must therefore occur infinitely slowly, and the system has time to relax to equilibrium at each stage of the process. The system passes through a sequence of equilibrium states during a reversible process. A reversible process is sometimes called a *quasi-equilibrium process* or a *quasi-static process*. There can be no truly reversible processes in the real universe, but we can often make calculations for them and apply the results to real processes, either exactly or approximately.

An approximate version of Eq. (1.2-6) can be written for a finite reversible process corresponding to increments ΔP, ΔT, and Δn:

$$\Delta V \approx \left(\frac{\partial V}{\partial T}\right)_{P,n} \Delta T + \left(\frac{\partial V}{\partial P}\right)_{T,n} \Delta P + \left(\frac{\partial V}{\partial n}\right)_{T,P} \Delta n \tag{1.2-12}$$

where ≈ means "is approximately equal to" and where we use the common notation

$$\Delta V = V(\text{final}) - V(\text{initial}) \tag{1.2-13}$$

and so on. Calculations made with Eq. (1.2-12) will usually be more nearly correct if the finite increments ΔT, ΔP, and Δn are small, and less nearly correct if the increments are large.

Variables Related to Partial Derivatives

The *isothermal compressibility* κ_T is defined by

$$\kappa_\mathrm{T} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right) \quad \text{(definition of the isothermal compressibility)} \tag{1.2-14}$$

The factor $1/V$ is included so that the compressibility is an intensive variable. The fact that T and n are fixed in the differentiation means that measurements of the isothermal compressibility are made on a closed system at constant temperature. It is found experimentally that the compressibility of any system is positive. That is, every system decreases its volume when the pressure on it is increased.

The *coefficient of thermal expansion* is defined by

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{P,n} \quad \text{(definition of the coefficient of thermal expansion)} \tag{1.2-15}$$

The coefficient of thermal expansion is an intensive quantity and is usually positive. That is, if the temperature is raised the volume usually increases. There are a few systems with negative values of the coefficient of thermal expansion. For example, liquid water has a negative value of α between 0°C and 3.98°C. In this range of temperature the volume of a sample of water decreases if the temperature is raised. Values of the isothermal compressibility for a few pure liquids at several temperatures and at two different pressures are given in Table A.1 of Appendix A. The values of the coefficient of thermal expansion for several substances are listed in Table A.2. Each value applies only to a single temperature and a single pressure, but the dependence on temperature and pressure is not large for typical liquids, and these values can usually be used over fairly wide ranges of temperature and pressure.

For a closed system (constant n) Eq. (1.2-12) can be written

$$\Delta V \approx V\alpha\Delta T - V\kappa_\mathrm{T}\Delta P \tag{1.2-16}$$

EXAMPLE 1.5

The isothermal compressibility of liquid water at 298.15 K and 1.000 atm is equal to $4.57 \times 10^{-5}\ \mathrm{bar}^{-1} = 4.57 \times 10^{-10}\ \mathrm{Pa}^{-1}$. Find the fractional change in the volume of a sample of water if its pressure is changed from 1.000 bar to 50.000 bar at a constant temperature of 298.15 K.

Solution

The compressibility is relatively small in magnitude so we can use Eq. (1.2-16):

$$\Delta V \approx -V\kappa_\mathrm{T}\Delta P \tag{1.2-17}$$

The fractional change is

$$\frac{\Delta V}{V} \approx -\kappa_T \Delta P = -(4.57 \times 10^{-5}\ \text{bar}^{-1})(49.00\ \text{bar}) = -2.24 \times 10^{-3}$$

EXAMPLE 1.6

For liquid water at 298.15 K and 1.000 atm, $\alpha = 2.07 \times 10^{-4}\ \text{K}^{-1}$. Find the fractional change in the volume of a sample of water at 1.000 atm if its temperature is changed from 298.15 K to 303.15 K.

Solution

To a good approximation,

$$\Delta V \approx V\alpha\Delta T$$

The fractional change in volume is

$$\frac{\Delta V}{V} \approx \alpha\Delta T = (2.07 \times 10^{-4}\ \text{K}^{-1})(5.000\ \text{K}) = 1.04 \times 10^{-3}$$

Exercise 1.4

a. Find expressions for the isothermal compressibility and coefficient of thermal expansion for an ideal gas.

b. Find the value of the isothermal compressibility in atm^{-1}, in bar^{-1}, and in Pa^{-1} for an ideal gas at 298.15 K and 1.000 atm. Find the ratio of this value to that of liquid water at the same temperature and pressure, using the value from Table A.1.

c. Find the value of the coefficient of thermal expansion of an ideal gas at 20°C and 1.000 atm. Find the ratio of this value to that of liquid water at the same temperature and pressure, using the value from Table A.2.

In addition to the coefficient of thermal expansion there is a quantity called the *coefficient of linear thermal expansion*, defined by

$$\alpha_L = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_P \quad \text{(definition of the coefficient of linear thermal expansion)} \tag{1.2-18}$$

where L is the length of the object. This coefficient is usually used for solids, whereas the coefficient of thermal expansion in Eq. (1.2-15) is used for gases and liquids. Unfortunately, the subscript L is sometimes omitted on the symbol for the coefficient of linear thermal expansion, and the name "coefficient of thermal expansion" is also sometimes used for it. Because the units of both coefficients are the same (reciprocal temperature) there is opportunity for confusion between them.

We can show that the linear coefficient of thermal expansion is equal to one-third of the coefficient of thermal expansion. Subject a cubical object of length L to an infinitesimal change in temperature, dT. The new length of the object is

$$L(T + dT) = L(T) + \left(\frac{\partial L}{\partial T}\right)_P dT = L(T)(1 + \alpha_L dT) \tag{1.2-19}$$

The volume of the object is equal to L^3, so

$$\begin{aligned} V(T+dT) &= L(T)^3\left(1+\alpha_{\mathrm{L}}dT^3\right) \\ &= L(T)^3\left(1+3\alpha_{\mathrm{L}}dT+3(\alpha_{\mathrm{L}}dT)^2+(\alpha_{\mathrm{L}}dT)^3\right) \end{aligned} \tag{1.2-20}$$

Since dT is small, the last two terms are insignificant compared with the term that is proportional to dT.

$$V(T+dT) = L(T)^3(1+3\alpha_{\mathrm{L}}dT) \tag{1.2-21}$$

The volume at temperature $T + dT$ is given by

$$V(T+dT) = V(T) + \left(\frac{\partial V}{\partial T}\right)dT = V(T)(1+\alpha dT) \tag{1.2-22}$$

Comparison of Eq. (1.2-22) with Eq. (1.2-21) shows that

$$\alpha = 3\alpha_{\mathrm{L}} \tag{1.2-23}$$

This relationship holds for objects that are not necessarily shaped like a cube.

EXAMPLE 1.7

The linear coefficient of expansion of borosilicate glass, such as Pyrex® or Kimax®, is equal to $3.2 \times 10^{-6}\ \mathrm{K}^{-1}$. If a volumetric flask contains 2.000000 L at 20.0°C, find its volume at 25.0°C.

Solution

$$\begin{aligned} V(25^\circ\mathrm{C}) &= V(20^\circ\mathrm{C})(1+3\alpha_{\mathrm{L}}(5.0^\circ\mathrm{C})) \\ &= (2.000000\ \mathrm{L})(1+3(3.2\times10^{-6})(5.0^\circ\mathrm{C})) = 2.000096\ \mathrm{L} \end{aligned}$$

Exercise 1.5

Find the volume of the volumetric flask in Example 1.7 at 100.0°C.

Moderate changes in temperature and pressure produce fairly small changes in the volume of a liquid, as in the examples just presented. The volumes of most solids are even more nearly constant. We therefore recommend the following practice: *For ordinary calculations, assume that liquids and solids have fixed volumes. For more precise calculations, calculate changes in volume proportional to changes in pressure or temperature as in Examples 1.5 and 1.6.*

Exercise 1.6

The compressibility of acetone at 20°C is $12.39 \times 10^{-10}\ \mathrm{Pa}^{-1}$, and its density is $0.7899\ \mathrm{g\ cm}^{-3}$ at 20°C and 1.000 bar.

a. Find the molar volume of acetone at 20°C and a pressure of 1.000 bar.
b. Find the molar volume of acetone at 20°C and a pressure of 100.0 bar.

PROBLEMS

Section 1.2: Systems and States in Physical Chemistry

1.13 Show that the three partial derivatives obtained from $PV = nRT$ with n fixed conform to the cycle rule, Eq. (B-15) of Appendix B.

1.14 For 1.000 mol of an ideal gas at 298.15 K and 1.000 bar, find the numerical value of each of the three partial derivatives in the previous problem and show numerically that they conform to the cycle rule.

1.15 Finish the equation for an ideal gas and evaluate the partial derivatives for $V = 22.4$ L, $T = 273.15$ K, and $n = 1.000$ mol.

$$dP = \left(\frac{\partial P}{\partial V}\right)_{T,n} dV + ?$$

1.16 Take $z = aye^{x/b}$, where a and b are constants.

a. Find the partial derivatives $(\partial z/\partial x)_y$, $(\partial x/\partial y)_z$, and $(\partial y/\partial z)_x$.

b. Show that the derivatives of part a conform to the cycle rule, Eq. (B-15) of Appendix B.

1.17 **a.** Find the fractional change in the volume of a sample of liquid water if its temperature is changed from 20.00°C to 30.00°C and its pressure is changed from 1.000 bar to 26.000 bar.

b. Estimate the percent change in volume of a sample of benzene if it is heated from 0°C to 45°C at 1.000 atm.

c. Estimate the percent change in volume of a sample of benzene if it is pressurized at 55°C from 1.000 atm to 50.0 atm.

1.18 **a.** Estimate the percent change in the volume of a sample of carbon tetrachloride if it is pressurized from 1.000 atm to 10.000 atm at 25°C.

b. Estimate the percent change in the volume of a sample of carbon tetrachloride if its temperature is changed from 20°C to 40°C.

1.19 Find the change in volume of 100.0 cm^3 of liquid carbon tetrachloride if its temperature is changed from 20.00°C to 25.00°C and its pressure is changed from 1.000 atm to 10.000 atm.

1.20 Let $f(u) = \sin(au^2)$ and $u = x^2 + y^2$, where a is a constant. Using the chain rule, find $(\partial f/\partial x)_y$ and $(\partial f/\partial y)_x$. (See Appendix B.)

1.21 Show that for any system,

$$\frac{\alpha}{\kappa_T} = \left(\frac{\partial P}{\partial T}\right)_{V,n}$$

1.22 The coefficient of linear expansion of borosilicate glass is equal to $3.2 \times 10^{-6}\ \mathrm{K}^{-1}$.

a. Calculate the pressure of a sample of helium (assumed ideal) in a borosilicate glass vessel at 150°C if its pressure at 0°C is equal to 1.000 atm. Compare with the value of the pressure calculated assuming that the volume of the vessel is constant.

b. Repeat the calculation of part a using the virial equation of state truncated at the B_2 term. The value of B_2 for helium is 11.8 $\mathrm{cm^3 mol^{-1}}$ at 0°C and 11.0 $\mathrm{cm^3 mol^{-1}}$ at 150°C.

1.23 Assuming that the coefficient of thermal expansion of gasoline is roughly equal to that of benzene, estimate the fraction of your gasoline expense that could be saved by purchasing gasoline in the morning instead of in the afternoon, assuming a temperature difference of 5°C.

1.24 The volume of a sample of a liquid at constant pressure can be represented by

$$V_m(t_C) = V_m(0°C)(1 + \alpha' t_C + \beta' t_C^2 + \gamma' t_C^3)$$

where α', β', and γ' are constants and t_C is the Celsius temperature.

a. Find an expression for the coefficient of thermal expansion as a function of t_C.

b. Evaluate the coefficient of thermal expansion of benzene at 20.00°C, using $\alpha' = 1.17626 \times 10^{-3}(°C)^{-1}$, $\beta' = 1.27776 \times 10^{-6}(°C)^{-2}$, and $\gamma' = 0.80648 \times 10^{-8}(°C)^{-3}$. Compare your value with the value in Table A.2.

1.25 The coefficient of thermal expansion of ethanol equals $1.12 \times 10^{-3}\ \mathrm{K}^{-1}$ at 20°C and 1.000 atm. The density at 20°C is equal to 0.7893 g cm^{-3}.

a. Find the volume of 1.000 mol of ethanol at 10.00°C and 1.000 atm.

b. Find the volume of 1.000 mol of ethanol at 30.00°C and 1.000 atm.

1.3

Real Gases

The van der Waals equation of state is named for Johannes Diderik van der Waals,1837–1923, a Dutch physicist who received the 1910 Nobel Prize in physics for his work on equations of state.

Most gases obey the ideal gas law to a good approximation when near room temperature and at a moderate pressure. At higher pressures one might need a better description. Several equations of state have been devised for this purpose. The *van der Waals equation of state* is

$$\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT \tag{1.3-1}$$

The symbols a and b represent constant parameters that have different values for different substances. Table A.3 in Appendix A gives values of van der Waals parameters for several substances.

We solve the van der Waals equation for P and note that P is actually a function of only two intensive variables, the temperature T and the molar volume V_m, defined to equal V/n.

$$P=\frac{nRT}{V-nb}-\frac{an^2}{V^2}=\frac{RT}{V_m-b}-\frac{a}{V_m^2} \tag{1.3-2}$$

This dependence illustrates the fact that *intensive variables such as pressure cannot depend on extensive variables* and that the *intensive state of a gas or liquid of one substance is specified by only two intensive variables*.

EXAMPLE 1.8

Use the van der Waals equation to calculate the pressure of nitrogen gas at 273.15 K and a molar volume of 22.414 L mol^{-1}. Compare with the pressure of an ideal gas at the same temperature and molar volume.

Solution

$$P=\frac{\left(8.134\ \mathrm{J\ K^{-1}mol^{-1}}\right)(273.15\ \mathrm{K})}{0.022414\ \mathrm{m^3\ mol^{-1}}-0.0000391\ \mathrm{m^3\ mol^{-1}}}-\frac{0.1408\ \mathrm{Pa\ m^3\ mol^{-1}}}{\left(0.022414\ \mathrm{m^3\ mol^{-1}}\right)^2}$$

$$=1.0122\times10^5\ \mathrm{Pa}=0.9990\ \mathrm{atm}$$

For the ideal gas

$$P=\frac{RT}{V_m}=\frac{\left(8.134\ \mathrm{J\ K^{-1}mol^{-1}}\right)(273.15\ \mathrm{K})}{0.022414\ \mathrm{m^3\ mol^{-1}}}=1.0132\times10^5\ \mathrm{Pa}=1.0000\ \mathrm{atm}$$

Exercise 1.7

a. Show that in the limit that V_m becomes large, the van der Waals equation becomes identical to the ideal gas law.

b. Find the pressure of 1.000 mol of nitrogen at a volume of 24.466 L and a temperature of 298.15 K using the van der Waals equation of state. Find the pressure of an ideal gas under the same conditions.

c. Find the pressure of 1.000 mol of nitrogen at a volume of 1.000 L and a temperature of 298.15 K using the van der Waals equation of state. Find the pressure of an ideal gas under the same conditions.

Another common equation of state is the *virial equation of state*:

$$\frac{PV_{\mathrm{m}}}{RT} = 1 + \frac{B_2}{V_{\mathrm{m}}} + \frac{B_3}{V_{\mathrm{m}}^2} + \frac{B_4}{V_{\mathrm{m}}^3} + \cdots \tag{1.3-3}$$

which is a power series in the independent variable $1/V_{\mathrm{m}}$. The B coefficients are called *virial coefficients*. The first virial coefficient, B_1, is equal to unity. The other virial coefficients must depend on temperature in order to provide an adequate representation. Table A.4 gives values of the second virial coefficient for several gases at several temperatures.

An equation of state that is a power series in P is called the *pressure virial equation of state*:

$$PV_{\mathrm{m}} = RT + A_2P + A_3P^2 + A_4P^3 + \cdots \tag{1.3-4}$$

The coefficients A_2, A_3, etc., are called *pressure virial coefficients* and also must depend on the temperature. It can be shown that A_2 and B_2 are equal.

EXAMPLE 1.9

Show that $A_2 = B_2$.

Solution

We solve Eq. (1.3-3) for P and substituting this expression for each P in Eq. (1.3-4).

$$P = \frac{RT}{V_{\mathrm{m}}} + \frac{RT\,B_2}{V_{\mathrm{m}}^2} + \frac{RT\,B_3}{V_{\mathrm{m}}^3} + \cdots$$

We substitute this expression into the left-hand side of Eq. (1.3-4).

$$PV_{\mathrm{m}} = RT + \frac{RT\,B_2}{V_{\mathrm{m}}} + \frac{RT\,B_3}{V_{\mathrm{m}}^2} + \cdots$$

We substitute this expression into the second term on the right-hand side of Eq. (1.3-4).

$$PV_{\mathrm{m}} = RT + A_2\frac{RT}{V_{\mathrm{m}}} + \frac{RT\,B_2}{V_{\mathrm{m}}^2} + \frac{RT\,B_3}{V_{\mathrm{m}}^3} + \cdots$$

If two power series in the same variable are equal to each other for all values of the variable, the coefficients of the terms of the same power of the variable must be equal to each other. We equate the coefficients of the $1/V_{\mathrm{m}}$ terms and obtain the desired result:

$$A_2 = B_2$$

Exercise 1.8

Show that $A_3 = \frac{1}{RT}\left(B_3 - B_2^2\right)$.

Table 1.1 displays several additional equations of state, and values of parameters for several gases are found in Table A.3. The parameters for a given gas do not necessarily have the same values in different equations even if the same letters are used. The accuracy of several of the equations of state has been evaluated.[2] The *Redlich–Kwong equation of state* seemed to perform better than the other two-parameter equations, with the van der Waals equation coming in second best. The Gibbons–Laughton modification of the Redlich–Kwong equation (with four parameters) is more accurate than the two-parameter equations.

Table 1.1 Some Equations of State

The letters a and b stand for constant parameters that have different values for different substances. These parameters do not necessarily have the values for the same substance in different equations of state.

The Berthelot Equation of State

$$\left(P + \frac{a}{TV_{\mathrm{m}}^2}\right)(V_{\mathrm{m}} - b) = RT$$

The Dieterici Equation of State

$$Pe^{a/V_{\mathrm{m}}RT}(V_{\mathrm{m}} - b) = RT$$

The Redlich–Kwong Equation of State

$$P = \frac{RT}{V_{\mathrm{m}} - b} - \frac{a}{T^{1/2}V_{\mathrm{m}}(V_{\mathrm{m}} + b)}$$

The Soave Modification of the Redlich–Kwong Equation of State

$$P = \frac{RT}{V_{\mathrm{m}} - b} - \frac{a\alpha(T)}{V_{\mathrm{m}}(V_{\mathrm{m}} + b)}$$

where $\alpha(T) = \{1 + m\,1 - (T/T_{\mathrm{c}})^{1/2}\}^2$, where m is a constant parameter and where T_{c} is the critical temperature. See the article by Soave for values of the parameter m.

The Gibbons–Laughton Modification of the Redlich–Kwong-Soave Equation of State

The equation is the same as the Soave modification, but $\alpha(T)$ is given by

$$\alpha(T) = 1 + X(T/T_{\mathrm{c}}) - 1 + Y(T/T_{\mathrm{c}})^{1/2} - 1$$

where X and Y are constant parameters. See the article by Gibbons and Laughton for values of these parameters.

Other equations of state can be found in the book by Hirschfelder, Curtiss, and Bird, including the Beattie–Bridgeman equation, with five parameters, and the Benedict–Webb–Rubin equation, with eight parameters.

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[2] J. B. Ott, J. R. Goates, and H. T. Hall, Jr., *J. Chem. Educ.*, **48**, 515 (1971); M. W. Kemp, R. E. Thompson, and D. J. Zigrang, *J. Chem. Educ.*, **52**, 802 (1975).

Graphical Representation of Volumetric Data for Gases

The *compression factor*, denoted by Z, is sometimes used to describe the behavior of real gases:

$$Z = \frac{PV_\mathrm{m}}{RT} \tag{1.3-5}$$

Some authors call Z the *compressibility factor*. We avoid this name because it might be confused with the compressibility. The compression factor equals unity for an ideal gas. Figure 1.3 shows a graph of the compression factor of nitrogen gas as a function of pressure at several temperatures. At low temperatures, the value of Z is less than unity for moderate pressures, but rises above unity for larger pressures. At higher temperatures, the value of Z is greater than unity for all pressures. Attractions between the molecules tend to reduce the value of Z and repulsions between the molecules tend to increase the value of Z. Attractions are more important at lower temperatures and smaller pressures, and repulsions are more important at higher temperatures and higher pressures. The temperature at which the curve has zero slope at zero pressure is called the *Boyle temperature*. This is the temperature at which the gas most nearly approaches ideality for small pressures.

For a van der Waals gas, the compression factor is given by

$$Z = \frac{PV_\mathrm{m}}{RT} = \frac{V_\mathrm{m}}{V_\mathrm{m} - b} - \frac{a}{RTV_\mathrm{m}} = \frac{1}{1 - by} - \frac{ay}{RT} \tag{1.3-6}$$

where we let $y = 1/V_\mathrm{m}$. Since a and b are both positive for all gases, the first term on the right-hand side of Eq. (1.3-6) gives a positive contribution to Z, and the second term gives a negative contribution. The parameter b describes the effect of repulsive

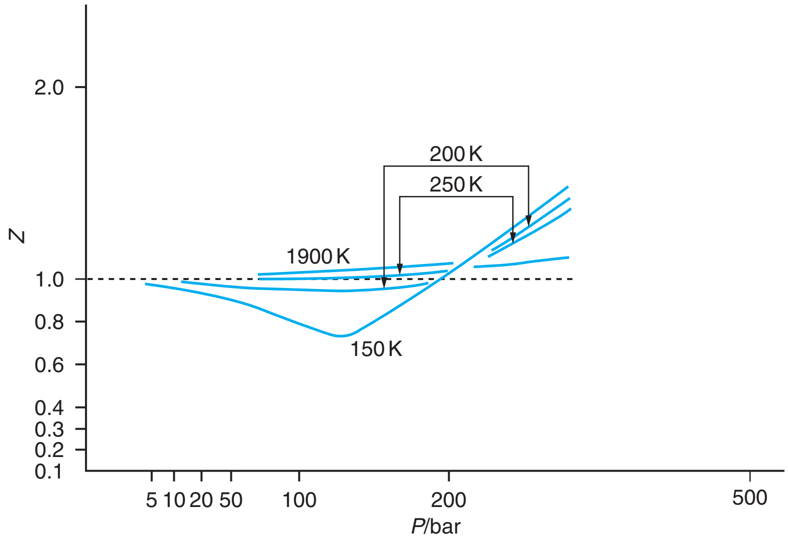

Figure 1.3 The Compression Factor of Nitrogen as a Function of Pressure at Several Temperatures.

intermolecular forces and the parameter a describes the effect of attractive intermolecular forces. For higher temperatures the second term is relatively unimportant, and the compression factor will exceed unity for all values of y. For temperatures below the Boyle temperature the second term becomes relatively more important, and a value of Z less than unity will occur if y is not too large.

EXAMPLE 1.10

a. Find an expression for the Boyle temperature of a van der Waals gas.

b. Find the value of the Boyle temperature of nitrogen gas as predicted by the van der Waals equation.

Solution

a. Since y is proportional to P for small values of P, we seek the temperature at which

$$\left(\frac{\partial Z}{\partial y}\right)\Bigg|_{y=0} = 0 = \left(\frac{b}{(1-by)^2} - \frac{a}{RT}\right)\Bigg|_{y=0} = b - \frac{a}{RT}$$

where the subscript $y = 0$ indicates the value of y at which the derivative is evaluated. The Boyle temperature is

$$T_{\text{Boyle}} = a/Rb$$

b. For nitrogen,

$$T_{\text{Boyle}} = \frac{0.1408\ \text{Pa m}^2\ \text{mol}^{-1}}{\left(8.134\ \text{J K}^{-1}\ \text{mol}^{-1}\right)\left(3.913 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1}\right)} = 433\ \text{K}$$

Exercise 1.9

a. Find an expression for the Boyle temperature of a gas obeying the Dieterici equation of state.

b. Find the value of the Boyle temperature of nitrogen according to the Dieterici equation of state.

c. Find the expression for the molar volume at which $Z = 1$ for the van der Waals gas for a given temperature below the Boyle temperature. Hint: Find the nonzero value of y in Eq. (1.3-6) that makes $Z = 1$.

d. Find the value of the molar volume and the pressure at which $Z = 1$ for nitrogen at 273.15 K, according to the van der Waals equation.

PROBLEMS

Section 1.3: Real Gases

1.26 For the van der Waals equation of state, obtain formulas for the partial derivatives $(\partial P/\partial T)_{V,n}$, $(\partial P/\partial V)_{T,n}$, and $(\partial P/\partial n)_{T,V}$.

1.27 For the virial equation of state,

a. Find the expressions for $(\partial P/\partial V)_{T,n}$ and $(\partial P/\partial T)_{V,n}$.

b. Show that $(\partial^2 P/\partial V\partial T)_n = (\partial^2 P/\partial T\partial V)_n$.

1.28 Evaluate each of the partial derivatives in Problem 1.26 for carbon dioxide at 298.15 K and 10.000 bar.

1.29 **a.** Derive an expression for the isothermal compressibility of a gas obeying the van der Waals equation of state. Hint: Use the reciprocal identity, Eq. (B-8).

b. Evaluate the isothermal compressibility of carbon dioxide gas at a temperature of 298.15 K and a molar volume of $0.01000\,\mathrm{m}^3\,\mathrm{mol}^{-1}$. Compare with the value obtained from the ideal gas law.

1.30 Write the expressions giving the compression factor Z as a function of temperature and molar volume for the van der Waals, Dieterici, and Redlich–Kwong equations of state.

1.31 **a.** For the van der Waals equation of state at temperatures below the Boyle temperature, find an expression for a value of the pressure other than $P = 0$ for which $PV_\mathrm{m} = RT$.

b. Find the value of this pressure for nitrogen gas at 298.15 K.

1.32 **a.** By differentiation, find an expression for the isothermal compressibility of a gas obeying the Dieterici equation of state.

b. Find the value of the isothermal compressibility of nitrogen gas at 298.15 K and $V_\mathrm{m} = 24.4\,\mathrm{L}$. Compare with that of an ideal gas.

1.33 **a.** By differentiation, find an expression for the coefficient of thermal expansion of a gas obeying the van der Waals equation of state.

b. Find the value of the coefficient of thermal expansion of nitrogen gas at 298.15 K and $V_\mathrm{m} = 24.4\,\mathrm{L\,mol}^{-1}$.

1.34 By differentiation, find an expression for the coefficient of thermal expansion of a gas obeying the Dieterici equation of state.

1.35 Manipulate the Dieterici equation of state into the virial form. Use the identity

$$e^{-x} = 1 - x + \frac{x^2}{2!} - \frac{x^3}{3!} + \cdots + (-1)^n \frac{x^n}{n!} + \cdots$$

where $n! = n(n-1)(n-2)(n-3)\ldots(3)(2)(1)$. Write expressions for the second, third, and fourth virial coefficients.

1.36 Write an expression for the isothermal compressibility of a nonideal gas obeying the Redlich–Kwong equation of state.

1.37 The experimental value of the compression factor $Z = PV_\mathrm{m}/RT$ for hydrogen gas at $T = 273.15\,\mathrm{K}$ and $V_\mathrm{m} = 0.1497\,\mathrm{L\,mol}^{-1}$ is 1.1336. Find the values of Z predicted by the van der Waals, Dieterici, and Redlich–Kwong equations of state for these conditions. Calculate the percent error for each.

1.38 The parameters for the van der Waals equation of state for a mixture of gases can be approximated by use of the *mixing rules*:

$$a = a_1x_1^2 + a_{12}x_1x_2 + a_2x_2^2$$

$$b = b_1x_1^2 + b_{12}x_1x_2 + b_2x_2^2$$

where x_1 and x_2 are the mole fractions of the two substances and where a_1, b_1, a_2, and b_2 are the van der Waals parameters of the two substances. The quantities a_{12} and b_{12} are defined by

$$a_{12} = (a_1a_2)^{1/2}$$

and

$$b_{12} = \left(\frac{b_1^{1/3} + b_2^{1/3}}{3}\right)^3$$

a. Using these mixing rules and the van der Waals equation of state, find the pressure of a mixture of 0.79 mol of N_2 and 0.21 mol of O_2 at 298.15 K and at a *mean molar volume* (defined as V/n_total) of $0.00350\,\mathrm{m}^3\,\mathrm{mol}^{-1}$. Compare your answer with the pressure of an ideal gas under the same conditions.

b. Using the van der Waals equation of state, find the pressure of pure N_2 at 298.15 K and at a molar volume of $0.00350\,\mathrm{m}^3\,\mathrm{mol}^{-1}$.

c. Using the van der Waals equation of state, find the pressure of pure O_2 at 298.15 K and at a molar volume of $0.00350\,\mathrm{m}^3\,\mathrm{mol}^{-1}$.

1.39 Find the value of the isothermal compressibility of carbon dioxide gas at 298.15 K and a molar volume of $24.4\,\mathrm{L\,mol}^{-1}$,

a. According to the ideal gas law.

b. According to the truncated virial equation of state

$$\frac{PV_\mathrm{m}}{RT} = 1 + \frac{B_2}{V_\mathrm{m}}$$

For carbon dioxide at 298.15 K, $B_2 = -12.5 \times 10^{-5}\,\mathrm{m}^3\,\mathrm{mol}^{-1}$.

1.40 Considering P to be a function of T, V, and n, obtain the expression for dP for a gas obeying the van der Waals equation of state.

1.4 The Coexistence of Phases and the Critical Point

Transitions from a gaseous state to a liquid state or from a liquid state to a solid state, and so forth, are called *phase transitions* and the samples of matter in the different states are called *phases*. Such transitions can take place abruptly. If a gas is initially at a temperature slightly above its condensation temperature, a small decrease in the temperature can produce a liquid phase that coexists with the gas phases, and a further small decrease in the temperature can cause the system to become a single liquid phase. This remarkable behavior is an exception to the general rule that in nature small changes produce small effects and large changes produce large effects.

It is an experimental fact that for any pure substance the pressure at which two phases can coexist at equilibrium is a smooth function of the temperature. Equivalently, the temperature is a smooth function of the pressure. Figure 1.4 shows schematic curves representing these functions for a typical substance. The curves are called *coexistence curves* and the figure is called a *phase diagram*. The three curves shown are the solid–gas (sublimation) curve at the bottom of the figure, the liquid–gas (vaporization) curve at the upper right, and the solid–liquid (fusion, melting, or freezing) curve at the upper left. The three curves meet at a point called the *triple point*. This point corresponds to

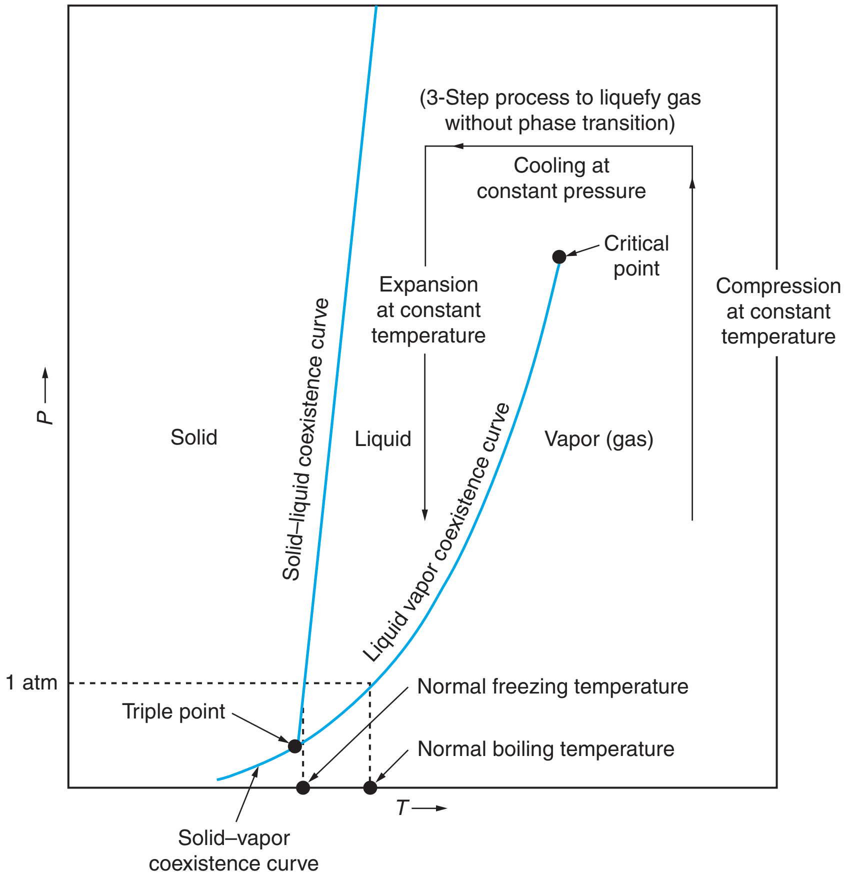

Figure 1.4 The Coexistence Curves for a Typical Pure Substance (Schematic).

the unique value of the pressure and the unique value of the temperature at which all three phases can coexist.

The equilibrium temperature for coexistence of the liquid and solid at a pressure equal to 1 atmosphere is called the *normal melting temperature* or *normal freezing temperature*. The equilibrium temperature for coexistence of the liquid and gas phases at a pressure equal to 1 atmosphere is called the *normal boiling temperature*. These temperatures are marked on Figure 1.4. If the triple point is at a higher pressure than 1 atmosphere the substance does not have a normal freezing temperature or a normal boiling temperature, but has a *normal sublimation temperature* at which the solid and gas coexist at a pressure equal to 1 atmosphere. The triple point of carbon dioxide occurs at a pressure of 5.112 atm and a temperature of 216.55 K (−56.60°C) and its normal sublimation temperature is equal to 194.6 K (−78.5°C). Equilibrium liquid carbon dioxide can be observed only at pressures greater than 5.112 atm. At lower pressures the solid sublimes directly into the vapor phase.

The Critical Point

There is a remarkable feature that is shown in Figure 1.4. The liquid–vapor coexistence curve terminates at a point that is called the *critical point*. The temperature, molar volume, and pressure at this point are called the *critical temperature*, denoted by T_c, the *critical molar volume*, denoted by V_mc, and the *critical pressure*, denoted by P_c. These three quantities are called *critical constants*. Table A.5 in the appendix gives values of the critical constants for several substances. At temperatures higher than the critical temperature and pressures higher than the critical pressure there is no transition between liquid and gas phases. It is possible to heat a gas to a temperature higher than the critical temperature, then to compress it until its density is as large as that of a liquid, and then to cool it until it is a liquid without ever having passed through a phase transition. A path representing this kind of process is drawn in Figure 1.4. Fluids at supercritical temperatures are often referred to as gases, but it is better to refer to them as *supercritical fluids*. Some industrial extractions, such as the decaffeination of coffee, are carried out with supercritical fluids such as carbon dioxide.[3] Supercritical carbon dioxide is also used as a solvent in some HPLC applications.[4] Using a chiral stationary phase, enantiomers can be separated. The liquid–solid coexistence curve apparently does not terminate at a critical point. Nobody has found such a termination, and it seems reasonable that the presence of a lattice structure in the solid, which makes it qualitatively different from the liquid, makes the existence of such a point impossible.

Figure 1.5 schematically shows the pressure of a fluid as a function of molar volume for several fixed temperatures, with one curve for each fixed temperature. These constant-temperature curves are called *isotherms*. For temperatures above the critical temperature there is only one fluid phase, and the isotherms are smooth curves. The liquid branch is nearly vertical since the liquid is almost incompressible while the gas branch of the curve is similar to the curve for an ideal gas. For subcritical temperatures, the isotherm consists of two smooth curves (branches) and a horizontal line segment, which is called a *tie line*. A tie line connects the two points representing the molar volumes of the coexisting liquid and gas phases. As subcritical temperatures closer and closer to the critical temperature are chosen the tie lines become shorter and shorter

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[3] *Chem. Eng. Sci.*, **36**(11), 1769(1981); *Env. Sci. Technol.*, **20**(4), 319 (1986); *Chemtech.*, **21**(4), 250 (1991), *Anal. Chem.*, **66**(12), 106R (1994).

[4] A.M. Thayer, *Chem. Eng. News*, **83**, 49 (September 5, 2005).

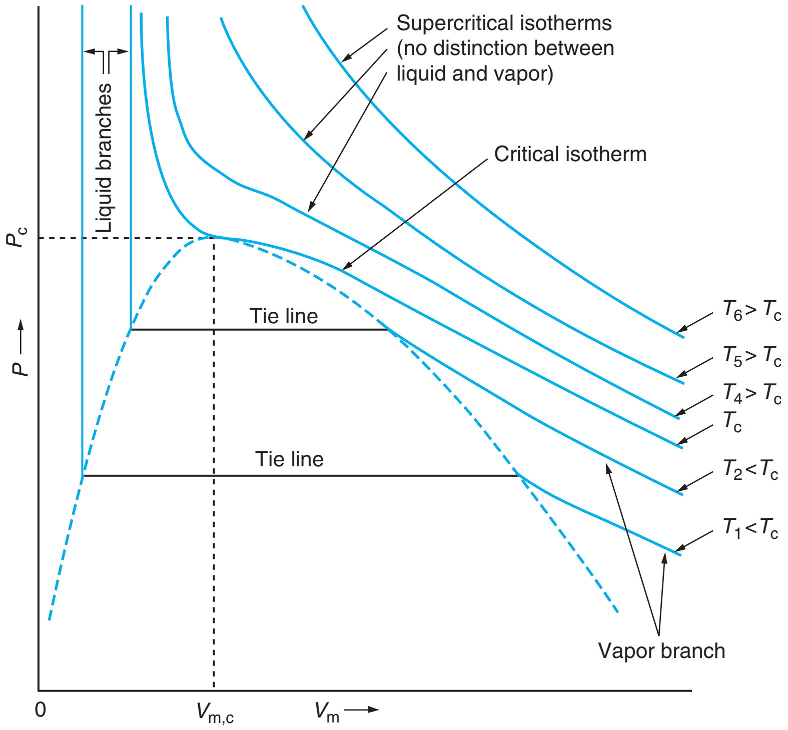

Figure 1.5 Isotherms for a Typical Pure Substance (Schematic).

until they shrink to zero length at the critical point. No two isotherms can intersect, so the isotherm that passes through the critical point must have a horizontal tangent line at the critical point. This point on the critical isotherm is an *inflection point*, with a zero value of $(\partial P/\partial V_m)_T$ and a zero value of $(\partial^2 P/\partial V_m^2)_T$.

At the critical point, a fluid exhibits some unusual properties such as strong scattering of light, infinite heat capacity, and infinite compressibility. If a sample of a pure fluid is confined in a rigid closed container such that the average molar volume is equal to that of the critical state and if the temperature is raised through the critical temperature, the meniscus between the liquid and gas phases becomes diffuse and then disappears at the critical temperature. Figure 1.6 shows photographs illustrating this behavior in carbon dioxide.[5] The system contains three balls that are slightly different in density, with densities close to the critical density of carbon dioxide.

Figure 1.7 depicts a perspective view of a three-dimensional graph with a surface representing the pressure of a fluid as a function of temperature and molar volume. The isotherms in Figure 1.5 are produced by passing planes of constant temperature through the surface of this graph. Several isotherms are drawn on the surface in Figure 1.7. The liquid–gas tie lines are seen in the tongue-shaped region. When the three-dimensional graph is viewed in a direction perpendicular to the T–P plane each liquid–gas tie line is seen as a point. The set of all such points makes up the gas–liquid coexistence curve seen in Figure 1.4.

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[5] J. V. Sengers and A. L. Sengers, *Chem. Eng. News.*, **46**, 54 (June 10, 1968). This figure can be seen on the Web at http://sfu.ca/chemcai/critical.html, courtesy of Dr. Steven Lower of Simon Fraser University.

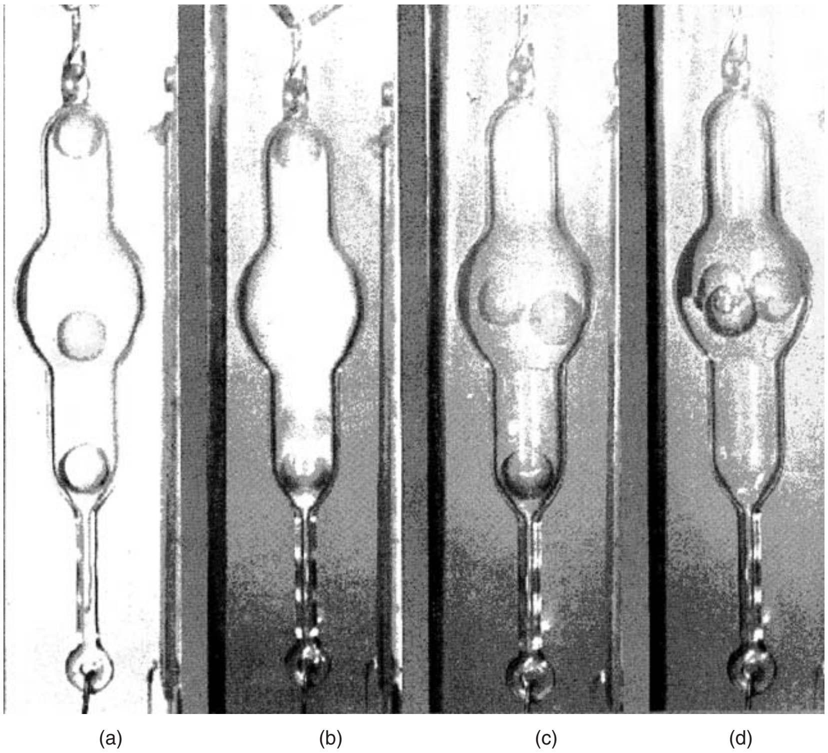

Figure 1.6 Liquid–Gas Equilibrium near the Critical Point. (a) At a temperature slightly above the critical temperature. The density of the fluid depends slightly on height, due to gravity. (b) At the critical temperature, and showing the scattering of light known as critical opalescence. (c) and (d) At subcritical temperatures, showing a definite meniscus. From J. V. Sengers and A. L. Sengers, *Chem. Eng. News*, June 10, 1968, p. 104. Used by permission of the copyright holder.

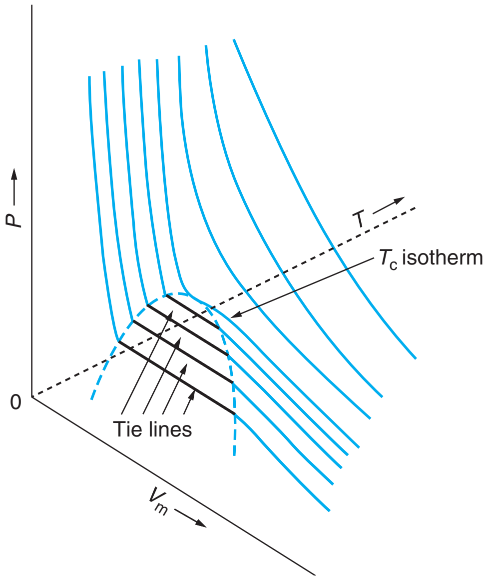

Figure 1.7 Surface Giving Pressure as a Function of Molar Volume and Temperature for a Typical Pure Substance in the Liquid–Vapor Region (Schematic).

Because the entire fluid (liquid and gas) surface in Figure 1.7 is connected, a completely successful equation of state should represent the entire surface. The equations of state that we have discussed yield surfaces that resemble the true surface in the liquid region as well as in the gas region, although they do not represent the tie lines. In Chapter 5 we will discuss a technique for constructing the tie lines for a particular equation of state. The modified Redlich–Kwong–Soave equation of Gibbons and Laughton seems to be fairly accurate in representing both the liquid and the gas, and the van der Waals equation is often used to give qualitative information. For any equation of state, we can obtain equations that locate the critical point.

EXAMPLE 1.11

Derive formulas for the critical temperature and critical molar volume for a gas obeying the van der Waals equation of state.

Solution

We seek the point at which

$$(\partial P/\partial V_{\mathrm{m}})_T = 0 \tag{1.4-1}$$

$$(\partial^2 P/\partial V_{\mathrm{m}}^2)_T = 0 \tag{1.4-2}$$

The first derivative of Eq. (1.3-2) with respect to V_{m} is

$$\left(\frac{\partial P}{\partial V_{\mathrm{m}}}\right)_T = -\frac{RT}{(V_{\mathrm{m}}-b)^2} + \frac{2a}{V_{\mathrm{m}}^3} \tag{1.4-3}$$

and the second derivative is

$$\left(\frac{\partial^2 P}{\partial V_{\mathrm{m}}^2}\right)_T = -\frac{2RT}{(V_{\mathrm{m}}-b)^3} + \frac{6a}{V_{\mathrm{m}}^4} \tag{1.4-4}$$

Setting the right-hand side of each of these two equations equal to zero gives us two simultaneous algebraic equations, which are solved to give the values of the critical temperature T_{c} and the critical molar volume V_{mc}:

$$T_{\mathrm{c}} = \frac{8a}{27Rb}, \qquad V_{\mathrm{mc}} = 3b \tag{1.4-5}$$

Exercise 1.10

Solve the simultaneous equations to verify Eq. (1.4-5). One way to proceed is as follows: Obtain Eq. (I) by setting the right-hand side of Eq. (1.4-3) equal to zero, and Eq. (II) by setting the right-hand side of Eq. (1.4-4) equal to zero. Solve Eq. (I) for T and substitute this expression into Eq. (II).

When the values of T_{c} and V_{mc} are substituted into the van der Waals equation of state the value of the critical pressure for a van der Waals gas is obtained:

$$P_{\mathrm{c}} = \frac{a}{27b^2} \tag{1.4-6}$$

For a van der Waals gas, the compression factor at the critical point is

$$Z_c = \frac{P_c V_{mc}}{RT_c} = \frac{3}{8} = 0.375 \tag{1.4-7}$$

Exercise 1.11

Verify Eqs. (1.4-6) and (1.4-7).

Equations (1.4-5) and (1.4-6) can be solved for *a* and *b*:

$$a = 3V_{mc}^2 P_c = \frac{9R\,V_{mc}T_c}{8} = \frac{27R^2T_c^2}{64P_c} \tag{1.4-8}$$

$$b = \frac{V_{mc}}{3} = \frac{RT_c}{8P_c} \tag{1.4-9}$$

There are two or three formulas for each parameter. Since no substance exactly fits the equation different values can result from the different formulas. The best values of *a* and *b* are obtained by using P_c and T_c as independent variables. The values of the parameters for any two-parameter or three-parameter equation of state can be obtained from critical constants.

Exercise 1.12

a. Show that for the Dieterici equation of state,

$$V_{mc} = 2b, \quad T_c = \frac{a}{4bR}, \quad P_c = \frac{a}{4b^2}e^{-2} \tag{1.4-10}$$

b. Show that for the Dieterici equation of state,

$$Z_c = 2e^{-2} = 0.27067$$

c. Obtain the formulas giving the Dieterici parameters *a* and *b* as functions of P_c and T_c. Find the values of *a* and *b* for nitrogen and compare with the values in Table A.3.

The parameters *a* and *b* in the Redlich–Kwong equation of state can be obtained from the relations

$$a = \frac{R^2T_c^{5/2}}{9\left(2^{1/3}-1\right)P_c}, \quad b = \frac{\left(2^{1/3}-1\right)RT_c}{3P_c} \tag{1.4-11}$$

The value of the compression factor at the critical point according to the Redlich–Kwong equation of state is 1/3.

Exercise 1.13

Find the values of *a* and *b* in the Redlich–Kwong equation of state for nitrogen.

Figure 1.8 shows schematically a more complete view of the three-dimensional graph of Figure 1.7, including the solid–liquid and solid–gas phase transitions. There

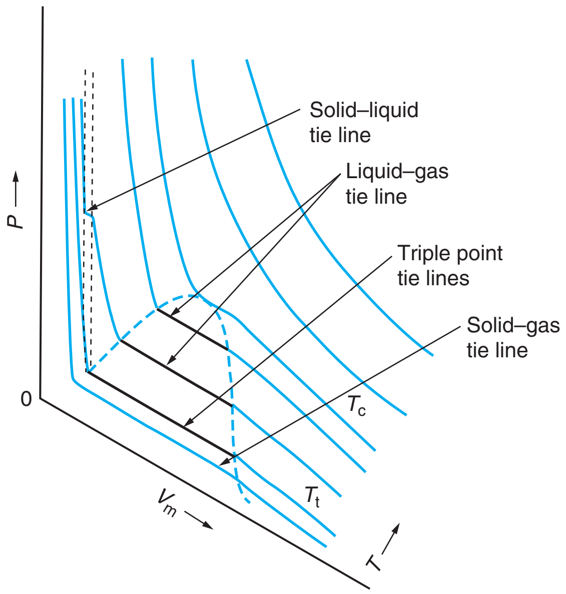

Figure 1.8 Surface Giving Pressure as a Function of Molar Volume and Temperature Showing All Three Phases (Schematic).

are three sets of tie lines, corresponding to the three curves in Figure 1.4. At the triple point, all three tie lines come together in a single tie line connecting three phases. As shown in Figures 1.7 and 1.8, the pressure of a one-phase system of one substance is a function of only two intensive variables, T and V_{m}. Any intensive variable in a one-component fluid system is also a function of two intensive variables. The *intensive state* of an equilibrium system is the state of the system so far as only intensive variables are concerned, and is specified by two independent intensive variables if an equilibrium system contains a single substance and a single fluid phase. The size of the system is not specified. For a one-phase fluid (liquid or gas) system of c substances, $c + 1$ intensive variables specify the intensive state of the system.

The Law of Corresponding States

The van der Waals equation predicts that the value of the compression factor at the critical point is equal to 0.375 for all substances. There is even a greater degree of generality, expressed by an empirical law called the *law of corresponding states*:[6] *All substances obey the same equation of state in terms of reduced variables.* The reduced variables are dimensionless variables defined as follows: The *reduced volume* is the ratio of the molar volume to the critical molar volume:

$$V_{\mathrm{r}} = \frac{V_{\mathrm{m}}}{V_{\mathrm{mc}}} \tag{1.4-12}$$

The *reduced pressure* is the ratio of the pressure to the critical pressure:

$$P_{\mathrm{r}} = \frac{P}{P_{\mathrm{c}}} \tag{1.4-13}$$

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[6] Hirschfelder, Curtiss, and Bird, *op. cit.*, p. 235 [see Table 2.1].

The *reduced temperature* is the ratio of the temperature to the critical temperature:

$$T_r = \frac{T}{T_c} \tag{1.4-14}$$

Using the definitions in Eqs. (1.4-12), (1.4-13), and (1.4-14) and the relations in Eqs. (1.4-5) and (1.4-6) we obtain for a fluid obeying the van der Waals equation of state:

$$P = \frac{aP_r}{27b^2}, \quad V_m = 3bV_r, \quad T = \frac{8aT_r}{27Rb}$$

When these relations are substituted into Eq. (1.3-1), the result is

$$\left(P_r + \frac{3}{V_r^2}\right)\left(V_r - \frac{1}{3}\right) = \frac{8T_r}{3} \tag{1.4-15}$$

Exercise 1.14

Carry out the algebraic steps to obtain Eq. (1.4-15).

In Eq. (1.4-15), the parameters a and b have canceled out. The van der Waals equation of state thus conforms to the law of corresponding states. The same equation of state without adjustable parameters applies to every substance that obeys the van der Waals equation of state if the reduced variables are used instead of P, V_m, and T. The other two-parameter equations of state also conform to the law of corresponding states.

Figure 1.9 is a graph of the experimentally measured compression factor of a number of polar and nonpolar fluids as a function of reduced pressure at a number of reduced

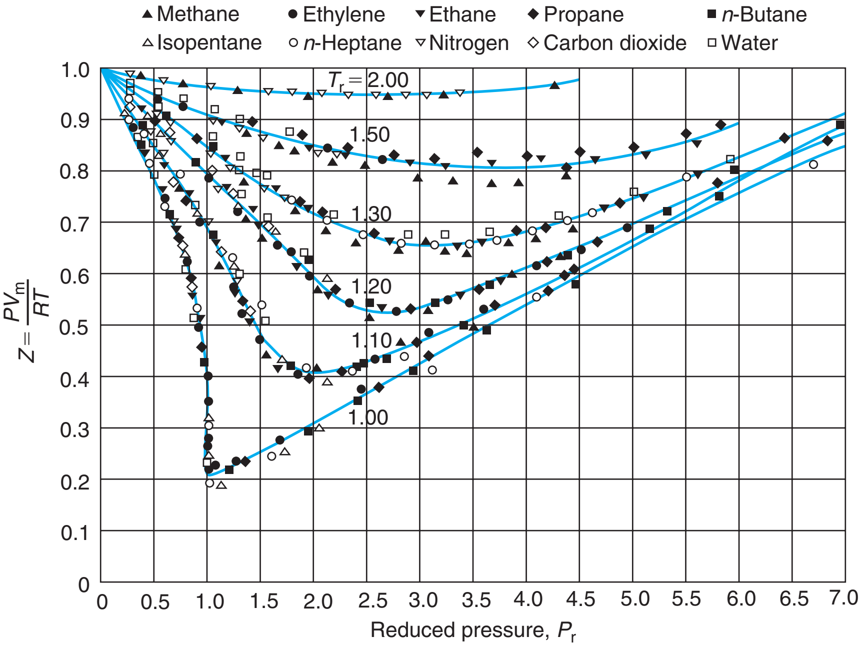

Figure 1.9 The Compression Factor as a Function of Reduced Pressure and Reduced Temperature for a Number of Gases. From G.-J. Su, *Ind. Eng. Chem.*, **38**, 803 (1946). Used by permission of the copyright holder.

temperatures.[7] The agreement of the data for different substances with the law of corresponding states is generally better than the agreement of the data with any simple equation of state.

Exercise 1.15

Show that the Dieterici equation of state conforms to the law of corresponding states by expressing it in terms of the reduced variables.

PROBLEMS

Section 1.4: The Coexistence of Phases and the Critical Point

1.41 **a.** Use the van der Waals equation of state in terms of reduced variables, Eq. (1.4-15), to calculate the pressure of 1.000 mol of CO_2 in a volume of 1.000 L at 100.0°C. The critical constants are in Table A.5 in Appendix A. Since the critical compression factor of carbon dioxide does not conform to the van der Waals value, $Z_c = 0.375$, you must replace the experimental critical molar volume by $V_{\mathrm{mc}}^{\mathrm{th}} = (0.375)RT_c/P_c$.

b. Repeat the calculation using the ordinary form of the van der Waals equation of state.

1.42 **a.** Find the formulas for the parameters a and b in the Soave and Gibbons–Laughton modifications of the Redlich–Kwong equation of state in terms of the critical constants. Show that information about the extra parameters is not needed.

b. Find the values of the parameters a and b for nitrogen.

1.43 The critical temperature of xenon is 289.73 K, and its critical pressure is 5.840 MPa (5.840×10^6 Pa).

a. Find the values of the van der Waals constants a and b for xenon.

b. Find the value of the compression factor, Z, for xenon at a reduced temperature of 1.35 and a reduced pressure of 1.75.

1.44 **a.** Evaluate the parameters in the Dieterici equation of state for argon from critical point data.

b. Find the Boyle temperature of argon according to the Dieterici equation of state.

Summary of the Chapter

A system is defined as the material object that one is studying at a specific time. The state of a system is the circumstance in which it is found, expressed by numerical values of a sufficient set of variables. A macroscopic system has two important kinds of states: the macroscopic state, which concerns only variables pertaining to the system as a whole, and the microscopic state, which pertains to the mechanical variables of individual molecules. The equilibrium macroscopic state of a one-phase fluid (liquid or gas) system of one component is specified by the values of three independent state variables. All other macroscopic state variables are dependent variables, with values given by mathematical functions of the independent variables.

The volumetric (P-V-T) behavior of gases under ordinary pressures is described approximately by the ideal gas law. For higher pressures, several more accurate equations of state were introduced. A calculation practice was introduced: for ordinary calculations: Gases are treated as though they were ideal. The volumes of solids and liquids are computed with the compressibility and the coefficient of thermal expansion. For ordinary calculations they are treated as though they had constant volume.

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[7] G.-J. Su, *Ind. Eng. Chem.*, **38**, 803 (1946).

When two phases of a single substance are at equilibrium, the pressure is a function only of the temperature. A phase diagram for a pure substance contains three curves representing this dependence for the solid–liquid, solid–gas, and liquid–gas equilibria. These three curves meet at a point called the triple point. The liquid–vapor coexistence curve terminates at the critical point. Above the critical temperature, no gas–liquid phase transition occurs and there is only one fluid phase. The law of corresponding states was introduced, according to which all substances obey the same equation of state in terms of reduced variables

ADDITIONAL PROBLEMS

1.45 Assume that when Julius Caesar exhaled for the last time he exhaled 1.0 L of air.

a. Estimate the number of nitrogen molecules that were exhaled in Julius Caesar's last breath. The mole fraction of nitrogen in air is approximately 0.78. (The mole fraction of a substance is its amount in moles divided by the total amount of all substances.)

b. Estimate the number of nitrogen molecules out of those in part a that are now present in the physical chemistry classroom. Assume that sufficient time has elapsed for the nitrogen molecules that Julius Caesar exhaled to mix randomly in the entire atmosphere of the earth. Take the average barometric pressure as 1.00 bar and estimate the total mass of the atmosphere from its pressure and the area of the earth. The radius of the earth is roughly 4000 miles. State any additional assumptions, including your estimates of the room dimensions.

1.46 **a.** Manipulate the van der Waals equation of state into the virial form of Eq. (1.3-3). Use the identity

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \cdots$$

b. For each of the temperatures in Table A.4 at which a value of the second virial coefficient is given for argon, calculate the value of the second virial coefficient from the values of the van der Waals parameters. Calculate the percent error for each value, assuming that the values in Table A.4 are correct.

c. In terms of intermolecular forces, what does it mean when a second virial coefficient is positive? What does it mean when a second virial coefficient is negative? Draw a graph of the second virial coefficient of argon as a function of temperature, and comment on the temperature dependence.

d. Calculate the value of the third virial coefficient of argon at 0°C and at 50°C, assuming that the van der Waals equation is a correct description.

e. Calculate the value of the compression factor of argon at 0°C and a molar volume of 2.271 L mol^{-1}. Do it once using the ideal gas equation, once using the van der Waals equation, once using the virial equation of state truncated at the second virial coefficient and using the correct value of the second virial coefficient, once using the virial equation of state truncated at the second virial coefficient and using the value of the second virial coefficient from the van der Waals parameters, and once using the virial equation of state truncated at the third virial coefficient and using the values of the virial coefficients from the van der Waals parameters.

1.47 The volume of a sample of liquid water at constant pressure can be represented by the formula

$$V(t_C) = V(0°C)(1 + \alpha' t_C + \beta' t_C^2 + \gamma' t_C^3 + \delta' t_C^4)$$

where α', β', γ', and δ' are constants and t_C is the Celsius temperature.

a. Find an expression for the coefficient of thermal expansion as a function of t_C.

b. Two different sets of values are used: The first set is said to be valid from 0°C to 33°C:

$$\begin{aligned}\alpha' &= -6.4268 \times 10^{-5}(°C)^{-1},\\ \beta' &= 8.505266 \times 10^{-6}(°C)^{-2},\\ \gamma' &= -6.78977 \times 10^{-8}(°C)^{-3},\\ \delta' &= 4.01209 \times 10^{-10}(°C)^{-4}.\end{aligned}$$

The second set is said to be valid from 0°C to 80°C:

$$\alpha' = -5.3255 \times 10^{-5}(°\mathrm{C})^{-1},$$
$$\beta' = 7.615323 \times 10^{-6}(°\mathrm{C})^{-2},$$
$$\gamma' = -4.37217 \times 10^{-8}(°\mathrm{C})^{-3},$$
$$\delta' = 1.64322 \times 10^{-10}(°\mathrm{C})^{-4}.$$

Calculate the volume of 1.000 g of liquid water at 25.000°C using the two sets of data. The density of liquid water at 0.000°C is equal to 0.99987 g mL^{-1}. Compare your calculated density with the correct value, 0.99707 g mL^{-1}.

c. Make a graph of the volume of 1.000 g of liquid water from 0.000°C to 10.00°C, using the first set of data.

d. Find the temperature at which the density of liquid water is at a maximum (the temperature at which the volume is at a minimum) using each of the sets of data. The correct temperature of maximum density is 3.98°C.

e. Derive a formula for the coefficient of thermal expansion of water. Calculate the value of this coefficient at 20°C. Compare your value with the value in Table A.2.

1.48 **a.** Calculate the values of the van der Waals parameters *a* and *b* for water, using the critical constants. Compare your values with those in Table A.3.

b. Construct a graph of the isotherm (graph of P as a function of V_m at constant T) for water at the critical temperature, using the van der Waals equation of state.

c. Construct a graph of the vapor branch of the water isotherm for 350°C using the van der Waals equation of state. Use the fact that the vapor pressure of water at 350°C is equal to 163.16 atm to locate the point at which this branch ends.

d. Construct a graph of the water isotherm for 350°C, using the van der Waals equation of state for the entire graph. Note that this equation of state gives a nonphysical "loop" instead of the tie line connecting the liquid and the vapor branches. This loop consists of a curve with a local maximum and a local minimum. The portion of the curve from the true end of the vapor branch to the maximum can represent metastable states (supercooled vapor). The portion of the curve from the end of the liquid branch to the minimum can also represent metastable states (superheated liquid). Find the location of the maximum and the minimum. What do you think about the portion of the curve between the minimum and the maximum?

e. For many temperatures, the minimum in the "loop" of the van der Waals isotherm is at negative values of the pressure. Such metastable negative pressures might be important in bringing water to the top of large trees, because a pressure of 1.000 atm can raise liquid water to a height of only 34 feet (about 10 m). What negative pressure would be required to bring water to the top of a giant sequoia tree with height 90 m? Find the minimum negative pressure in the van der Waals isotherm for a temperature of 25°C.

f. Find the Boyle temperature of water vapor, using the van der Waals equation of state.

g. Construct a graph of the compression factor of water vapor as a function of pressure at the Boyle temperature, ranging from 0 bar to 500 bar, using the van der Waals equation of state. To generate points for plotting, instead of choosing equally spaced values of P, it is likely best to choose a set of values of V_m, and then to calculate both a value of P and a value of Z for each value of V_m.

h. Construct an accurate graph of the compression factor of water at the critical temperature, ranging from 0 bar to 500 bar. Use the van der Waals equation of state. Tell how this graph relates to the graph of part b.

i. Calculate the density of liquid water at a temperature of 25°C and a pressure of 1000 bar, using the method of Examples 1.5 and 1.6. The density of liquid water at this temperature and 1.000 bar is equal to 0.997296 g mL^{-1}.

j. Assume that the van der Waals equation of state can be used for a liquid. Calculate the molar volume of liquid water at 100°C and 1.000 atm by the van der Waals equation of state. (Get a numerical approximation to the solution of the cubic equation by a numerical method.) Compare your answer with the correct value, 18.798 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$.

1.49 Identify each statement as either true or false. If a statement is true only under special circumstances, label it as false.

a. All gases approach ideal behavior at sufficiently low pressures.

b. All gases obey the ideal gas law within about 1% under all conditions.

c. Just as there is a liquid–vapor critical point, there must be a liquid–solid critical point.

d. For every macroscopic state of a macroscopic system, there must correspond many microscopic states.

e. The equilibrium state of a system is independent of the history of the system.

f. The macroscopic state of a one-phase fluid system containing one substance is specified by the value of three state variables.

g. Two gaseous systems containing the same substance and having the same values of T, P, and n can have different volumes.

h. Negative pressures can occur in metastable systems.

i. Negative pressures can occur in equilibrium systems.

j. Above the critical temperature and pressure, there is no distinction between the liquid and gaseous phases.

1.50 **a.** Find the expression for the isothermal compressibility of a gas obeying the truncated pressure virial equation of state:

$$PV = nRT + nA_2P$$

where A_2 depends on T but not on P or n.

b. Find the value of the isothermal compressibility of carbon dioxide at a temperature of 273.15 K and a pressure of 2.000 atm using the expression from part a.

c. Find the value of the isothermal compressibility of carbon dioxide at a temperature of 273.15 K and a pressure of 2.000 atm using the ideal gas law.

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R. M. Gibbons and A. P. Laughton, *J. Chem. Soc., Faraday Trans. 2*, **80**, 1019 (1984).
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2

Work, Heat, and Energy: The First Law of Thermodynamics

PRINCIPAL FACTS AND IDEAS

1. Thermodynamics is based on empirical laws.
2. The first law of thermodynamics asserts that the internal energy U is a state function if

   $$\Delta U = q + w$$

   where q is an amount of heat transferred to the system and w is an amount of work done on the system.
3. Heat is one way of transferring energy.
4. Work is another way of transferring energy.
5. The first law of thermodynamics provides the means to calculate amounts of work and heat transferred in various processes, including adiabatic processes.
6. The enthalpy is a state function whose change in a constant-pressure process is equal to the amount of heat transferred to the system in the process.
7. The enthalpy change of a chemical reaction can be calculated from the enthalpy changes of formation of all products and reactants.

2.1 Work and the State of a System

Thermodynamics involves work and heat. It began in the 19th century with the efforts of engineers to increase the efficiency of steam engines, but it has become the general theory of the macroscopic behavior of matter at equilibrium. It is based on empirical laws, as is classical mechanics. Although classical mechanics has been superseded by relativistic mechanics and quantum mechanics, thermodynamics is an unchallenged theory. No exceptions have been found to the laws of thermodynamics.

Mechanical Work

Nicolas Leonard Sadi Carnot, 1796–1832, was a French engineer who was the first to consider quantitatively the interconversion of work and heat and who is credited with founding the science of thermodynamics.

Gaspard de Coriolis, 1792–1843, was a French physicist best known for the Coriolis force.

The quantitative measurement of work was introduced by Carnot, who defined an amount of work done on an object as the height it is lifted times its weight. This definition was extended by Coriolis, who provided the presently used definition of work: *The amount of work done on an object equals the force exerted on it times the distance it is moved in the direction of the force.* If a force F_z is exerted on an object in the z direction, the work done on the object in an infinitesimal displacement dz in the z direction is

$$dw = F_z\,dz \quad \text{(definition of work)} \tag{2.1-1}$$

where dw is the quantity of work. The SI unit of force is the newton ($\mathrm{N} = \mathrm{kg\,m\,s^{-2}}$), and the SI unit of work is the joule ($\mathrm{J} = \mathrm{kg\,m^2\,s^{-2}} = \mathrm{N\,m}$),

If the force and the displacement are not in the same direction, they must be treated as vectors. A vector is a quantity that has both magnitude and direction. Vectors are discussed briefly in Appendix B. We denote vectors by boldface letters and denote the magnitude of a vector by the symbol for the vector between vertical bars or by the letter in plain type. The amount of work dw can be written as the *scalar product* of the two vectors $\mathbf{F}$ and $d\mathbf{r}$ where $\mathbf{F}$ is the force exerted on the object and $d\mathbf{r}$ is its displacement:

$$dw = \mathbf{F}\cdot d\mathbf{r} = |\mathbf{F}||d\mathbf{r}|\cos(\alpha) \tag{2.1-2}$$

where α denotes the angle between the vector $\mathbf{F}$ and the vector $d\mathbf{r}$. The scalar product of the vectors $\mathbf{F}$ and $d\mathbf{r}$, denoted by $\mathbf{F}\cdot d\mathbf{r}$, is defined by the second equality in Eq. (2.1-2), which contains the magnitudes of the vectors. The product $|d\mathbf{r}|\cos(\alpha)$ is the component of the displacement in the direction of the force, as shown in Figure 2.1. Only the component of the displacement in the direction of the force is effective in determining the amount of work. There is no work done if the object does not move or if the force and the displacement are perpendicular to each other. For example, if the earth's orbit around the sun were exactly circular, the sun would do no work on the earth.

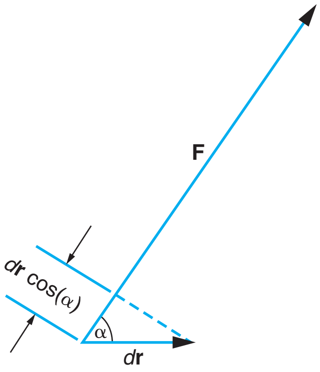

Figure 2.1 A Force and a Displacement

The formula in Eq. (2.1-2) can be written in terms of Cartesian components as in Eq. (B-35) of Appendix B:

$$dw = F_x dx + F_y dy + F_z dz \tag{2.1-3}$$

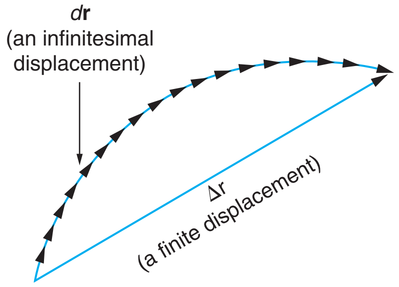

Figure 2.2 A Displacement Divided into Small Steps.

For a finite process we can divide the displacement into small steps such that the force is nearly constant in each step. This division is shown schematically in Figure 2.2. The work done on the object in the entire process is obtained by adding the work done in all of the steps. In the limit that the sizes of the steps approach zero the sum becomes an integral. If the displacement and force are both in the z direction this integral is

$$w = \int dw = \int F_z dz \tag{2.1-4}$$

where we denote an amount of work done in a finite process by w. In order to calculate w for an actual process, we must know how F_z depends on z.

EXAMPLE 2.1

An object is pushed in the z direction by a force given by $F_z = az + b$, where the constant a has the value $300.0\,\mathrm{N\,m^{-1}}$ and the constant b has the value 500.0 N. Find the work done in moving the object from $z = 0$ to $z = 10.0\,\mathrm{m}$.

Solution

Since the force is in the z direction, Eq. (2.1-4) applies:

$$w = \int_0^{10.0\,\mathrm{m}} F_z dz = \int_0^{10.0\,\mathrm{m}} (az + b)dz = \left(\frac{az^2}{2} + bz\right)\Bigg|_0^{10.0\,\mathrm{m}}$$

$$= \frac{(300.0\,\mathrm{N\,m^{-1}})(10.0\,\mathrm{m})^2}{2} + (500.0\,\mathrm{N})(10.0\,\mathrm{m}) = 2.00 \times 10^4\,\mathrm{J}$$

The Work Done on a Closed Fluid System

If a force is transmitted between a system and its surroundings and if the volume of the system changes there is work done by the surroundings on the system or by the system on the surroundings. Consider a gas confined in a cylinder with a piston as depicted in Figure 1.1. We assume that any friction is negligible. Let an external force F_{ext} be exerted downward on the system by the piston. If the external force is greater than the force exerted on the piston by the system, the piston will accelerate downward and the surroundings perform work on the system. If the external force is smaller, the piston will accelerate upward and the system performs work on the surroundings. If the height of the piston, z, increases by an infinitesimal amount dz, the amount of work done on the surroundings is given by Eq. (2.1-1):

$$dw_{\mathrm{surr}} = F(\mathrm{transmitted})dz \tag{2.1-5}$$

where F(transmitted) is the force that is actually transmitted to the surroundings.

Reversible Processes

At equilibrium, the force exerted on the piston by the gas is equal to

$$F = P\mathscr{A} \tag{2.1-6}$$

where P is the pressure of the gas and $\mathscr{A}$ is the area of the piston. We define the *external pressure* P_{ext} by

$$P_{\text{ext}} = \frac{F_{\text{ext}}}{\mathscr{A}} \quad (\text{definition of } P_{\text{ext}}) \tag{2.1-7}$$

At equilibrium there is no tendency for the piston to move so that

$$P = P_{\text{ext}} = P(\text{transmitted}) \quad (\text{at equilibrium}) \tag{2.1-8}$$

where we define the *transmitted pressure* by

$$P(\text{transmitted}) = \frac{F(\text{transmitted})}{\mathscr{A}} \tag{2.1-9}$$

A *reversible process* is defined to be one that can be reversed in direction by an infinitesimal change in the surroundings. In order for an infinitesimal change in P_{ext} to change the direction of motion of the piston, there can be no friction and there can be no more than an infinitesimal difference between P, P(transmitted), and P_{ext}. For an infinitesimal step of a reversible process the work done on the surroundings is given by

$$dw_{\text{surr,rev}} = PdV \quad (\text{reversible process}) \tag{2.1-10}$$

where V is the volume of the system. We will consistently use a subscript "surr" when a symbol pertains to the surroundings. If no subscript is attached to a symbol, the symbol refers to the system.

If a fluid system contains a single substance in a single phase, its equilibrium state can be specified by the values of three variables such as T, V, and n. We can define a three-dimensional space in which T, V, and n are plotted on the three axes. We call such mathematical space a *state space*. Each equilibrium state is represented by a *state point* located in the state space. A reversible process proceeds infinitely slowly, so that the system has sufficient time to come to equilibrium during any part of the process. The system passes through a succession of equilibrium states and the state point traces out a curve in the equilibrium state space, such as that shown in Figure 2.3 for a fixed value of n.

We reckon work done on the surroundings as a negative amount of work done on the system, so we write

$$\boxed{dw_{\text{rev}} = -PdV} \tag{2.1-11}$$

The signs we have used correspond to the following convention: *A positive value of* w *or* dw *corresponds to work being done on the system by the surroundings. A negative value of* w *or of* dw *corresponds to work being done on the surroundings by the system.* Unfortunately, the opposite convention has been used in some older books. We will consistently use the convention stated above.

We have obtained the relation of Eq. (2.1-11) for a gas in a cylinder with a movable piston. We assert that this relation applies to a fluid system of any shape. If a system can exchange work with its surroundings only by changing its volume, we say that it is a *simple system*. This kind of work is sometimes called *compression work* or *P-V work*. A gas is a simple system. A liquid is a simple system if the work required to create surface area by changing the shape of the system can be neglected. A spring or a rubber band is not a simple system because work is done to change its length. An electrochemical cell is also not a simple system since work can be done by passing a current through it.

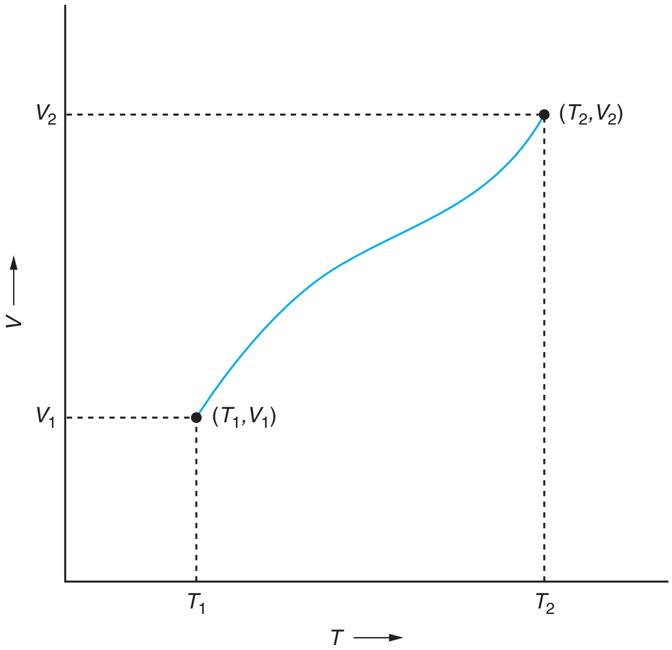

Figure 2.3 A Curve in State Space.

Work Done on an Ideal Gas in a Reversible Process

The ideal gas is a convenient system for example calculations, since it has simple properties but illustrates the principles involved. However, you should be careful not to apply ideal gas equations to other systems. For a finite reversible change in volume of n moles of an ideal gas,

$$w_{\mathrm{rev}} = \int_c dw_{\mathrm{rev}} = -\int_c P dV = -nR\int_c \frac{T}{V}dV \quad \text{(ideal gas)} \tag{2.1-12}$$

Because the integrand in this integral depends on T and V we must specify how T depends on V in order to carry out the integration. This dependence corresponds to a curve in state space, and the letter c under the integral stands for this curve. This kind of integral is called a *line integral*.

If the temperature is constant the process is called *isothermal*. For an isothermal process,

$$w_{\mathrm{rev}} = \int_c dw_{\mathrm{rev}} = -\int_{V_1}^{V_2} \frac{nRT}{V}dV = -nRT\int_{V_1}^{V_2} \frac{1}{V}dV$$

$$\boxed{w_{\mathrm{rev}} = nRT\ln\left(\frac{V_2}{V_1}\right) \quad \text{(closed ideal gas, isothermal process)}} \tag{2.1-13}$$

where V_1 is the initial value of the volume and V_2 is the final value.

EXAMPLE 2.2

a. Calculate the work done on a closed system consisting of 50.00 g of argon, assumed ideal, when it expands isothermally and reversibly from a volume of 5.000 L to a volume of 10.00 L at a temperature of 298.15 K.

b. Calculate the integral of dP for the same process.

Solution

a.
$$w = -(50.00\,\mathrm{g})\left(\frac{1\,\mathrm{mol}}{39.938\,\mathrm{g}}\right)(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})\ln\left(\frac{10.00\,\mathrm{L}}{5.000\,\mathrm{L}}\right)$$
$$= -2151\,\mathrm{J}$$

The negative sign indicates that work is done on the surroundings by the system.

b. For a sample of ideal gas with fixed n we have a two-term expression for dP:

$$dP = \left(\frac{\partial P}{\partial T}\right)_{V,n} dT + \left(\frac{\partial P}{\partial V}\right)_{T,n} dV = \frac{nR}{V}dT - \frac{nRT}{V^2}dV$$

The change in P for the finite process is given by integration:

$$\Delta P = \int_c dP = \int_{T_1}^{T_2} \frac{nR}{V}dT + \int_{V_1}^{V_2} \frac{nRT}{V^2}dV$$

In order to carry out a line integral like this we must know how V depends on T for the first term and must know how T depends on V for the second term. In this case the process is isothermal (T is constant). Because $dT = 0$ for each infinitesimal step of the process, the first term vanishes. In the second term the factor nRT can be factored out of the integral:

$$\Delta P = -nRT\int_{V_1}^{V_2} \frac{1}{V^2}dV = nRT\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$
$$= (50.00\,\mathrm{g})\left(\frac{1\,\mathrm{mol}}{39.938\,\mathrm{g}}\right)(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})$$
$$\times\ (298.15\,\mathrm{K})\left(\frac{1}{0.01000\,\mathrm{m^3}} - \frac{1}{0.005000\,\mathrm{m^3}}\right)$$
$$= -3.103\times10^5\,\mathrm{J\,m^{-3}} = -3.103\times10^5\,\mathrm{Pa} = -3.062\,\mathrm{atm}$$

Reversible Work Done on a Nonideal Gas

For any nonideal gas equation of state, the expression for the work done in an isothermal reversible volume change can be obtained by integration.

EXAMPLE 2.3

Obtain the formula for the work done on a sample of gas during an isothermal reversible volume change if it is represented by the truncated virial equation of state:

$$\frac{PV_\mathrm{m}}{RT} = 1 + \frac{B_2}{V_\mathrm{m}} \tag{2.1-14}$$

Solution

We first convert the equation of state to an expression in terms of T, V, and n instead of T and V_m:

$$P = \frac{nRT}{V} + \frac{n^2RTB_2}{V^2}$$

$$\begin{aligned} w_{\mathrm{rev}} &= \int_c PdV = -nRT\int_{V_1}^{V_2} \frac{1}{V}dV + n^2RTB_2\int_{V_1}^{V_2}\frac{1}{V^2}dV \\ &= -nRT\ln\left(\frac{V_2}{V_1}\right) + n^2RTB_2\left(\frac{1}{V_2} - \frac{1}{V_1}\right) \\ &= -nRT\ln\left(\frac{V_{\mathrm{m},2}}{V_{\mathrm{m},1}}\right) + nRTB_2\left(\frac{1}{V_{\mathrm{m},2}} - \frac{1}{V_{\mathrm{m},1}}\right) \end{aligned} \tag{2.1-15}$$

Exercise 2.1

a. Calculate the work done in the reversible expansion of 100.00 g of CO_2 from a volume of 10.000 L to a volume of 50.00 L at a constant temperature of 25.00°C. Use the truncated virial equation of state of Example 2.3. The second virial coefficient of CO_2 is equal to $-128\,\mathrm{cm^3\,mol^{-1}}$ at this temperature.

b. Recalculate the work done in the process of part a, assuming CO_2 to be an ideal gas.

Work and Irreversible Processes

All real processes with nonzero rates are irreversible. If we know P(transmitted) we can write

$$dw_{\mathrm{irrev}} = -P(\text{transmitted})dV \tag{2.1-16}$$

for a simple system. We cannot discuss irreversible processes in a general way, since P(transmitted) can differ from the equilibrium pressure in complicated ways. However, there are some processes for which we can obtain an adequate approximation for P(transmitted).

Constant-Pressure Processes

In some chemical reactions and some phase changes the system is open to the atmosphere and P_{ext} is equal to the barometric pressure, which is nearly constant. In this case we can assume that P(transmitted) is equal to P_{ext} and to P. We can write

$$w = -\int P_{\mathrm{ext}}dV = -P_{\mathrm{ext}}\Delta V = -P\Delta V \quad \text{(constant-pressure process)} \tag{2.1-17}$$

where "constant-pressure" means not only that the pressure is constant, but also that it is equal to P(transmitted) and to P_{ext}. This equation is valid for both increases and decreases in the volume of the system and is not restricted to reversible changes, so long as P is constant and equal to P(transmitted).

EXAMPLE 2.4

The thermal decomposition of a sample of solid $KClO_3$ produces 0.345 mol of CO_2 gas at a constant temperature of 245°C and a constant barometric pressure of 755 torr. Find the work done on the atmosphere, assuming that CO_2 is an ideal gas. Neglect the volume of the solid $KClO_3$ and the solid KCl that is produced.

Solution

$$\Delta V = \frac{(\Delta n)\,RT}{P} = \frac{(0.345\,\mathrm{mol})(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(518\,\mathrm{K})}{(755\,\mathrm{torr})\left(\dfrac{101325\,\mathrm{Pa}}{760\,\mathrm{torr}}\right)} = 0.0148\,\mathrm{m^3}$$

$$w_{\mathrm{surr}} = P\Delta V = (755\,\mathrm{torr})\left(\frac{101325\,\mathrm{Pa}}{760\,\mathrm{torr}}\right)(0.0148\,\mathrm{m^3}) = 1490\,\mathrm{J}$$

Expansion Processes

If P is larger than P_{ext} the system will expand against the surroundings. If the process is not too rapid, we can assume to a good approximation that P(transmitted) is equal to P_{ext}, although we cannot assume that is equal to P. The details of the nonuniformity of the system's pressure are not important, because P does not enter into the formula for w. We can write

$$\boxed{w = -\int P_{\mathrm{ext}}dV \quad \text{(irreversible expansion process)}} \tag{2.1-18}$$

EXAMPLE 2.5

A sample of 0.500 mol of nitrogen expands irreversibly from a volume of 5.00 L to a volume of 10.00 L at a constant external pressure of 1.000 atm (101,325 Pa). Assume that P(transmitted) is equal to P_{ext}. Calculate w for the process. Explain why the result does not depend on the temperature or the amount of gas. Does it matter if the gas is ideal or nonideal?

Solution

$$w = -\int P_{\mathrm{ext}}dV = -P_{\mathrm{ext}}\Delta V = -(101325\,\mathrm{Pa})(5.00\,\mathrm{L})\left(\frac{1\,\mathrm{m^3}}{1000\,\mathrm{L}}\right) = -507\,\mathrm{Pa\,m^3} = -507\,\mathrm{J}$$

The result depends only on the external pressure and the volume change. The amount of gas would affect the pressure of the system, but this pressure does not enter into the calculation. For the same reason it does not matter if the gas is assumed to be ideal.

Because P must be greater than P_{ext} for the irreversible process to occur, w_{surr} will be smaller for the irreversible expansion than for an equivalent reversible expansion.

Exercise 2.2

a. Calculate w if 0.500 mol of nitrogen expands irreversibly from a volume of 5.00 L to a volume of 10.00 L with a constant external pressure equal to 1.000 atm.

b. Calculate w if 0.500 mol of nitrogen expands reversibly from a volume of 5.00 L to a volume of 10.00 L at a constant temperature of 25.00°C.

Compression Processes

If P is smaller than P_{ext}, a fluid system will be compressed to a smaller volume. If the process is irreversible, the system's pressure will be nonuniform. It will be compressed to a greater extent near the piston than in the rest of the system, so that P(transmitted) will be greater than the equilibrium pressure of the gas, but smaller than P_{ext}. We are not prepared to discuss a nonuniform pressure and will not attempt calculations of w for an irreversible compression. We can obtain some limits for the work done.

EXAMPLE 2.6

Assume that 1.00 mol of an ideal gas is initially confined in a cylinder with a volume of 22.4 L at a temperature of 273.15 K. The external pressure is increased to 1.50×10^5 Pa and the gas is compressed irreversibly and isothermally until $P = 1.50 \times 10^5$ Pa. Find the largest and smallest values that w might have.

Solution

The final volume is

$$V(\text{final}) = \frac{(1.000\,\text{mol})(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(273.15\,\text{K})}{(1.50 \times 10^5\,\text{Pa})} = 0.0151\,\text{m}^3$$

Since P(transmitted) cannot exceed P_{ext},

$$w(\text{maximum}) = -P_{\text{ext}}\Delta V = -(1.50 \times 10^5\,\text{Pa})(0.0151\,\text{m}^3 - 0.0224\,\text{m}^3) = 2270\,\text{J}$$

Since P(transmitted) will exceed the equilibrium pressure that the gas would have at any volume,

$$w(\text{minimum}) = -(1.000\,\text{mol})(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(273.15\,\text{K})\ln\left(\frac{0.0151\,\text{m}^3}{0.0224\,\text{m}^3}\right)$$
$$= 890\,\text{J}$$

The actual value must lie between these values, but would depend on the rate of the process and other things that we cannot evaluate using thermodynamics.

In Chapter 10 we will discuss the rates of certain irreversible processes from a nonthermodynamic point of view. Thermodynamics has also been extended to include such irreversible processes by the use of additional assumptions,[1] but we will not discuss this subject.

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[1] See for example S. R. deGroot and P. Mazur, *Nonequilibrium Thermodynamics*, North Holland, Amsterdam, 1962.

Exact and Inexact Differentials

The differential of a function of two or more independent variables is called an *exact differential*. If f is a function of x and y, the differential

$$df = \left(\frac{\partial f}{\partial x}\right)_y dx + \left(\frac{\partial f}{\partial y}\right)_x dx \quad \text{(exact differential)} \tag{2.1-19}$$

is an exact differential. There is an important theorem of mathematics concerning the line integral of an exact differential: *A line integral of an exact differential is equal to the function evaluated at the final point of the integration curve minus the function evaluated at the initial point of the curve. The line integral of an exact differential therefore depends only on the end points, and not on the curve connecting them.* The line integral of an exact differential is said to be *path-independent*. The converse of this theorem is also true. *If the integral of a differential is path-independent for all paths between the same end points, the differential must be an exact differential.*

Since the pressure P is a state function, dP is an exact differential. The line integral of dP in part b of Example 2.2 is equal to the value of P at the end of the process minus the value of P at the beginning of the process:

$$\int_c dP = \Delta P = P(\text{final}) - P(\text{initial})$$

Exercise 2.3

Verify that ΔP in Example 2.2 is equal to the final pressure minus the initial pressure.

Work Is an Inexact Differential

A differential that is not exact is called an *inexact differential*. The differential

$$du = M(x, y)dx + N(x, y)dy \tag{2.1-20}$$

is an inexact differential if M and N are not the appropriate partial derivatives of the same function. The line integral of an inexact differential depends on the path of integration as well as on the initial point and the final point. We will show that dw is an inexact differential by showing that two processes with the same initial and final states can correspond to different amounts of work done on the system.

EXAMPLE 2.7

Consider a reversible process with the same initial and final states as the process of Example 2.2, but with a different path. Calculate the work done on the ideal gas system of Example 2.2 if it is reversibly cooled at constant volume of 5.000 L from 298.15 K to 200.00 K, then reversibly expanded from 5.000 L to 10.00 L at a constant temperature of 200.0 K, and then reversibly heated at a constant volume of 10.00 L from 200.0 K to 298.15 K.

Solution

The three parts of the process must be integrated separately. In the cooling process at constant volume, $dV = 0$ for each infinitesimal step, so that $w = 0$ for this step. The same is true for the heating process. The only nonzero contribution to w is from the isothermal expansion:

$$\begin{aligned} w &= -(50.00\,\mathrm{g})\left(\frac{1\,\mathrm{mol}}{39.948\,\mathrm{g}}\right)(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(200.00\,\mathrm{K})\ln\left(\frac{10.00\,\mathrm{L}}{5.000\,\mathrm{L}}\right) \\ &= -1443\,\mathrm{J} \end{aligned}$$

which is not equal to the amount of work in Example 2.2.

Since a single case of path dependence is sufficient to show that a differential is inexact, this example shows that dw_{rev} is not an exact differential.

EXAMPLE 2.8

a. Since dw_{rev} corresponds to Eq. (B-19) of Appendix B with $N = 0$, show that dw_{rev} does not satisfy the Euler reciprocity relation of Eq. (B-20) to be an exact differential.

b. Calculate the line integral of dP for the process of Example 2.2. Show that the integral is path-independent for the two paths of Example 2.2 and Example 2.7. For the second path the integral will have to be done in three sections, but in each section only one term of the line integral will be nonzero. For the heating and cooling processes, $dV = 0$ but $dT \neq 0$. For the isothermal process, $dV \neq 0$ but $dT = 0$.

Solution

a.

$$dw = P_{\mathrm{ext}}dV + 0 = PdV + 0 \text{ (reversible processes)}$$

$$\left(\frac{\partial P}{\partial T}\right)_V \neq \left(\frac{\partial 0}{\partial V}\right)_T = 0$$

b. Let 5.000 L be called V_1 and 10.00 L be called V_2. Let 298.15 K be called T_1 and 200.00 K be called T_2.

$$dP = \left(\frac{\partial P}{\partial T}\right)_V dT + \left(\frac{\partial P}{\partial V}\right)_T dV = \frac{nR}{V}dT - \frac{nRT}{V^2}dV$$

We carry out the three integration steps. For the first step, the second term vanishes. For the second step, the first term vanishes, and for the third step, the second term vanishes.

$$n = (50.00\,\mathrm{g})\left(\frac{1\,\mathrm{mol}}{39.948\,\mathrm{g}}\right) = 1.2516\,\mathrm{mol}$$

$$\begin{aligned}
\int dP &= \frac{nR}{V_1}\int_{T_1}^{T_2} dT - nRT_2\int_{V_1}^{V_2}\frac{1}{V^2} + \frac{nR}{V_2}\int_{T_2}^{T_1} dT \\
&= \frac{nR}{V_1}(T_2 - T_1) + nRT_2\left(\frac{1}{V_2} - \frac{1}{V_1}\right) + \frac{nR}{V_2}(T_1 - T_2) \\
&= (1.2516\,\mathrm{mol})(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\left(\frac{-98.15\,\mathrm{K}}{0.00500\,\mathrm{m^3}}\right) \\
&\quad + (1.2516\,\mathrm{mol})(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(200.00\,\mathrm{K})\left(\frac{1}{0.0100\,\mathrm{m^3}} - \frac{1}{0.0050\,\mathrm{m^3}}\right) \\
&\quad + (1.2516\,\mathrm{mol})(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\left(\frac{98.15\,\mathrm{K}}{0.01000\,\mathrm{m^3}}\right) \\
&= -2.0428 \times 10^5\,\mathrm{J\,m^3} - 2.0813 \times 10^5\,\mathrm{J\,m^3} + 1.0214 \times 10^5\,\mathrm{J\,m^3} \\
&= -3.103 \times 10^5\,\mathrm{J\,m^3} = 3.062\,\mathrm{atm}
\end{aligned}$$

This value is the same as in the previous example, showing that the integral of dP is path-independent so far as these two paths are concerned.

Exercise 2.4

a. Calculate the amount of work done on the surroundings if the isothermal expansion of Example 2.2 is carried out at a constant transmitted pressure of 1.000 atm instead of reversibly, but with the same initial and final states as in Example 2.2. Why is less work done on the surroundings in the irreversible process than in the reversible process?

b. What is the change in the pressure of the system for the irreversible process?

PROBLEMS

Section 2.1: Work and the State of a System

2.1 Calculate the work done on the surroundings if 1.000 mol of neon (assumed ideal) is heated from 0.0°C to 250.0°C at a constant pressure of 1.00 atm.

2.2 Calculate the work done on the surroundings if 100.0 g of water freezes at 0.0°C and a constant pressure of 1.00 atm. The density of ice is $0.916\,\mathrm{g\,cm^{-3}}$ and that of liquid water is $1.00\,\mathrm{g\,cm^{-3}}$.

2.3 Calculate the work done on 100.0 g of benzene if it is pressurized reversibly from 1.00 atm to 50.00 atm at a constant temperature of 293.15 K.

2.4 Calculate the work done on the surroundings if 1.000 kg of water is heated from 25.0°C to 100.0°C at a constant pressure of 1.00 atm.

2.5 **a.** The tension force for a spring that obeys Hooke's law is given by

$$\tau = -k(x - x_0)$$

where x is the length of the spring, x_0 is its equilibrium length, and k is a constant called the spring constant. Obtain a formula for the work done on the spring if its length is changed reversibly from x_0 to x' at constant volume.

b. Show that the force can be derived from a potential energy

$$\mathscr{V} = \frac{1}{2}k(x - x_0)^2$$

and that the work done on the spring in part a is equal to the change in the potential energy.

2.6 **a.** Obtain a formula for the work done in reversibly and isothermally compressing 1.000 mol of a gas from a volume V_1 to a volume V_2 if the gas obeys the Redlich–Kwong equation of state.

b. Using the formula from part a, find the work done in reversibly compressing 1.000 mol of carbon dioxide from 10.00 L to 5.000 L at 298.15 K. Compare with the result obtained by assuming that the gas is ideal.

c. Using the formula from part a, calculate the work done on the surroundings if 1.000 mol of carbon dioxide expands isothermally but irreversibly from 5.000 L to 10.00 L at an external pressure of 1.000 atm. Compare with the result obtained by assuming that the gas is ideal.

2.7 **a.** Obtain a formula for the work done in reversibly and isothermally compressing 1.000 mol of a van der Waals gas from a volume V_1 to a volume V_2.

b. Using the formula from part a, find the work done in reversibly compressing 1.000 mol of carbon dioxide from 10.00 L to 5.000 L at 298.15 K. Compare with the result obtained by assuming that the gas is ideal.

c. Using the formula from part a, calculate the work done on the surroundings if 1.000 mol of carbon dioxide expands isothermally but irreversibly from 5.000 L to 10.00 L at an external pressure of 1.000 atm. Compare with the result obtained by assuming that the gas is ideal.

2.8 Test the following differentials for exactness:

a. $T^2 dT + TV dV$

b. $xe^{xy} dx + ye^{xy} dy$

c. $xy dx + \frac{1}{2}x^2 dy$

2.9 Carry out the line integral:

$$\int_c \left(\frac{nR}{V} dT - \frac{nRT}{V^2} dV \right)$$

on the path from (300.0 K, 10.0 L) to (300.0 K, 20.0 L) to (400.0 K, 20.0 L). Take $n = 1.000$ mol.

2.2 Heat

Joseph Black, 1728–1799, was a Scottish chemist who discovered carbon dioxide ("fixed air") by heating calcium carbonate.

Joseph Black was the first to distinguish between the quantity of heat and the "intensity" of heat (temperature) and to recognize *latent heat* absorbed or given off in phase transitions. However, Black believed in the *caloric theory of heat*, which incorrectly asserted that heat was an "imponderable" fluid called "caloric." This incorrect theory was not fully discredited until several decades after Black's death.

Heat Transferred during Temperature Changes

A small amount of heat added to a system is proportional to its change in temperature of the system if there is no phase change or chemical reaction:

$$dq = C dT \tag{2.2-1}$$

where dq is an infinitesimal amount of heat transferred to the object and dT is a resulting infinitesimal change in temperature. The proportionality constant C is called the *heat capacity* of the system.

Equation (2.2-1) does *not* indicate that C is a derivative of q with respect to T. We will see that dq is an inexact differential so that the heat capacity C depends on the way in which the temperature of the system is changed. If the temperature is changed at constant pressure, the heat capacity is denoted by C_P and is called the *heat capacity at constant pressure*. If the temperature is changed at constant volume, the heat capacity is denoted by C_V and is called the *heat capacity at constant volume*. These two heat capacities are not generally equal to each other.

The *specific heat* (better called the *specific heat capacity*) is denoted by c and is defined as the heat capacity per unit mass,

$$c = \left(\frac{C}{m}\right) \tag{2.2-2}$$

where m is the mass of the object. For a pure substance the *molar heat capacity* is denoted by C_m and is defined as the heat capacity divided by the amount of the substance measured in moles. We will use both the molar heat capacity at constant pressure

$$C_\mathrm{P,m} = \left(\frac{C_\mathrm{P}}{n}\right) \tag{2.2-3}$$

and the molar heat capacity at constant volume

$$C_\mathrm{V,m} = \left(\frac{C_\mathrm{V}}{n}\right) \tag{2.2-4}$$

where n is the amount of the substance in moles. Both of these molar heat capacities are intensive variables. It is an experimental fact that *the heat capacity of any object is always positive*. There is no such thing as a system that lowers its temperature when heat is added to it.

If an object is heated from temperature T_1 to temperature T_2 without any chemical reaction or phase change occurring, the quantity of heat transferred to the object is given by

$$q = \int_c dq = \int_{T_1}^{T_2} C dT \tag{2.2-5}$$

If the heat capacity is independent of temperature

$$q = C\int_{T_1}^{T_2} dT = C(T_2 - T_1) = C\Delta T \quad \text{(if } C \text{ is independent of } T\text{)} \tag{2.2-6}$$

A positive value of q *indicates heat transferred to the system and a negative value indicates heat transferred from the system to its surroundings.*

The *calorie* was the first metric unit of heat and was originally defined as the amount of heat required to raise the temperature of 1 gram of liquid water by 1°C at 15°C. The specific heat capacity of liquid water equals $1.00\,\mathrm{cal\,K^{-1}\,g^{-1}}$ at 15°C. The heat capacity of liquid water is nearly temperature-independent and we can use this value for any temperature with good accuracy. The calorie is now defined to equal 4.184 J (exactly) so that heat capacities can be expressed in joules as well as in calories.

EXAMPLE 2.9

a. Find the amount of heat in calories needed to heat 3.20 mol of liquid water from 25.00°C to 95.00°C.

b. The specific heat of aluminum equals $0.215\,\mathrm{cal\,K^{-1}\,g^{-1}}$. Find the final temperature if a piece of aluminum with mass 25.00 g and at an initial temperature of 90.00°C is placed in 100.00 g of liquid water initially at 20.00°C.

Solution

a.

$$c = 1.000\,\mathrm{cal\,K^{-1}\,g^{-1}} = 4.184\,\mathrm{J\,K^{-1}\,g^{-1}}$$

$$q = (3.20\,\mathrm{mol})(18.015\,\mathrm{g\,mol^{-1}})(4.184\,\mathrm{J\,K^{-1}\,g^{-1}})(70.00\,\mathrm{K}) = 1690\,\mathrm{J} = 1.69\,\mathrm{kJ}$$

b.

$$q_{total} = 0 = q_{Al} + q_{water}$$

$$C_{Al} = (0.215\,\mathrm{cal\,K^{-1}\,g^{-1}})(25.00\,\mathrm{g}) = 5.38\,\mathrm{cal\,K^{-1}}$$

$$C_{water} = (1.000\,\mathrm{cal\,K^{-1}\,g^{-1}})(100.00\,\mathrm{g}) = 100.0\,\mathrm{cal\,K^{-1}}$$

$$(5.38\,\mathrm{cal\,K^{-1}})(T - 363.15\,\mathrm{K}) + (100.00\,\mathrm{cal\,K^{-1}})(T - 293.15\,\mathrm{K}) = 0$$

$$(5.38\,\mathrm{cal\,K^{-1}})(T - 1954\,\mathrm{cal}) + (100.00\,\mathrm{cal\,K^{-1}})(T - 29315\,\mathrm{cal}) = 0$$

$$T = \frac{31269\,\mathrm{cal}}{105.36\,\mathrm{cal\,K^{-1}}} = 296.8\,\mathrm{K}$$

$$t_C = 23.6°\mathrm{C}$$

Exercise 2.5

The *British thermal unit* (Btu) was originally defined as the amount of heat required to raise the temperature of 1 pound of water by 1 degree Fahrenheit (°F). It equals 252.0 cal. Express the amount of heat in part a of the previous example in Btu.

The heat capacities of gases are often more strongly temperature dependent than those of liquids. If the heat capacity depends on temperature, it can be represented by a polynomial or other function.

EXAMPLE 2.10

The molar heat capacity of water vapor at a constant pressure of 1.000 atm is represented by

$$C_{\mathrm{P,m}} = 30.54\,\mathrm{J\,K^{-1}\,mol^{-1}} + (0.01029\,\mathrm{J\,K^{-2}\,mol^{-1}})T$$

where T is the Kelvin temperature. Find the amount of heat required to raise the temperature of 2.000 mol of water vapor from 100.0°C to 500.0°C.

Solution

$$q = (2.000\,\mathrm{mol})\int_{373.15\,\mathrm{K}}^{773.15\,\mathrm{K}} \left[30.54\,\mathrm{J\,K^{-1}\,mol^{-1}} + \left(0.01029\,\mathrm{J\,K^{-2}\,mol^{-1}}\right)T\right]dT$$

$$= (2.000\,\mathrm{mol})\left\{(30.54\,\mathrm{J\,K^{-1}\,mol^{-1}})(400\,\mathrm{K})\right.$$

$$\left. + (0.01029\,\mathrm{J\,K^{-2}\,mol^{-1}})\frac{1}{2}\left[(773.15\,\mathrm{K})^2 - (373.15\,\mathrm{K})^2\right]\right\}$$

$$= (2.000\,\mathrm{mol})(12216\,\mathrm{J\,mol^{-1}} + 2359\,\mathrm{J\,mol^{-1}}) = 2.915 \times 10^4\,\mathrm{J}$$

Heat Transferred during Phase Changes

When a phase change occurs, heat can be transferred to or from the system without changing its temperature or its pressure. This heat is sometimes called *latent heat*. The amount of latent heat per unit mass is characteristic of the substance and the phase transition. The latent heat of fusion (melting) is denoted by $\Delta_{\text{fus}}H$. For water at 0°C and a constant pressure of 1.000 atm $\Delta_{\text{fus}}H$ equals 79.72 cal g^{-1}. The latent heat of vaporization (boiling) is denoted by $\Delta_{\text{vap}}H$. For water at 100°C and 1.000 atm $\Delta_{\text{vap}}H$ equals 539.55 cal g^{-1}.

EXAMPLE 2.11

Find the mass of liquid water that can be brought to 100.0°C from 25.00°C by contact with 100.0 g of steam at 100.0°C.

Solution

Define the steam as subsystem 1, the liquid water as subsystem 2. Assume that the heat capacity of liquid water can be assumed to be constant and equal to 4.18 J K^{-1} g^{-1}. The heat lost by subsystem 1 must equal the heat gained by subsystem 2.

$$\Delta_{\text{vap}}H = \left(539.55\ \text{cal g}^{-1}\right)\left(\frac{4.184\ \text{J}}{1\ \text{cal}}\right) = 22575\ \text{J g}^{-1}$$

$$q_1 = -(2257.5\ \text{J g}^{-1})(100.0\ \text{g}) = -225750\ \text{J}$$

$$q_2 = (4.18\ \text{J K}^{-1}\ \text{g}^{-1})\,m(75.00\ \text{K}) = (314\ \text{J g}^{-1})m = -q_1 = 225750\ \text{J}$$

$$m = \frac{225750\ \text{J}}{314\ \text{J g}^{-1}} = 719\ \text{g}$$

PROBLEMS

Section 2.2: Heat

2.10 Calculate the amount of heat required to bring 1.000 mol of water from solid at 0.0°C to gas at 100.0°C at a constant pressure of 1.000 atm. Calculate w for the process.

2.11 Compute the rise in temperature of water if it is brought to rest after falling over a waterfall 50.0 m high. Assume that no heat is transferred to the surroundings.

2.12 The normal boiling temperature of ethanol is 78.5°C, and its molar enthalpy change of vaporization at this temperature is 40.3 kJ mol^{-1}. Find q and w if 3.000 mol of ethanol are vaporized at 78.5°C and a constant pressure of 1.000 atm.

2.13 **a.** If a sample of 2.000 mol of helium gas is isothermally and reversibly expanded at 298.15 K from a pressure of 2.500 atm to a pressure of 1.000 atm, find w and q.

b. If the sample of helium from part a is isothermally and irreversibly expanded from the same initial state to the same final state with $P_{\text{ext}} = 1.000$ atm, find w and q.

2.14 Calculate q and w if 2.000 mol of helium is heated reversibly from a volume of 20.0 L and a temperature of 300.0 K to a volume of 40.0 L and a temperature of 600.0 K. The heating is done in such a way that the temperature remains proportional to the volume.

2.15 The normal boiling temperature of ethanol is 78.5°C, and its molar enthalpy change of vaporization at this temperature is 40.3 kJ mol^{-1}. Find q and w if 3.000 mol of ethanol are reversibly vaporized at 78.5°C and a constant pressure of 1.000 atm. Neglect the volume of the liquid compared with that of the vapor.

2.16 A sample of 2.000 mol of CO_2 gas is heated from 0.00°C to 100.0°C at a constant pressure of 1.000 atm. Find q and w for this process. State any assumptions or approximations.

a. Assume that $C_{P,m}$ is constant and equal to its value in Table A.8 at 298.15 K. Assume that the gas is ideal.

b. Assume that $C_{P,m}$ is given by the formula in Table A.6 with the parameters given there and that the gas is described by the truncated pressure virial equation of state:

$$PV_m = RT + A_2 P$$

and use the fact that $A_2 = B_2$.

2.3 Internal Energy: The First Law of Thermodynamics

Although Lavoisier discredited the phlogiston theory of combustion, which held that combustion was the loss of an "imponderable" fluid called *phlogiston*, he was one of the principal promoters of the equally incorrect *caloric theory of heat* espoused by Black, which asserted that heat was an imponderable fluid called "caloric." The first experimental studies that discredited the caloric theory were done by Count Rumford. Rumford was at one time in charge of manufacturing cannons for the Elector of Bavaria, the ruler who made him a count. Rumford noticed that when a cannon was bored with a dull boring tool, more heat was produced than when a sharp tool was used. He carried out a systematic set of experiments and was able to show by using a very dull tool that there was no apparent limit to the amount of heat that could be generated by friction. He immersed the cannon in water to transfer the heat from the cannon and even generated enough heat to have melted the cannon. Rumford's results showed that "caloric" was not simply being extracted from the cannon, because if caloric existed only a definite amount could be stored in a cannon without melting it. Work must have been converted to heat.

Benjamin Thompson, Count Rumford, 1753–1814, was an American-British physicist who abandoned his family and left America after the American revolution because of his royalist sympathies. He pursued a checkered career in various countries, including Bavaria (where he ingratiated himself with the Elector of Bavaria), France (where he married Lavoisier's widow), and England (where he founded the Royal Institution and hired Humphrey Davy as a lecturer).

Rumford calculated an approximate value for the "mechanical equivalent of heat," or the amount of heat to which a joule of work could be converted. Better values were obtained by Mayer in 1842 and Joule in 1847. Joule carried out experiments in which changes of temperature were produced either by doing work on a system or by heating it. His apparatus is schematically depicted in Figure 2.4. A falling mass turned a stirring paddle in a sample of water, doing work on the liquid. The rise in temperature of the water was measured and the amount of work done by the falling mass was compared with the amount of heat required to produce the same change in temperature. Joule found that the ratio of the work to the amount of heat was always the same, approximately 4.18 J of work for 1.00 cal of heat. The calorie is now defined to be exactly 4.184 J.

Julius Robert Mayer, 1814–1878, was a German physicist originally trained as a physician. He was apparently the first to assert that heat and work are two different means by which energy is transferred, and that energy can neither be created nor destroyed.

EXAMPLE 2.12

Calculate the rise in temperature of 100.0 g of water if the falling weight of Figure 2.4 has a mass of 5.00 kg and drops by 0.800 m. Neglect friction in the pulleys.

Solution

Let $\mathscr{V}$ be the potential energy of the mass.

$$\Delta\mathscr{V} = (5.00\,\mathrm{kg})(9.80\,\mathrm{m\,s^{-2}})(-0.800\,\mathrm{m}) = -39.2\,\mathrm{J}$$

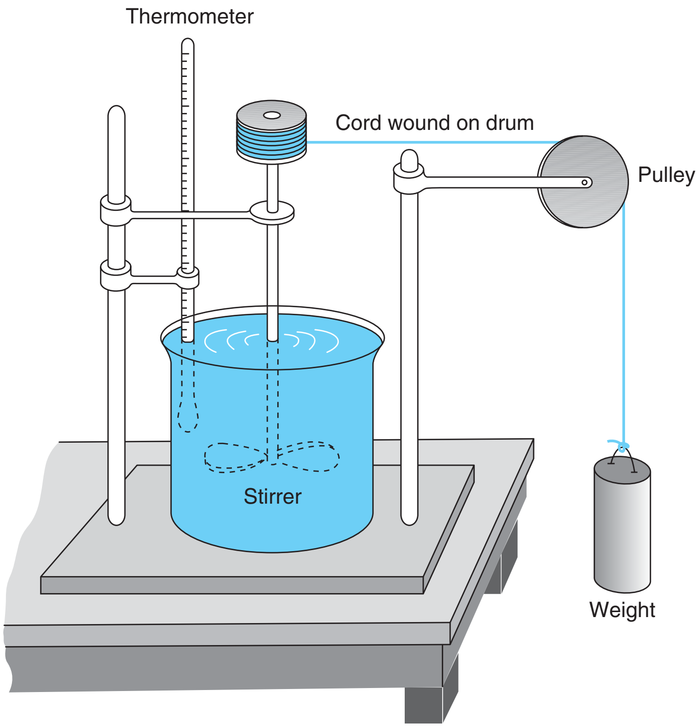

Figure 2.4 Joule's Apparatus for Determining the Mechanical Equivalent of Heat (Schematic).

$$q = C\Delta T = (4.18\,\mathrm{J\,K^{-1}\,g^{-1}})(100.0\,\mathrm{g})\Delta T = 418\,\mathrm{J\,K^{-1}} = -\Delta\mathcal{V}$$

$$\Delta T = \frac{39.2\,\mathrm{J}}{418\,\mathrm{J\,K^{-1}}} = 0.0937\,\mathrm{K}$$

Joule found that there was no detectable difference in the final state of the system whether its temperature was raised by doing work on it or by heating it. This shows that heat and work are two different means of changing a single property of the system. Since energy is defined as the capacity to do work, the work done on the sample of water must have increased its energy. Therefore the heat transferred must also have increased its energy. Joule's sample of water could have kinetic energy if its center of mass were moving, and it could have gravitational potential energy. The work and heat that Joule added to his system did not change either of these forms of energy, so there must be an additional form of energy, which we call the *internal energy* or the *thermodynamic energy* and denote by U. If the system is close to the surface of the earth, the total energy of the system is

$$E_{\mathrm{total}} = \frac{1}{2}mv_c^2 + Mgz_c + U \tag{2.3-1}$$

where m is the mass of the system, v_c is the speed of its center of mass, z_c is the vertical coordinate of its center of mass, and g is the acceleration due to gravity.

Based on the experiments of Rumford, Mayer, Helmholtz, Joule, and many others since the time of Joule, we now state the *first law of thermodynamics* as it applies to a system whose kinetic and potential energy do not change: *For a closed system and for any process that begins and ends with equilibrium states*

$$\boxed{\Delta U = q + w} \tag{2.3-2}$$

where q *is the amount of heat transferred to the system and* w *is the work done on the system and where* ΔU *is the change in the value of* U, *the internal energy, which is a state function:*

$$\Delta U = U(\text{final}) - U(\text{initial}) \tag{2.3-3}$$

Hermann Ludwig von Helmholtz, 1821–1894, was a German physicist and physiologist who studied the energy of muscle contraction and who was one of the first to propose that the energy for all processes on the earth ultimately came from solar radiation.

In spite of the work of Rumford, Mayer, and Joule the credit for announcing the first law of thermodynamics went to Helmholtz.

We accept the first law of thermodynamics as an experimentally established law and accept the internal energy as a state function. This law is a version of the law of conservation of energy, which is a general law of physics to which there are no known exceptions. Apparent violations of energy conservation led particle physicists to search for previously unknown particles that could be transferring energy to or from a system, leading to the discovery of the *neutrino*.[2] Occasionally an unknown inventor in search of gullible investors announces a machine that will produce more energy than it takes in, violating the first law of thermodynamics. Such nonexistent machines are known as *perpetual motion machines of the first kind*.

It is the total energy of a system that is governed by conservation of energy. The first law of thermodynamics as stated in Eq. (2.3-2) applies to a closed system whose center of mass is not accelerated and whose gravitational potential energy does not change. If work is done to change the kinetic or potential energy of the system as a whole this amount of work must be subtracted from the total work done to obtain the amount of work that changes the internal energy.

The internal energy includes the rest-mass energy of the system. We always deal only with energy changes or measure energy relative to some specified reference state in order to avoid including the rest-mass energy in our calculations.

EXAMPLE 2.13

Find the value of the rest-mass energy of 1.000 mol of argon gas, using Einstein's equation, $E = mc^2$.

Solution

$$E_{\text{rest-mass}} = (0.039948\ \text{kg})(2.9979 \times 10^8\ \text{m s}^{-1})^2 = 3.5903 \times 10^{15}\ \text{J}$$

---

[2] E. Fermi, *Z. Physik*, **88**, 161 (1934).

Exercise 2.6

a. Assume that argon is an ideal gas with $C_{V,m} = 12.47\,\mathrm{J\,K^{-1}\,mol^{-1}}$. Find ΔU if 1.000 mol of argon gas is heated at constant volume from 298.15 K to 500.0 K. Find the ratio of this energy difference to the rest-mass energy of the system. Find the difference between the observed mass of the system at 298.15 K and at 500.0 K.

b. Explain why it would be difficult to use values of total energies for chemical purposes if the rest-mass energy were included.

For a one-phase simple system containing one component the equilibrium state is specified by the values of three variables, at least one of which must be extensive. Since the internal energy is a state function we can write

$$U = U(T, V, n) \tag{2.3-4}$$

or

$$U = U(T, P, n) \tag{2.3-5}$$

The internal energy is a state function, but heat and work are not state functions. Because heat and work are both means of changing the value of the internal energy, they do not maintain separate identities after a transfer of energy is finished. The following analogy has been used.[3] Heat transferred to the system is analogous to rain falling on a pond, work done on the system is analogous to the influx of a stream into the pond, and energy is analogous to water in the pond. Evaporation (counted as negative rainfall) is analogous to heat flow to the surroundings, and efflux from the pond into a second stream is analogous to work done on the surroundings. Once rain falls into the pond, it is no longer identifiable as rain, but only as water. Once stream flow is in the pond, it also is identifiable only as water, and not as stream flow. The amount of water in the pond is a well-defined quantity (a state function), but one cannot separately state how much rain and how much stream flow are in the pond. Similarly, there is no such thing as the heat content of a system in a given state and no such thing as the work content of a system in a given state.

The Molecular Interpretation of the Internal Energy

Although the internal energy U is a macroscopic state function, it must include the energies of the atoms or molecules making up the system. In Chapter 9 we will discuss a model system that represents a dilute monatomic gas. In this model, the molecules are represented by structureless mass points with no intermolecular forces. The constant potential energy is set equal to zero. The only energy is the translational kinetic energy of the molecules, and it will be found that the energy of the model gas of N molecules is

$$E = \frac{3}{2}Nk_{\mathrm{B}}T = \frac{3}{2}nRT \quad \text{(dilute monotonic gas)} \tag{2.3-6}$$

---

[3] Herbert B. Callen, *Thermodynamics*, Wiley, New York, 1960, p. 19.

where k_B is Boltzmann's constant, n is the amount of gas in moles, R is the ideal gas constant, and T is the absolute temperature. Since this energy does not include the gravitational potential energy and the kinetic energy of the entire system, this energy is the internal energy of the model gas:

$$U = \frac{3}{2}nRT \quad \text{(dilute monotonic gas)} \tag{2.3-7}$$

Real atoms and molecules are not structureless particles. Real atoms and molecules have translational energy and electronic energy, and molecules also have rotational and vibrational energy. The translational energy of all dilute gases is accurately represented by Eq. (2.3-7). The other contributions to the energy of a dilute gas are studied in statistical mechanics, which is discussed in later chapters of this textbook. At ordinary temperatures the electrons of nearly all atoms and molecules are in their lowest possible energy states, and the electronic energy is a constant, which we can set equal to zero. The vibrational contribution to the energy is not quite so small as the electronic contribution at ordinary temperatures, but we will neglect it for now. Statistical mechanics gives the following results for the rotational contributions:

$$U_{\text{rot}} = nRT \quad \text{(diatomic gas or linear polyatomic gas)} \tag{2.3-8}$$

$$U_{\text{rot}} = \frac{3}{2}nRT \quad \text{(nonlinear polyatomic gas)} \tag{2.3-9}$$

We can now write formulas for the internal energy of dilute gases:

$$U \approx \frac{3}{2}nRT + U_0 \quad \text{(monatomic gas)} \tag{2.3-10}$$

$$U \approx \frac{5}{2}nRT + U_0 \quad \text{(diatomic gas or linear polyatomic gas)} \tag{2.3-11}$$

$$U \approx 3nRT + U_0 \quad \text{(nonlinear polyatomic gas)} \tag{2.3-12}$$

We can set the zero of energy at any convenient energy, so we ordinarily set the constants denoted by U_0 equal to zero. We will later use experimental heat capacity data to test these equations. Near room temperature, Eq. (2.3-10) is a very good approximation and Eqs. (2.3-11) and (2.3-12) are fairly good approximations.

The atoms or molecules of a solid or liquid have the same average translational energy as the molecules of a gas at the same temperature, although the translational motion is a kind of rattling back instead of motion in a straight line between collisions. In some liquids containing small molecules the rotational and vibrational contributions will also be nearly the same, although in other cases the rotation is restricted. However, the molecules of a liquid or solid are packed closely together, and the potential energy makes an important contribution to the internal energy. There is no simple representation of this potential energy, and it is not possible to represent the internal energy of a solid or liquid by a general mathematical formula.

PROBLEMS

Section 2.3: Internal Energy: The First Law of Thermodynamics

2.17 According to special relativity, the total energy of a system is given by

$$E = mc^2$$

where m is the mass of the system and c is the speed of light.

a. Assuming a substance with a molar mass of $0.100\ \mathrm{kg\ mol^{-1}}$, calculate the amount of energy necessary to change the molar mass from its rest-mass value to a value larger by 1.0 ppm (part per million).

b. Compare this energy with a typical chemical bond energy, roughly $400\ \mathrm{kJ\ mol^{-1}}$.

c. If the energy in part a were all kinetic energy of the center of mass of the system, calculate the speed of the center of mass of the system of 1.000 mol.

2.18 **a.** Calculate q, w, and ΔU if 2.000 mol of neon (assumed ideal) is heated at a constant pressure of 1.000 atm from a temperature of 0.00°C to a temperature of 250.00°C.

b. Calculate q, w, and ΔU if the same sample of neon is heated at a constant volume from the same initial state to 250.00°C and is then expanded isothermally to the same final volume as in part a.

2.19 Calculate q, w, and ΔU for melting 100.0 g of ice at 0.0°C and a constant pressure of 1.000 atm. The density of ice is $0.916\ \mathrm{g\ mL^{-1}}$.

2.20 Calculate q, w, and ΔU for vaporizing 2.000 mol of liquid water at 100.0°C to steam at 100.0°C at a constant pressure of 1.000 atm.

2.21 Consider the following three processes: (1) A sample of 2.000 mol of helium gas is isothermally and reversibly expanded from a volume of 10.00 L and a temperature of 400.0 K to a volume of 40.00 L. (2) The same sample is reversibly cooled at a constant volume of 10.00 L from 400.0 K to a temperature of 300.0 K, then expanded reversibly and isothermally to a volume of 40.00 L, and then heated reversibly from 300.0 K to 400.0 K at a constant volume of 40.00 L. (3) The same sample is expanded irreversibly and isothermally at a temperature of 400.0 K from a volume of 10.00 L to a volume of 40.00 L with a constant external pressure of 1.000 atm. Calculate ΔU, q, and w for each process.

2.22 1.000 kg of water is pressurized isothermally at 298.15 K from a pressure of 1.000 atm to a pressure of 10.00 atm. Calculate w for this process. State any assumptions.

2.4 Calculation of Amounts of Heat and Energy Changes

Like work, heat is not a state function. The amount of heat put into a system can depend on the path taken from the initial to the final state, as was the case with work.

Exercise 2.7

Show that if

$$dU = dw + dq$$

and if dU is an exact differential and if dw is an inexact differential then dq must be an inexact differential.

The Heat Capacity at Constant Volume

For a closed simple system at equilibrium n is fixed and we can choose T and V as independent variables:

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,n} dT + \left(\frac{\partial U}{\partial V}\right)_{T,n} dV \quad \text{(closed simple system)} \tag{2.4-1}$$

From the first law of thermodynamics an infinitesimal amount of heat is given by

$$dq = dU - dw = dU + P(\text{transmitted})dV \quad \text{(closed simple system)} \tag{2.4-2}$$

If V is constant, $dV = 0$ and $dw = 0$:

$$dq = dU = \left(\frac{\partial U}{\partial T}\right)_{V,n} dT \quad (V \text{ constant, simple system}) \tag{2.4-3}$$

Comparison of this equation with Eq. (2.2-1) shows that

$$C_{\mathrm{V}} = \left(\frac{\partial U}{\partial T}\right)_{V,n} \quad \text{(simple system)} \tag{2.4-4}$$

where C_{V} is the heat capacity at constant volume. Although the heat capacity in general is not a derivative of any function, the heat capacity at constant volume of a simple closed system is equal to the partial derivative of U with respect to T.

The Ideal Gas as an Example System

It is found experimentally that all gases at sufficiently low pressure (dilute gases) obey the ideal gas equation of state to an adequate approximation:

$$PV \approx nRT \quad \text{(dilute gas)} \tag{2.4-5}$$

Dilute gases also have an internal energy that is independent of the volume or the pressure:

$$U \approx U(T, n) \quad \text{(dilute gas)} \tag{2.4-6}$$

We now define an *ideal gas* as one that obeys Eqs. (2.4-5) and (2.4-6) exactly for all temperatures and pressures. We will show in Chapter 4 that Eq. (2.4-6) is a consequence of Eq. (2.4-5).

To an excellent approximation, the heat capacities at constant volume of monatomic gases are given from Eq. (2.3-10) by

$$C_{\mathrm{V}} = \left(\frac{\partial U}{\partial T}\right)_{V,n} \approx \frac{3}{2}nR \quad \text{(dilute monatomic gas)} \tag{2.4-7}$$

where n is the amount of the gas in moles and R is the ideal gas constant. If the vibrational and electronic motions of molecules can be ignored, Eqs. (2.3-11) and (2.3-12) give

$$C_{\mathrm{V}} \approx \frac{5}{2}nR \quad \text{(diatomic or linear polyatomic dilute gas)} \tag{2.4-8}$$

$$C_V \approx 3nR \quad \text{(nonlinear polyatomic dilute gas)} \tag{2.4-9}$$

This ascribes the internal energy to the translational energy and rotational energy of the molecules. Equations (2.4-8) and (2.4-9) are usable approximations for some substances near room temperature.

Amounts of Heat Transferred to an Ideal Gas

In an isothermal reversible expansion or compression of a closed ideal gas, ΔU vanishes so that

$$q_{\text{rev}} = \Delta U - w_{\text{rev}} = -w_{\text{rev}} = \int_{V_1}^{V_2} P\,dV = nRT \int_{V_1}^{V_2} \frac{1}{V}dV$$

$$q_{\text{rev}} = nRT \ln\left(\frac{V_2}{V_1}\right) \quad \text{(ideal gas; reversible isothermal change)} \tag{2.4-10}$$

where V_2 is the final volume and V_1 is the initial volume. We will apply this equation to dilute gases, but must remember not to apply it to other systems.

EXAMPLE 2.14

Find the amount of heat put into 5.000 mol of argon (assumed ideal) in expanding reversibly and isothermally at 298.15 K from a volume of 20.00 L to 100.00 L.

Solution

$$w = -(5.000\,\text{mol})(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K}) \ln\left(\frac{100.0\,\text{L}}{20.00\,\text{L}}\right) = -19950\,\text{J}$$

$$q = \Delta U - w = -w = 19950\,\text{J}$$

Exercise 2.8

Calculate the amount of heat put into the system of the previous example if it expands irreversibly and isothermally at 298.15 K at a constant external pressure of 1.000 atm from a volume of 20.00 L to a volume of 100.00 L. Assume that $P(\text{transmitted}) = P_{\text{ext}}$. *Hint:* ΔU is the same as in the example because U is a state function.

Since U depends only on T and n for an ideal gas,

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = 0 \quad \text{(ideal gas)} \tag{2.4-11}$$

For an ideal gas with fixed n (a closed system)

$$dU = C_V dT \quad \text{(closed ideal gas)} \tag{2.4-12}$$

Exercise 2.9

The Euler reciprocity relation, Eq. (B-13) of Appendix B, implies that for any system

$$\left(\frac{\partial^2 U}{\partial V \partial T}\right)_n = \left(\frac{\partial^2 U}{\partial T \partial V}\right)_n$$

Show that Eqs. (2.4-11) and (2.4-12) are consistent with this requirement.

The Joule Experiment

The first attempt to determine whether $(\partial U/\partial V)_{T,n}$ vanishes for real gases was made by Joule around 1843. His apparatus is schematically depicted in Figure 2.5. A sample of a gas (the system) was placed in one side of the apparatus and the other side of the apparatus was evacuated. Mechanical vacuum pumps were not yet invented, so a water aspirator was used. The system was allowed to equilibrate and the initial temperature of the apparatus was measured. The stopcock was then opened and the gas expanded irreversibly into the vacuum.

Because the surroundings were not affected during the expansion into a vacuum, w was equal to zero. The gas expanded rapidly so there was little opportunity for heat to be transferred to or from the surroundings, and q therefore vanished to a good approximation. From the first law, ΔU was equal to zero. If a change in temperature of the gas occurred, heat would be transferred to or from the surroundings after the expansion was complete, and the final temperature of the surroundings

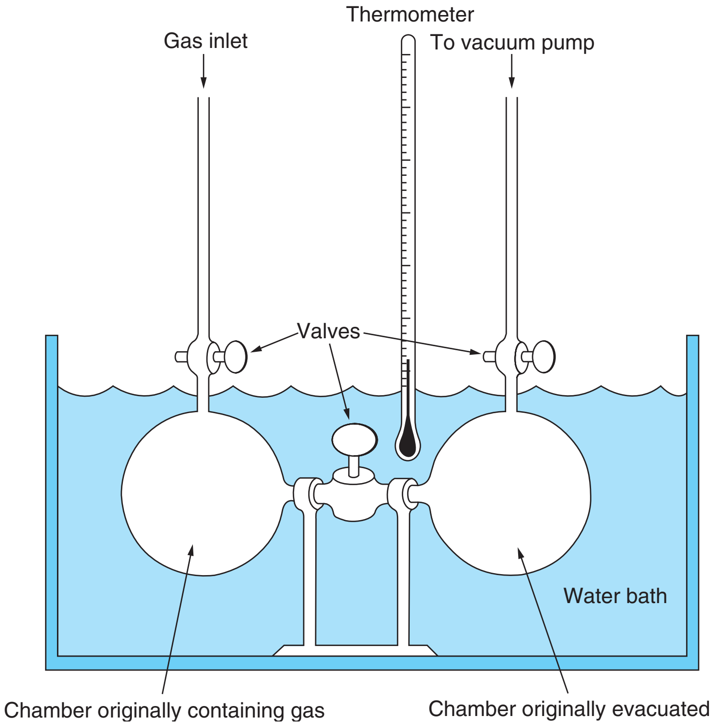

Figure 2.5 The Apparatus for the Joule Experiment (Schematic).

would differ from the initial temperature. If the heat capacity of the apparatus and the heat capacity of the gas are known, the change in temperature of the gas could be calculated.

The Joule experiment was carried out several times with various volumes for the second chamber. The ratio $\Delta T/\Delta V$ would be determined for each experiment and extrapolated to zero value of ΔV, where ΔV is the final volume of the gas minus its initial volume. This extrapolation is equivalent to taking the mathematical limit, so the result is a partial derivative, called the *Joule coefficient* and denoted by μ_{J}:

$$\mu_{\text{J}} = \lim_{\Delta V \to 0} \left(\frac{\Delta T}{\Delta V}\right) = \left(\frac{\partial T}{\partial V}\right)_{U,n} \tag{2.4-13}$$

The Joule coefficient is related to $(\partial U/\partial V)_{T,n}$ by use of the cycle rule, Eq. (B-15), and the reciprocal identity, Eq. (B-8):

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = -\left(\frac{\partial T}{\partial V}\right)_{U,n}\left(\frac{\partial U}{\partial T}\right)_{V,n} = -\mu_{\text{J}} C_{\text{V}} \tag{2.4-14}$$

Exercise 2.10

Verify Eq. (2.4-14).

Joule was unsuccessful in his attempt to measure the Joule coefficient because the changes in temperature that occurred were too small to be measured by his thermometers, even though he used pressures up to 22 atm. Later versions of the experiment with better apparatus have given nonzero values of $(\partial U/\partial V)_{T,n}$ for real gases.

There are better ways than the Joule experiment to determine values of $(\partial U/\partial V)_{T,n}$, and we will discuss them in Chapter 4. Once values for C_{V} and for $(\partial U/\partial V)_{T,n}$ are obtained, ΔU can be calculated for any process that begins with one equilibrium state and ends with another equilibrium state.

EXAMPLE 2.15

If the virial equation of state, Eq. (1.3-3), is truncated at the second term it can be shown that

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = \left(\frac{\partial U_m}{\partial V_{\text{m}}}\right)_{T,n} = \frac{RT^2}{V_{\text{m}}^2}\frac{dB_2}{dT} \tag{2.4-15}$$

where R is the gas constant and where V_{m} is the molar volume. The derivation of this equation is found in Example 4.8. For argon gas at 298.15 K, B_2 is approximately equal to $-15.8\ \text{cm}^3\ \text{mol}^{-1}$ and dB_2/dT is approximately equal to $0.20\ \text{cm}^3\ \text{mol}^{-1}\ \text{K}^{-1}$. Assume that $C_{\text{V,m}} = 3R/2$.

a. Find ΔU, q, and w for a reversible isothermal expansion of 1.000 mol of argon at 298.15 K from a volume of 2.000 L to a volume of 20.00 L. Compare with values obtained assuming ideal gas behavior.

b. Find the value of the Joule coefficient for 1.000 mol of argon at 298.15 K and a volume of 20.000 L.

Solution

Since our system consists of 1.000 mol, we calculate the change in the molar energy, $U_{\mathrm{m}} = U/n$. We also calculate the work done per mole.

a. $$\Delta U_{\mathrm{m}} = \int_c \left(\frac{\partial U_{\mathrm{m}}}{\partial V_{\mathrm{m}}}\right)_{T,n} dV_{\mathrm{m}} = \int_{V_{\mathrm{m1}}}^{V_{\mathrm{m2}}} \left(\frac{RT^2 B_2'}{V_{\mathrm{m}}^2}\right) dV_{\mathrm{m}} = -RT^2 B_2' \left(\frac{1}{V_{\mathrm{m2}}} - \frac{1}{V_{\mathrm{m1}}}\right)$$

$$= -(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}} 298.15\,\mathrm{K})^2 (0.20 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}\,K^{-1}})$$

$$\times \left(\frac{1}{0.0200\,\mathrm{m^3\,mol^{-1}}} - \frac{1}{0.00200\,\mathrm{m^3\,mol^{-1}}}\right)$$

$$= 66.5\,\mathrm{J\,mol^{-1}} \approx 67\,\mathrm{J\,mol^{-1}}$$

$$w = -\int_c P dV_{\mathrm{m}} = -RT \int_{V_{\mathrm{m1}}}^{V_{\mathrm{m2}}} \left(\frac{1}{V_{\mathrm{m}}} - \frac{B_2}{V_{\mathrm{m}}^2}\right) dV_{\mathrm{m}}$$

$$w = -RT \left[\ln\left(\frac{V_{\mathrm{m2}}}{V_{\mathrm{m1}}}\right) - B_2 \left(\frac{1}{V_{\mathrm{m2}}} - \frac{1}{V_{\mathrm{m1}}}\right)\right]$$

$$= -(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})$$

$$\times \left[\ln\left(\frac{20.0\,\mathrm{L}}{2.00\,\mathrm{L}}\right) - \left(-15.8\,\mathrm{cm^3\,mol^{-1}}\right)\left(\frac{1}{20000\,\mathrm{cm^3\,mol^{-1}}} - \frac{1}{2000\,\mathrm{cm^3\,mol^{-1}}}\right)\right]$$

$$= -\left(2479\,\mathrm{J\,mol^{-1}}\right)\left[2.303 - 7.11 \times 10^{-3}\right] = -5690\,\mathrm{J\,mol^{-1}}$$

$$q = \Delta U - w = 67\,\mathrm{J\,mol^{-1}} - (-5690\,\mathrm{J\,mol^{-1}}) = 5757\,\mathrm{J\,mol^{-1}}$$

Compare these values with those obtained if ideal behavior is assumed: $\Delta U = 0$, $w = -5708\,\mathrm{J\,mol^{-1}}$, $q = 5708\,\mathrm{J\,mol^{-1}}$.

b. $$\left(\frac{\partial U}{\partial V}\right)_{T,n} = (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})^2 \left(\frac{0.20 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}\,K^{-1}}}{\left(0.02000\,\mathrm{m^3\,mol^{-1}}\right)^2}\right)$$

$$= 370\,\mathrm{J\,m^{-3}}$$

$$\mu_{\mathrm{J}} = -\left(\frac{\partial U}{\partial V}\right)_{T,n} \frac{1}{C_{\mathrm{V}}} = -\frac{370\,\mathrm{J\,m^{-3}}}{12.17\,\mathrm{J\,K^{-1}}} = -30\,\mathrm{K\,m^{-3}}$$

Exercise 2.11

a. Find ΔU, q, and w for an irreversible isothermal expansion at 298.15 K of 1.000 mol of argon with the same initial and final molar volumes as in the previous example but with a constant external pressure of 1.000 atm. Assume that $P(\text{transmitted}) = P_{\text{ext}}$ and assume the same equation of state as in the previous example. Compare your results with the values obtained in the previous example.

b. Find the change in temperature if 1.000 mol of argon initially at 298.15 K is expanded adiabatically (without any transfer of heat) into a vacuum so that its volume changes from 2.000 L to 20.00 L. Since it expands into a vacuum the surroundings are not affected.

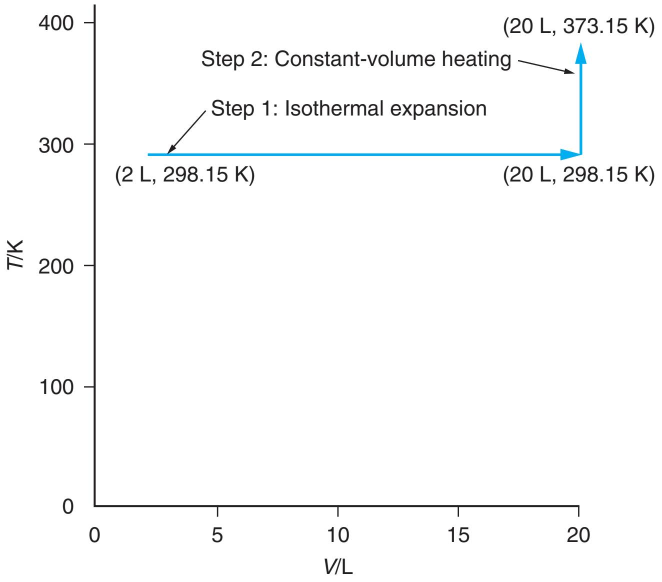

Figure 2.6 The Curve Representing the Path for the ΔU Line Integral.

A change in internal energy for a nonisothermal process can be calculated by carrying out a line integral of dU.

EXAMPLE 2.16

Calculate ΔU for a process that takes 1.000 mol of argon from $T = 298.15\,\mathrm{K}$ and $V = 2.000\,\mathrm{L}$ to $T = 373.15\,\mathrm{K}$ and $V = 20.000\,\mathrm{L}$. Does the result depend on whether the process is reversible?

Solution

Since U is a state function, we can choose any path with the same initial state and final state to calculate ΔU. We choose to integrate along the reversible path shown in Figure 2.6, consisting of an isothermal expansion and a constant-volume change in temperature. The first step of the path is that of the previous example, so ΔU_1, the change in energy for that part, is equal to $67\,\mathrm{J\,mol^{-1}}$. For the second step

$$\Delta U_2 = \int_{T_1}^{T_2} C_V dT = C_V(T_2 - T_1) = nC_{V,m}(T_2 - T_1)$$

$$= (1.000\,\mathrm{mol})\left(\frac{3}{2}\right)R(T_2 - T_1) = \left(12.472\,\mathrm{J\,K^{-1}}\right)(75.0\,\mathrm{K}) = 935\,\mathrm{J}$$

$$\Delta U = \Delta U_1 + \Delta U_2 = 67\,\mathrm{J} + 935\,\mathrm{J} = 1002\,\mathrm{J}$$

Because U is a state function, the result does not depend on whether the actual process is reversible, so long as the initial and final states are metastable or equilibrium states.

Exercise 2.12

a. Calculate q and w for the reversible process that follows the path used in the solution of the previous example.

b. Calculate q and w for the reversible process corresponding to the following path. Step 1: The system is heated from 298.15 K to 373.15 K at a constant volume of 2.000 L; step 2: It is then expanded isothermally to a volume of 20.000 L.

c. Comment on the difference between the q and w values for parts a and b. What is the value of ΔU for the process of part b?

Reversible Adiabatic Processes

An *adiabatic process* is one in which no heat is transferred to or from a closed system, so that dq is equal to zero for every infinitesimal step of the process:

$$dU = dq + dw = dw \quad \text{(adiabatic process)} \tag{2.4-16}$$

Consider a reversible adiabatic process of an ideal gas.

$$dU = C_V dT \quad \text{(closed ideal gas, reversible process)} \tag{2.4-17}$$

$$dw = -PdV = -\frac{nRT}{V}dV \quad \text{(closed ideal gas, reversible process)} \tag{2.4-18}$$

Because $dq = 0$ for an adiabatic process, we equate dU and dw:

$$C_V dT = -\frac{nRT}{V}dV \quad \text{(closed ideal gas, reversible adiabatic process)} \tag{2.4-19}$$

This is a *differential equation* that can be solved to give T as a function of V if the dependence of C_V on T and V is known.

We first assume that C_V is constant. We can solve Eq. (2.4-19) by separation of variables. We divide by T to separate the variables (remove any V dependence from the left-hand side and any T dependence from the right-hand side):

$$\frac{C_V}{T}dT = -\frac{nR}{V}dV \tag{2.4-20}$$

Because each integrand contains only one variable we can integrate Eq. (2.4-20) from the initial state, denoted by V_1 and T_1, to the final state, denoted by V_2 and T_2. A definite integration gives

$$C_V \ln\left(\frac{T_2}{T_1}\right) = -nR\ln\left(\frac{V_2}{V_1}\right)$$

We divide by C_V and take the exponential (antilogarithm) of both sides of this equation:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{nR/C_V} = \left(\frac{V_1}{V_2}\right)^{R/C_{V,m}} \quad \text{(reversible adiabatic process, ideal gas, } C_V \text{ constant)} \tag{2.4-21a}$$

If the initial values V_1 and T_1 are specified, this equation gives T_2 as a function of V_2. If we drop the subscripts on V_2 and T_2, we can write Eq. (2.4-21a) in the form:

$$T = T(V) = T_1\left(\frac{V_1}{V}\right)^{R/C_{V,m}} \quad \text{(reversible adiabatic process, ideal gas, } C_V \text{ constant)} \tag{2.4-21b}$$

Equation (2.4-21) can be used for a reversible adiabatic compression as well as for an expansion. It is an example of an important fact that holds for any system, not just an ideal gas: *For a reversible adiabatic process in a simple system the final temperature is a function of the final volume for a given initial state.* All of the possible final state points for reversible adiabatic processes starting at a given initial state lie on a single curve in the state space, called a *reversible adiabat*. This fact will be important in our discussion of the second law of thermodynamics in Chapter 3.

EXAMPLE 2.17

A system consisting of 2.000 mol of argon expands adiabatically and reversibly from a volume of 5.000 L and a temperature of 373.15 K to a volume of 20.00 L. Find the final temperature. Assume argon to be ideal with C_V equal to $3nR/2$.

Solution

$$T = T_1\left(\frac{V_1}{V}\right)^{nR/C_V} = (373.15\ \text{K})\left(\frac{5.000\ \text{L}}{20.00\ \text{L}}\right)^{2/3} = 148.1\ \text{K}$$

Figure 2.7 shows the reversible adiabat that represents the final temperature as a function of the final volume for this example. For each initial state, there is only one such curve.

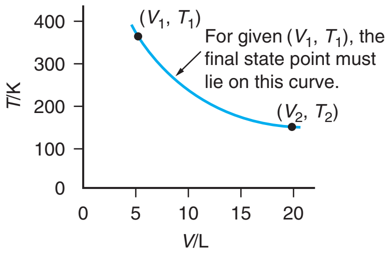

Figure 2.7 Final Temperature as a Function of Final Volume for the Adiabatic Expansion of an Ideal Gas.

Exercise 2.13

Find the volume to which the system of the previous example must be adiabatically and reversibly expanded in order to reach a final temperature of 273.15 K.

Exercise 2.14

Find the final temperature, ΔU, and w for a reversible adiabatic compression of 1.000 mol of helium gas (assumed ideal with $C_V = 3nR/2$) from a volume of 20.00 L and a temperature of 298.15 K to a volume of 10.00 L.

An equation analogous to Eq. (2.4-19) can be written for a real gas if C_V is independent of V and if an adequate equation of state is available. For a gas obeying the van der Waals equation of state it can be shown (see Problem 4.10) that

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = \left(\frac{\partial U_m}{\partial V_m}\right)_{T,n} = \frac{a}{V_m^2} \quad \text{(van der Waals gas)} \tag{2.4-22}$$

This can be used to derive an equation analogous to Eq. (2.4-21). For each such equation, there is a unique curve in the V–T plane containing all of the points that can be reached by adiabatic reversible processes from a given initial state.

EXAMPLE 2.18

Show that for a reversible adiabatic process the van der Waals gas obeys

$$C_V dT = -\frac{nRT}{V - nb} dV \tag{2.4-23}$$

Solution

Consider a system containing 1.000 mol of gas. Using Eq. (2.4-22) we can write for a closed system

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,n} dT + \left(\frac{\partial U}{\partial V}\right)_{T,n} dV = C_V dT + \frac{a}{V_m^2} dV$$

For a reversible process

$$dw = -P dV = -\left(\frac{RT}{V_m - b} - \frac{a}{V_m^2}\right) dV$$

For an adiabatic process

$$dU = C_V dT + \frac{a}{V_m^2} dV = dw = -\left(\frac{RT}{V_m - b} - \frac{a}{V_m^2}\right) dV$$

so that when terms are canceled

$$C_V dT = -\frac{RT}{V_m - b} dV$$

Exercise 2.15

Show that for a reversible adiabatic process in a van der Waals gas with constant $C_{V,m}$,

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_1 - nb}{V_2 - nb}\right)^{nR/C_V} \tag{2.4-24}$$

EXAMPLE 2.19

Find the final temperature for the process of Example 2.17, using Eq. (2.4-24) instead of Eq. (2.4-21), but still assuming that $C_V = 3nR/2$.

Solution

From Table A.3, the van der Waals parameter b is equal to $3.219 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}$ for argon.

$$T_2 = (373.15\ \mathrm{K})\left(\frac{5.000 \times 10^{-3}\ \mathrm{m^3\ mol^{-1}} - 3.22 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}}{20.00 \times 10^{-3}\ \mathrm{m^3\ mol^{-1}} - 3.22 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}}\right)^{2/3}$$

$$= 147.6\ \mathrm{K}$$

This value differs from the ideal value by 0.5 K.

If the molar heat capacity of a van der Waals gas is represented by

$$C_{\text{V,m}} = \alpha + \beta T \tag{2.4-25}$$

the equation analogous to Eqs. (2.4-21) and (2.4-24) is

$$\frac{T_2}{T_1}\exp\left(\frac{\beta(T_2 - T_1)}{\alpha}\right) = \left(\frac{V_{\text{m}1} - b}{V_{\text{m}2} - b}\right)^{R/\alpha} \tag{2.4-26}$$

Exercise 2.16

Show that Eq. (2.4-26) is correct.

For a reversible adiabatic process, not only is T a function of V, but P is also a function of V. For an ideal gas with constant heat capacity, we can substitute the ideal gas equation, $T = PV/nR$, into Eq. (2.4-21) to obtain

$$P = P_1\left(\frac{V_1}{V}\right)^{1+R/C_{\text{V,m}}} \tag{2.4-27}$$

The temperature can also be considered to be a function of the pressure:

$$T = T_1\left(\frac{P}{P_1}\right)^{R/(C_{\text{V,m}}+R)} \tag{2.4-28}$$

Exercise 2.17

Verify Eqs. (2.4-27) and (2.4-28).

EXAMPLE 2.20

The “Santa Ana” winds of California are winds that begin in the mountains and drop to an altitude near sea level. Assume that the air begins at a pressure of 0.81 atm (roughly the barometric pressure at 6000 feet above sea level) and a temperature of 25°C and that it is adiabatically and reversibly compressed to a pressure of 1.00 atm as it moves to near sea level. Assume that air is an ideal gas with $C_{\text{V,m}} = 5R/2$. Find the final temperature. This approximate treatment ignores other factors that raise the temperature, such as frictional heating as the air passes along the ground.

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/(C_{\text{V,m}}+R)} = \left(\frac{1.00\ \text{atm}}{0.81\ \text{atm}}\right)^{2/7} = 1.062$$

$$T_2 = (1.062)(298\ \text{K}) = 316\ \text{K}$$

$$t_{C,2} = 43^\circ\text{C}$$

Exercise 2.18

a. Using Eq. (2.4-27) find the final pressure for the adiabatic expansion of Example 2.17. Use the ideal gas law to find the initial pressure.

b. Use the ideal gas law and the final temperature from Example 2.17 to find the final pressure.

Irreversible Adiabatic Processes

We have assumed that we can equate $P(\text{transmitted})$ and P_{ext} for a relatively slow irreversible expansion processes. As an example, consider the expansion of Example 2.17 if it occurs irreversibly with a constant external pressure.

EXAMPLE 2.21

A system consisting of 2.000 mol of argon expands adiabatically and irreversibly from a volume of 5.000 L and a temperature of 373.15 K to a volume of 20.00 L at a constant $P_{\text{ext}} = 1.000$ atm. Find the final temperature, assuming that $P(\text{transferred}) = P_{\text{ext}}$. Assume argon to be ideal with $C_V = 3nR/2$.

Solution

$$w = -P_{\text{ext}} \int dV = -P_{\text{ext}} \Delta V$$

$$= (1.000\,\text{atm})\left(101325\,\text{Pa atm}^{-1}\right)(15.00\,\text{L})\left(0.001\,\text{m}^3\,\text{L}^{-1}\right) = 1520\,\text{J}$$

$$\Delta U = w = -1520\,\text{J}$$

$$\Delta T = \frac{\Delta U}{C_V} = \frac{-1520\,\text{J}}{(1.5)(1.000\,\text{mol})\left(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}\right)} = 121.9\,\text{K}$$

$$T_{\text{final}} = 373.15\,\text{K} - 121.9\,\text{K} = 251.3\,\text{K}$$

This final temperature is higher than the temperature reached reversibly, and this will always be the case.

Exercise 2.19

For an irreversible adiabatic expansion of 5.00 mol of neon from an initial temperature of 500.0 K and an initial volume of 50.00 L to a final volume of 100.00 L, find the final temperature, ΔU, and w if $P(\text{transferred}) = 1.000$ atm. Compare with the values for a reversible expansion from the same initial state to the same final volume.

We cannot equate P_{ext} and $P(\text{transmitted})$ or P and $P(\text{transmitted})$ for an irreversible compression, but we can assert that $P(\text{transmitted})$ will be greater than P. We will not attempt calculations for irreversible adiabatic compressions.

Exercise 2.20

Since $dw > -PdV$ for an irreversible compression process, show that the final temperature for an irreversible adiabatic compression of an ideal gas must be higher than the final temperature of the reversible adiabatic compression with the same initial state and the same final volume.

PROBLEMS

Section 2.4: Calculation of Amounts of Heat and Energy Changes

2.23 **a.** Calculate the Joule coefficient for carbon dioxide at 298.15 K, using the truncated virial equation of state. Approximate dB_2/dT by the quotient of finite differences of the values for 0°C and 50°C. Use the value of $C_{P,m}$ in Table A.8 to obtain a value of $C_{V,m}$. State any assumptions or approximations.

b. Find the final temperature if 1.000 mol of carbon dioxide at 298.15 K and 33 atm is expanded into an evacuated vessel with a volume of 20.00 L.

2.24 A sample of 3.00 mol of argon is heated from 25.00°C to 100.00°C, beginning at a pressure of 1.000 atm (101,325 Pa).

a. Find q, w, and ΔU if the heating is done at constant volume.

b. Find q, w, and ΔU if the heating is done at constant pressure.

2.25 Find the final pressure if 2.000 mol of nitrogen is expanded adiabatically and reversibly from a volume of 20.00 L to a volume of 40.00 L, beginning at a pressure of 2.500 atm. Assume nitrogen to be ideal with $C_{V,m} = 5R/2$.

2.26 A sample of 1.000 mol of neon gas is expanded from a volume of 5.000 L and a temperature of 400.0 K to a volume of 8.000 L.

a. Find the final temperature if the expansion is adiabatic and reversible. Assume that the gas is ideal and that $C_V = 3nR/2 = \text{constant}$.

b. Find ΔU, q, and w for the expansion of part a.

c. Find ΔU, q, w, and the final temperature if the expansion is adiabatic but at a constant external pressure of 1.000 atm, starting from the same state as in part a and ending at the same volume as in part a.

d. Find ΔU, q, and w if the expansion is reversible and isothermal, starting at the same state as in part a and ending at the same volume as in part a. State any assumptions and approximations.

2.27 Find the final temperature and the final volume if 2.000 mol of nitrogen is expanded adiabatically and reversibly from STP to a pressure of 0.600 atm. Assume nitrogen to be ideal with $C_{V,m} = 5R/2$.

2.28 1.000 mol of carbon dioxide is expanded adiabatically and reversibly from 298.15 K and a molar volume of 5.000 L mol^{-1} to a volume of 20.00 L mol^{-1}.

a. Find the final temperature, assuming the gas to be ideal with $C_{V,m} = 5R/2 = \text{constant}$.

b. Find the final temperature, assuming the gas to be described by the van der Waals equation with $C_{V,m} = 5R/2 = \text{constant}$.

2.29 A sample of 20.00 g of acetylene, C_2H_2, is expanded reversibly and adiabatically from a temperature of 500 K and a volume of 25.00 L to a volume of 50.00 L. Use the value of $C_{V,m}$ obtained from the value in Table A.8 for 500 K with the assumption that acetylene is an ideal gas.

a. Find the percent difference between this value of $C_{V,m}$ that you obtain and $5R/2$.

b. Find the final temperature.

c. Find the values of ΔU, q, and w for the process.

2.30 **a.** A sample of 2.000 mol of argon gas is adiabatically and reversibly expanded from a temperature of 453.15 K and a volume of 15.0 L to a final temperature of 400.0 K. Find the final volume, ΔU,

w, and q for the process. Assume argon to be ideal and assume that $C_{V,m} = \frac{3}{2}R$.

b. Consider an irreversible adiabatic expansion with the same initial state and the same final volume, carried out with P(transferred) $= 1.000$ atm. Find the final temperature, ΔU, w, and q for this process.

2.31 **a.** Find the final temperature, ΔU, q, and w for the reversible adiabatic expansion of O_2 gas from 373.15 K and a molar volume of 10.00 L to a molar volume of 20.00 L. Assume the gas to be ideal with $C_{V,m} = 5R/2$.

b. Repeat the calculation of part a for argon instead of oxygen. Assume that $C_{V,m} = 3R/2$.

c. Explain in physical terms why your answers for parts a and b are as they are.

2.32 **a.** 2.000 mol of O_2 gas is compressed isothermally and reversibly from a pressure of 1.000 atm and a temperature of 100.0°C to a pressure of 3.000 atm. Find ΔU, q, w, and ΔH for this process. State any assumptions or approximations. Assume that the gas is ideal.

b. The same sample is compressed adiabatically and reversibly from a pressure of 1.000 atm and a temperature of 100.0°C to a pressure of 3.000 atm. Find ΔU, q, and w for this process. State any assumptions or approximations. Assume that $C_{V,m} = 5RT/2$ and that the gas is ideal.

2.33 For each of the following monatomic gases, calculate the percent difference between the tabulated value of $C_{P,m}$ in Table A.8 in the appendix and $5R/2$ for each temperature in the table.

a. Ar

b. H

c. He

d. O

e. C

2.34 For each of the following diatomic gases, calculate the percent difference between the tabulated value of $C_{P,m}$ in Table A.8 in the appendix and $7R/2$ for each temperature in the table.

a. CO

b. O_2

c. NO

d. HCl

2.35 A sample of 1.000 mol of water vapor originally at 500.0 K and a volume of 10.0 L is expanded reversibly and adiabatically to a volume of 20.0 L. Assume that the water vapor obeys the van der Waals equation of state and that its heat capacity at constant volume is described by Eq. (2.4-25) with $\alpha = 22.2\ \mathrm{J\,K^{-1}\,mol^{-1}}$ and $\beta = 10.3 \times 10^{-3}\ \mathrm{J\,K^{-2}\,mol^{-1}}$.

a. Find the final temperature.

b. Find the value of w and ΔU.

c. Compare your values with those obtained if water vapor is assumed to be an ideal gas and its heat capacity at constant pressure is constant and equal to its value at 500 K.

2.36 **a.** A sample of 2.000 mol of H_2 gas is reversibly and isothermally expanded from a volume of 20.00 L to a volume of 50.00 L at a temperature of 300 K. Find q, w, and ΔU for this process.

b. The same sample of H_2 gas is reversibly and adiabatically (without any transfer of heat) expanded from a volume of 20.00 L and a temperature of 300 K to a final volume of 50.00 L. Find the final temperature. Find q, w, and ΔU for this process.

2.37 A sample of 2.000 mol of N_2 gas is expanded from an initial pressure of 1.000 atm and an initial temperature of 450.0 K to a pressure of 0.400 atm.

a. Find the final temperature if the expansion is adiabatic and reversible. Assume that $C_V = 5nR/2$, so that $\gamma = 7/5 = 1.400$.

b. Find ΔU, q, and w for the expansion of part a.

c. Find ΔU, q, w, and the final temperature if the expansion is adiabatic but at a constant external pressure of 0.400 atm, starting from the same state as in part a and ending at the same volume as in part a.

d. Find ΔU, q, and w if the expansion is reversible and isothermal, ending at the same pressure as in part a.

2.5 Enthalpy

Many liquid systems in the laboratory are contained in vessels that are open to the atmosphere and are thus maintained at a nearly constant pressure.[4] For convenient analysis of constant-pressure processes we define a new variable, denoted by H and called the enthalpy:

$$\boxed{H = U + PV \quad \text{(definition of the enthalpy)}} \tag{2.5-1}$$

The enthalpy is a state function because U, P, and V are state functions.

Consider a simple system with a pressure that remains equal to a constant external pressure. We will refer to these conditions simply as *constant-pressure conditions* and assume that $P(\text{transferred}) = P = P_{\text{ext}}$. For a process under such conditions,

$$dw = -P_{\text{ext}}dV = -PdV \quad \text{(constant pressure)} \tag{2.5-2}$$

This expression for dw is the same as that for reversible processes, Eq. (2.1-11). We do not assert that all processes that occur at constant pressure are reversible processes, but only that the reversible expression for dw applies. If the volume changes from V_1 to V_2 at constant pressure,

$$w = \int_c dw = -\int_c P_{\text{ext}}dV = -\int_c PdV = -P(V_2 - V_1)$$
$$\text{(simple system, constant pressure)} \tag{2.5-3}$$

The heat transferred to the system is given by

$$dq = dU - dw = dU + PdV \quad \text{(simple system, constant pressure)} \tag{2.5-4}$$

From Eq. (2.5-1)

$$dH = dU + PdV + VdP \tag{2.5-5}$$

At constant pressure the VdP term vanishes, so that

$$\boxed{dq = dH \quad \text{(simple system, constant pressure)}} \tag{2.5-6}$$

For a finite process,

$$\boxed{q = \Delta H \quad \text{(simple system, constant pressure)}} \tag{2.5-7}$$

Although q is generally path-dependent, it is path-independent for constant-pressure processes, for which $q = \Delta H$. Enthalpy changes of constant-pressure processes are sometimes called "heats" of the processes.

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[4] The extreme observed sea-level barometric pressures are 1083.8 mbar (1.069 atm) and 877 mbar (0.866 atm): *Guinness Book of World Records*, Guinness, 1998, p. 95.

The Heat Capacity at Constant Pressure

The heat capacity at constant pressure is given by

$$C_{\mathrm{P}} = \lim_{\Delta T \to 0} \left(\frac{q}{\Delta T} \right)_{P,n} = \lim_{\Delta T \to 0} \left(\frac{\Delta H}{\Delta T} \right)_{P,n} = \left(\frac{\partial H}{\partial T} \right)_{P,n} \tag{2.5-8}$$

The heat capacity at constant pressure is the most commonly measured heat capacity for solids and liquids. We now obtain an expression for the difference between C_{P} and C_{V}. We begin with

$$C_{\mathrm{P}} = \left(\frac{\partial H}{\partial T} \right)_{P,n} = \left(\frac{\partial (U + PV)}{\partial T} \right)_{P,n} = \left(\frac{\partial U}{\partial T} \right)_{P,n} + P \left(\frac{\partial V}{\partial T} \right)_{P,n} \tag{2.5-9}$$

There is no $V(\partial P/\partial T)$ term because P is held constant in the differentiation. Equation (B-7) of Appendix B gives, as an example of the *variable-change identity*, the relation

$$\left(\frac{\partial U}{\partial T} \right)_{P,n} = \left(\frac{\partial U}{\partial T} \right)_{V,n} + \left(\frac{\partial U}{\partial V} \right)_{T,n} \left(\frac{\partial V}{\partial T} \right)_{P,n} \tag{2.5-10}$$

We substitute this equation into Eq. (2.5-9) and use the fact that $C_{\mathrm{V}} = (\partial U/\partial T)_{V,n}$ to write

$$C_{\mathrm{P}} = C_{\mathrm{V}} + \left(\left(\frac{\partial U}{\partial V} \right)_{T,n} + P \right) \left(\frac{\partial V}{\partial T} \right)_{P,n} \tag{2.5-11}$$

For an ideal gas, $(\partial U/\partial V)_{T,n} = 0$ and $(\partial V/\partial T)_{P,n} = nR/P$, so that

$$C_{\mathrm{P}} = C_{\mathrm{V}} + nR \quad \text{(ideal gas)} \tag{2.5-12}$$

The physical explanation for this difference between C_{P} and C_{V} is that heating an ideal gas at constant volume does not work on the surroundings. In heating at constant pressure some of the heat is turned into work against the external pressure as the gas expands. A larger amount of heat is therefore required for a given change in the temperature than for a constant-volume process. In Chapter 4 we will be able to show that C_{P} cannot be smaller than C_{V} for any system.

Equations (2.3-10) through (2.3-12) together with Eq. (2.5-12) give the following relations for dilute gases:

$$C_{\mathrm{P}} \approx \frac{5}{2} nR \quad \text{(dilute monatomic gases)} \tag{2.5-13a}$$

$$C_{\mathrm{P}} \approx \frac{7}{2} nR \quad \text{(dilute diatomic or linear polyatomic gases)} \tag{2.5-13b}$$

$$C_{\mathrm{P}} \approx 4nR \quad \text{(dilute nonlinear polyatomic gases)} \tag{2.5-13c}$$

Equation (2.5-13a) is a good approximation. The other two equations are fairly good approximations near room temperature.

Exercise 2.21

a. Look up $C_{\mathrm{P,m}}$ for helium, neon, and argon at 298.15 K in Appendix A. Compare each value with $5R/2$. Your results will test our assertion in Eq. (2.5-13a).

b. Look up $C_{\mathrm{P,m}}$ for N_2, O_2, and CO at 298.15 K in Appendix A. Compare each value with $7R/2$.

If the approximations in Eq. (2.5-13) are not adequate, $C_{\mathrm{P,m}}$ can be represented by the polynomial

$$C_{\mathrm{P,m}} = a + bT + cT^{-2} \tag{2.5-13d}$$

Table A.6 in Appendix A gives the values of the constant parameters a, b, and c for several gases.

Exercise 2.22

Evaluate $C_{\mathrm{P,m}}$ for CO_2 at 298.15 K, 500 K, and 1000 K using the formula of Eq. (2.5-13d) and compare your result with the values in Table A.8.

The ratio of the constant-pressure heat capacity to the constant-volume heat capacity is denoted by γ:

$$\gamma = \frac{C_{\mathrm{P}}}{C_{\mathrm{V}}} \quad \text{(definition of } \gamma\text{)} \tag{2.5-14}$$

The values in Eq. (2.5-13) give the following approximations:

$$\gamma \approx 5/3 \quad \text{(dilute monatomic gas)} \tag{2.5-15a}$$

$$\gamma \approx 7/5 \quad \text{(dilute diatomic or linear polyatomic gases)} \tag{2.5-15b}$$

$$\gamma \approx 4/3 \quad \text{(dilute nonlinear polyatomic gases)} \tag{2.5-15c}$$

For many liquids and solids near room temperature, heat capacities are nearly constant and $C_{\mathrm{P,m}}$ and $C_{\mathrm{V,m}}$ are nearly equal to each other, so that

$$\gamma \approx 1 \quad \text{(many liquids and solids)} \tag{2.5-15d}$$

Equations (2.4-21), (2.4-27), and (2.4-28) can be written in terms of γ as follows:

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1} \tag{2.5-16a}$$

$$\frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{\gamma} \tag{2.5-16b}$$

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{1-1/\gamma} \tag{2.5-16c}$$

Exercise 2.23

Verify Eq. (2.5-16).

Pierre Louis Dulong, 1785–1838, was a French chemist originally trained as a physician. Alexis Thérèse Petit, 1791–1820, was a French physicist.

For many solids in which a single atom is the formula unit, the molar heat capacity at room temperature is approximately equal to $3R = 24.94\ \mathrm{J\ K^{-1}\ mol^{-1}}$. This is the *law of Dulong and Petit*, which is a good approximation near room temperature and becomes more nearly accurate at higher temperatures.

EXAMPLE 2.22

Find the percent differences between $C_{\mathrm{P,m}}$ of solid silver and $3R$ at 298.15 K.

Solution

From the appendix, $C_{\mathrm{P,m}} = 25.351\ \mathrm{J\ K^{-1}\ mol^{-1}}$

$$\text{percent difference} = \frac{25.351\ \mathrm{J\ K^{-1}\ mol^{-1}} - 24.944\ \mathrm{J\ K^{-1}\ mol^{-1}}}{24.944\ \mathrm{J\ K^{-1}\ mol^{-1}}} \times 100\% = -1.6\%$$

Exercise 2.24

Repeat the calculation of the previous example for iron.

The Joule–Thomson Experiment

For an ideal gas U depends only on T and n, so that H depends only on T and n:

$$H = U + PV = U(T, n) + nRT = H(T, n) \quad \text{(ideal gas)} \tag{2.5-17}$$

Therefore,

$$\left(\frac{\partial H}{\partial P}\right)_{T,n} = 0 \quad \text{(ideal gas)} \tag{2.5-18}$$

Joule and Thomson carried out experiments in the 1850s to determine the value of $(\partial H/\partial P)_{T,n}$ for real gases. They used an apparatus equivalent to that sketched in Figure 2.8. This apparatus consists of two cylinders fitted with pistons and a porous

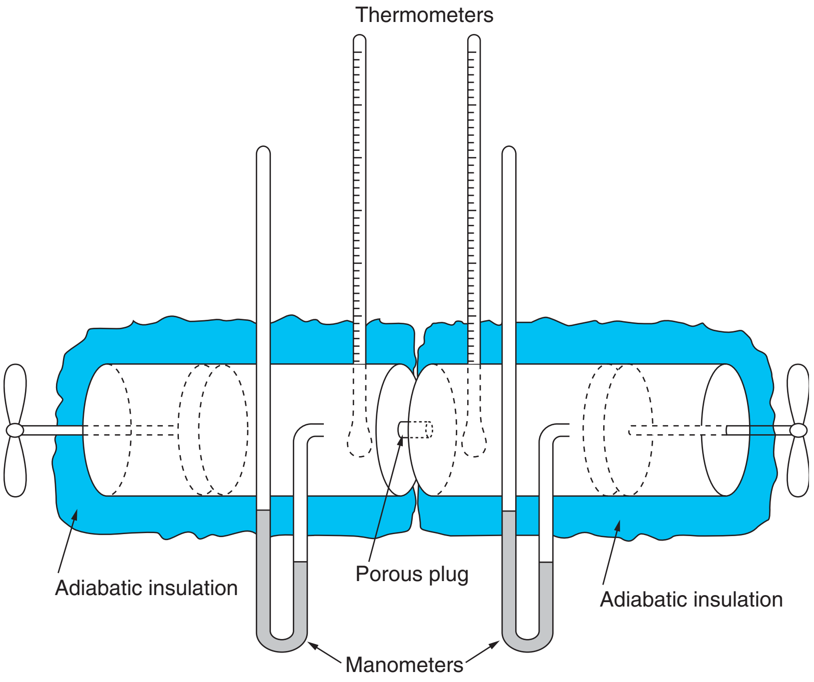

Figure 2.8 The Apparatus for the Joule–Thomson Experiment (Schematic).

plug separating the two cylinders. Each side has a manometer to measure the pressure and a thermometer to measure the temperature of the gas. The entire apparatus is adiabatically insulated from the surroundings. During the experiment, one of the pistons is moved into its cylinder and the other piston is withdrawn in a way such that the pressure on each side remains constant as the gas flows irreversibly through the porous plug. If the process is slow enough a time-independent nonequilibrium state (a steady state) will be attained with a different constant temperature and constant pressure on each side. Several experiments are carried out on a given gas with different values of the pressure difference. The *Joule–Thomson coefficient* μ_{JT} is defined as the extrapolated limit

William Thomson, 1824–1907, later Lord Kelvin, was a great Scottish mathematician and physicist who was an early supporter of Joule and became a close personal friend. He had many accomplishments, including the absolute temperature scale and the introduction of the Bell telephone into Great Britain. However, he is reported to have stated around 1880 that all possible discoveries in physics had already been made.

$$\mu_{\mathrm{JT}} = \lim_{P_{\mathrm{R}}\to P_{\mathrm{L}}}\left(\frac{T_{\mathrm{R}} - T_{\mathrm{L}}}{P_{\mathrm{R}} - P_{\mathrm{L}}}\right) = \lim_{\Delta P\to 0}\left(\frac{\Delta T}{\Delta P}\right) \quad \text{(definition of } \mu_{\mathrm{JT}}\text{)} \tag{2.5-19}$$

where the subscripts R and L indicate the right and left sides of the apparatus. We now show that the limit in this equation is a partial derivative at fixed enthalpy.

We choose as our system a sample of n moles of gas that flows through the porous plug after a steady state is established. We assume that irreversible processes take place only within the porous plug so that the initial and final states of our system can be treated as equilibrium states. The work done on the gas on the left side is given by

$$w_{\mathrm{L}} = -\int_{V_{\mathrm{L}1}}^{V_{\mathrm{L}2}} P_{\mathrm{L}} dV_{\mathrm{L}} = -P_{\mathrm{L}}(V_{\mathrm{L}2} - V_{\mathrm{L}1}) \tag{2.5-20}$$

where V_{L1} is the initial volume of the left side of the apparatus and V_{L2} is the final volume of the left side of the apparatus. The work done on the gas on the right side is given by

$$w_R = -\int_{V_{R1}}^{V_{R2}} = -P_R(V_{R2} - V_{R1}) \tag{2.5-21}$$

Prior to the transfer, the pressure P_1 of the system was equal to P_L, and the initial volume of the system must have been equal to the magnitude of the change in volume of the left side:

$$V_1 = V_{L1} - V_{L2} \tag{2.5-22}$$

The final pressure P_2 must be equal to P_R, and the final volume V_2 must be equal to the change in volume of the right side:

$$V_2 = V_{R2} - V_{R1} \tag{2.5-23}$$

From Eqs. (2.5-20) through (2.5-23), the total work done on the system is

$$w = w_L + w_R = P_1V_1 - P_2V_2 = -\Delta(PV) \tag{2.5-24}$$

Exercise 2.25

a. Show that for any change in state

$$\Delta(PV) = P_1\Delta V + V_1\Delta P + (\Delta P\Delta V) \tag{2.5-25}$$

b. When can $\Delta(PV)$ equal $P\Delta V$? When can it equal $V\Delta P$? When can it equal $P\Delta V + V\Delta P$?

Because the apparatus is adiabatically insulated from the laboratory, no heat is transferred to or from the laboratory. Also, no heat is transferred from the system to the apparatus after the steady state is established, because the chamber on the right is then at the same temperature as the gas that exits from the plug. Therefore,

$$q = 0 \tag{2.5-26}$$

$$\Delta U = q + w = w = -\Delta(PV) \tag{2.5-27}$$

$$\Delta H = \Delta U + \Delta(PV) = 0 \tag{2.5-28}$$

The Joule–Thomson process therefore occurs at constant enthalpy, and the Joule–Thomson coefficient is equal to a partial derivative at constant H and n:

$$\boxed{\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_{H,n}} \tag{2.5-29}$$

We can use the cycle rule, Eq. (B-15) of Appendix B, to write

$$\left(\frac{\partial H}{\partial P}\right)_{T,n} = -\left(\frac{\partial H}{\partial T}\right)_{P,n}\left(\frac{\partial T}{\partial P}\right)_{H,n} - C_{P}\mu_{JT} \tag{2.5-30}$$

The Joule–Thomson coefficient of an ideal gas vanishes because $(\partial H/\partial P)_{T,n}$ vanishes. Joule and Thomson found that the Joule–Thomson coefficient is measurably different from zero for ordinary gases at ordinary pressures. It depends on temperature and is positive at room temperature for most common gases except for hydrogen and helium. Even for these gases it is positive at some range of temperatures below room temperature. This means that for some range of temperature any gas cools on expansion through a porous plug. Expansion of a gas can be used to cool the gas enough to liquefy part of it, and the final step in the production of liquid nitrogen or liquid helium is ordinarily carried out in this way.

EXAMPLE 2.23

For air at 300 K and 25 atm, $\mu_{JT} = 0.173\ \mathrm{K\ atm^{-1}}$. If a Joule–Thomson expansion is carried out from a pressure of 50.00 atm to a pressure of 1.00 atm, estimate the final temperature if the initial temperature is equal to 300 K.

Solution

$$\Delta T \approx \left(\frac{\partial T}{\partial P}\right)_{T,n} \Delta P = \left(0.173\ \mathrm{K\ atm^{-1}}\right)(49\ \mathrm{atm}) = 8\ \mathrm{K}$$

$$T_2 \approx 292\ \mathrm{K}$$

The molecular explanation for the fact that the Joule–Thomson coefficient is positive at sufficiently low temperature is that at low temperatures the attractive intermolecular forces are more important than the repulsive intermolecular forces. When the gas expands, work must be done to overcome the attractions and the potential energy increases. If no heat is added, the kinetic energy decreases and the temperature decreases.

PROBLEMS

Section 2.5: Enthalpy

2.38 Show that if $dU = dq + dw$, if dU is exact, and if dq is inexact, then dw must be inexact.

2.39 The work done on a nonsimple system such as a spring or a rubber band is given by

$$dw = P(\text{transferred})dV + \tau dL$$

where τ is the tension force and L is the length of the spring or rubber band. One must specify whether a heat capacity is measured at constant τ or at constant L, in addition to specifying constant P or constant V. Find a relation analogous to Eq. (2.5-11) relating $C_{P,\tau}$ and $C_{P,L}$.

2.40 **a.** The Joule–Thomson coefficient of nitrogen gas at 50 atm and 0°C equals .044 K atm^{-1}. Estimate the final temperature if nitrogen gas is expanded through a porous plug from a pressure of 60.0 atm to a pressure of 1.00 atm at 0°C.

b. Estimate the value of $(\partial H_m/\partial P)_T$ for nitrogen gas at 50 atm and 0°C. State any assumptions.

2.41 A sample of 3.00 mol of argon is heated from 25.00°C to 100.00°C, beginning at a pressure of 1.000 atm (101,325 Pa).

a. Find q, w, ΔU, and ΔH if the heating is done at constant volume.

b. Find q, w, ΔU, and ΔH if the heating is done at constant pressure.

2.6 Calculation of Enthalpy Changes of Processes without Chemical Reactions

The most useful calculations of ΔH are for constant-pressure processes in closed systems. If no phase change or chemical reaction occurs,

$$\Delta H = q = \int_c dH = \int_{T_1}^{T_2} \left(\frac{\partial H}{\partial T}\right)_{P,n} dT = \int_{T_1}^{T_2} C_P dT \qquad (2.6\text{-}1)$$

The integration in this formula is carried out on a constant-pressure path.

EXAMPLE 2.24

a. Find a formula for ΔH for the heating of a sample of a gas from temperature T_1 to temperature T_2 at constant pressure if $C_{P,m}$ is represented by

$$C_{P,m} = a + bT + cT^{-2}$$

b. Find ΔH and q for the heating of 2.000 mol of oxygen gas from 25.00°C to 100.00°C at a constant pressure of 1.000 atm.

Solution

a.

$$\Delta H = q = n\int_{T_1}^{T_2}\left(a + bT + cT^{-2}\right)dT$$

$$= n\left[a(T_2 - T_1) + \frac{b}{2}\left(T_2^2 - T_1^2\right) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]$$

b. Using the values of the parameters for oxygen from Table A.6,

$$\Delta H = q = (2.000\ \text{mol})\left\{\left(30.0\ \text{J K}^{-1}\ \text{mol}^{-1}\right)(75.00\ \text{K})\right.$$
$$+ \frac{1}{2}\left(4.18\times 10^{-3}\ \text{J K}^{-2}\ \text{mol}^{-1}\right)(373.15\ \text{K})^2 - (298.15\ \text{K})^2$$
$$\left. - (-1.67\times 10^5\ \text{J K mol}^{-1})\left(\frac{1}{373.15\ \text{K}} - \frac{1}{298.15\ \text{K}}\right)\right\}$$

$$= (2.000\ \text{mol})\left(2250\ \text{J mol}^{-1} + 105\ \text{J mol}^{-1} - 113\ \text{J mol}^{-1}\right) = 4484\ \text{J}$$

Exercise 2.26

Using the values of a, b, and c from Table A.6, calculate the values of $C_{P,m}$ for O_2 gas at 298.15 K, 500.0 K, 1000.0 K, and 2000.0 K. Compare with the values in Table A.8.

A transition between two phases of a single substance takes place at a definite temperature if the pressure is fixed. For example, if the pressure is fixed at 1.000 atm, the boiling temperature of water is 100.00°C or 373.15 K and its freezing temperature is 0.00°C or 273.15 K. Table A.7 gives specific enthalpy changes (enthalpy changes per gram) for reversible fusion (melting) and vaporization (boiling) transitions for a number of substances at a constant pressure of 1.000 atm.

To obtain the molar enthalpy change from the specific enthalpy change, one multiplies the specific enthalpy change by the molar mass in grams per mole. To calculate ΔH for the fusion of n moles of a substance we write

$$\Delta H = n\Delta_{\mathrm{fus}}H_{\mathrm{m}} \tag{2.6-2}$$

where $\Delta_{\mathrm{fus}}H_{\mathrm{m}}$ is the molar enthalpy change of fusion. For the vaporization of n moles of a substance

$$\Delta H = n\Delta_{\mathrm{vap}}H_{\mathrm{m}} \tag{2.6-3}$$

where $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ is the molar enthalpy change of vaporization of the substance.

EXAMPLE 2.25

Find ΔH and q if 2.000 mol of liquid water at 0.00°C is reversibly frozen to ice at 0.00°C at a constant pressure of 1.000 atm.

Solution

$$q = \Delta H = (2.000\,\mathrm{mol})\left(18.02\,\mathrm{g\,mol^{-1}}\right)\left(-333.5\,\mathrm{J\,g^{-1}}\right) = -1.202 \times 10^{4}\,\mathrm{J}$$

Since the enthalpy is a state function, we can calculate ΔH for a given process by calculating ΔH for any process having the same initial and final states.

EXAMPLE 2.26

Calculate ΔH for the change of state of 1.000 mol of helium from a volume of 5.000 L and a temperature of 298.15 K to a volume of 10.000 L and a temperature of 373.15 K. Assume that $C_{P,m} = 5R/2$ and assume that the gas is ideal.

Solution

The value of ΔH is path-independent. For purposes of calculation, assume that the gas first expands isothermally and reversibly to a pressure equal to the final pressure (step 1), and is then heated at constant pressure to its final temperature (step 2). Since the enthalpy depends only on n and T, ΔH for the first step vanishes. For the second step

$$\Delta H_2 = \int_{T_1}^{T_2} C_P dT = nC_{P,m}\Delta T$$

$$= (1.000\,\text{mol})\left(\frac{5}{2}\right)\left(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}\right)(75.00\,\text{K}) = 1559\,\text{J}$$

$$\Delta H = \Delta H_1 + \Delta H_2 = 0 + 1559\,\text{J} = 1559\,\text{J}$$

Although ΔH is the same for any process with the same initial and final states as the overall process in Example 2.26, q and w are dependent on the path of a particular process. If the pressure is not constant during the entire process, q is not necessarily equal to ΔH.

EXAMPLE 2.27

Find q and w for the process used in the calculation of Example 2.26.

Solution

We first find V_2 and P_2, the volume and pressure at the end of step 2. From the ideal gas law,

$$V_2 = (10.00\,\text{L})\frac{298.15\,\text{K}}{373.15\,\text{K}} = 7.990\,\text{L}$$

$$P_2 = \frac{(1.000\,\text{mol})\left(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}\right)(298.15\,\text{K})}{0.007990\,\text{m}^3} = 3.103 \times 10^5\,\text{Pa}$$

$$q_1 = (1.000\,\text{mol})\left(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}\right)(298.15\,\text{K})\ln\left(\frac{7.990\,\text{L}}{5.000\,\text{L}}\right) = 1162\,\text{J}$$

Because the pressure was constant during step 2,

$$q_2 = \Delta H_2 = 1559\,\text{J}$$

$$q = q_1 + q_2 = 1162\,\text{J} + 1559\,\text{J} = 2721\,\text{J}$$

This differs considerably from the value of ΔH, 1559 J.

We can calculate w for the process. For the first step

$$w_1 = \Delta U_1 - q_1 = -q_1 = -1162\,\text{J}$$

For the second step, we let V_3 be the final volume

$$w_2 = -\int_{V_2}^{V_3} PdV = -P\int_{V_2}^{V_3} dV = -P\Delta V$$

$$= -\left(3.103 \times 10^5\,\text{Pa}\right)\left(0.01000\,\text{m}^3 - 0.007990\,\text{m}^3\right) = -623.6\,\text{J}$$

$$w = w_1 + w_2 = -1162\,\text{J} - 624\,\text{J} = -1786\,\text{J}$$

Exercise 2.27

a. Find ΔU for the process of the previous example.

b. Find ΔH, q, and w for the process in which the system of the previous example is first heated at constant volume from 298.15 K to 373.15 K and then expanded isothermally from a volume of 5.000 L to a volume of 10.000 L.

Enthalpy Changes for Irreversible Processes

Consider an irreversible process that begins with an equilibrium or metastable state and ends with an equilibrium state. To calculate ΔH for such an irreversible process, we find a reversible process with the same initial and final states, calculate ΔH for that process, and assign that value to the irreversible process, using the fact that H is a state function.

EXAMPLE 2.28

Find ΔH and q if 2.000 mol of supercooled liquid water at $-15.00°\mathrm{C}$ freezes irreversibly at a constant pressure of 1.000 atm and a temperature of $-15.00°\mathrm{C}$. Assume that $C_{\mathrm{P,m}}$ of liquid water is constant and equal to $75.48\ \mathrm{J\ K^{-1}\ mol^{-1}}$, and that $C_{\mathrm{P,m}}$ of ice is constant and equal to $37.15\ \mathrm{J\ K^{-1}\ mol^{-1}}$.

Solution

We assume that the supercooled water is metastable and treat it as though it were at equilibrium. We calculate ΔH along the reversible path shown in Figure 2.9. Step 1 is the reversible heating of the supercooled liquid to 0.00°C, the equilibrium freezing temperature. Step 2 is the reversible freezing of the system at 0.00°C, and step 3 is the reversible cooling of the solid to $-15.00°\mathrm{C}$. The enthalpy change for the irreversible process is equal to the enthalpy change of this reversible process.

$$\Delta H_1 = \int_{258.15\ \mathrm{K}}^{273.15\ \mathrm{K}} C_{\mathrm{P}}(\mathrm{l})dT = C_{\mathrm{P}}(\mathrm{l})\Delta T$$

$$= (2.000\ \mathrm{mol})\left(75.48\ \mathrm{J\ K^{-1}\ mol^{-1}}\right)(15.00\ \mathrm{K}) = 2264\ \mathrm{J}$$

The enthalpy change of step 2 was calculated in an earlier example:

$$\Delta H_2 = -12020\ \mathrm{J}$$

The enthalpy change of step 3 is similar to that of step 1.

$$\Delta H_3 = \int_{273.15\ \mathrm{K}}^{258.15\ \mathrm{K}} C_{\mathrm{P}}(\mathrm{s})dT = C_{\mathrm{P}}(\mathrm{s})\Delta T$$

$$= (2.000\ \mathrm{mol})\left(37.15\ \mathrm{J\ K^{-1}\ mol^{-1}}\right)(15.00\ \mathrm{K}) = 1114\ \mathrm{J}$$

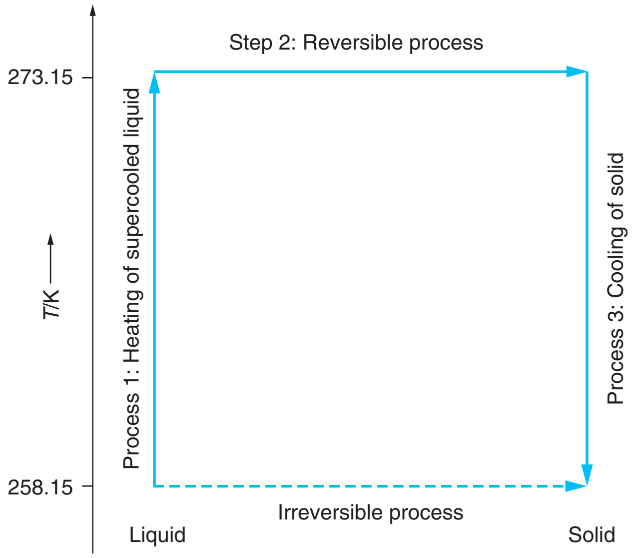

Figure 2.9 Irreversible and Reversible Paths for Example 2.28.

The total enthalpy change is

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = -10870\,\text{J} = -10.87\,\text{kJ}$$

Because the process is at constant pressure, $q = \Delta H$.

PROBLEMS

Section 2.6: Calculation of Enthalpy Changes of Processes without Chemical Reactions

2.42 **a.** Calculate ΔH and ΔU for heating 1.00 mol of argon from 100 K to 300 K at a constant pressure of 1.00 atm. State any assumptions.

b. Calculate ΔH and ΔU for heating 1.00 mol of argon from 100 K to 300 K at a constant volume of 30.6 L.

c. Explain the differences between the results of parts a and b.

2.43 **a.** Find q, w, ΔU, and ΔH for heating 1.000 mol of neon gas from 273.15 K to 373.15 K at a constant pressure of 1.000 atm. State any approximations and assumptions.

b. Find q, w, ΔU, and ΔH for heating 1.000 mol of neon gas from 273.15 K to 373.15 K at a constant volume of 22.4 L. State any approximations and assumptions.

2.44 Supercooled steam is condensed irreversibly but at a constant pressure of 1.000 atm and a constant temperature of 96.5°C. Find the molar enthalpy change. State any assumptions and approximations.

2.45 The enthalpy change of fusion of mercury is 2331 J mol^{-1}. Find ΔH for converting 100.0 g of solid mercury at −75.0°C to liquid mercury at 25.0°C at a constant pressure of 1.000 atm. Assume that the heat capacities are constant and equal to their values in Table A.6 of the appendix.

2.46 Find ΔH if 100.0 g of supercooled liquid mercury at −50.0°C freezes irreversibly at constant temperature and a constant pressure of 1.000 atm. The enthalpy change of fusion at the normal melting temperature is 2331 J mol^{-1}.

Assume that the heat capacities are constant and equal to their values in Table A.6 of the appendix.

2.47 Find the value of q and the value of ΔH if 2.000 mol of solid water (ice) at -10.00°C is turned into liquid water at 80.00°C, with the process at a constant pressure of 1.000 atm. Assume that the heat capacities are constant and equal to their values in Table A.6 of the appendix.

2.7 Calculation of Enthalpy Changes of a Class of Chemical Reactions

A chemical reaction involves the breaking of some chemical bonds and/or the formation of other chemical bonds. The breaking of bonds requires an input of energy and the formation of bonds gives off energy, so that nearly every constant-temperature chemical reaction is accompanied by energy and enthalpy changes. If the system gives off heat when a reaction takes place at constant temperature, the reaction is called *exothermic*. If the system absorbs heat at constant temperature, the reaction is called *endothermic*.

In this chapter we will consider only chemical reactions in which every reactant or product is either a gas or a pure liquid or solid, and we will assume that all gases are ideal gases. Three reactions in this class are:

$$2\mathrm{H_2(g)} + \mathrm{O_2(g)} \longrightarrow 2\mathrm{H_2O(l)} \tag{2.7-1}$$

$$\mathrm{CaCO_3(s)} \longrightarrow \mathrm{CaO(s)} + \mathrm{CO_2(g)} \tag{2.7-2}$$

$$\mathrm{N_2O_4(g)} \longrightarrow 2\mathrm{NO_2(g)} \tag{2.7-3}$$

The label "s" refers to solid, the label "l" refers to liquid, and the label "g" refers to gas. We will consider solution reactions in a later chapter.

Physical chemists like to write a single equation that can apply to every possible case. In order to do this, we write chemical reaction equations with the symbols for all substances on the right-hand side and replace the ⟶ symbol by an equals sign. The three reactions of Eqs. (2.7-1) through (2.7-3) become

$$0 = 2\mathrm{H_2O(l)} - 2\mathrm{H_2(g)} - \mathrm{O_2(g)} \tag{2.7-4}$$

$$0 = \mathrm{CaO(s)} + \mathrm{CO_2(g)} - \mathrm{CaCO_3(s)} \tag{2.7-5}$$

$$0 = 2\mathrm{NO_2(g)} - \mathrm{N_2O_4(g)} \tag{2.7-6}$$

We denote the stoichiometric coefficient of substance number i by ν_i or by $\nu(\mathscr{F}_i)$, where $\mathscr{F}_i$ represents the chemical formula of the substance. If substance number i is a product, ν_i is positive, and if substance number j is a reactant, ν_j is negative. If $\mathrm{NO_2}$ is called substance number 1 and $\mathrm{N_2O_4}$ is called substance number 2, then $\nu_1 = \nu(\mathrm{NO_2}) = 2$ and $\nu_2 = \nu(\mathrm{N_2O_4}) = -1$ in Eq. (2.7-6). If the number of substances involved in the reaction is represented by s, we number the substances from 1 to s, and represent any chemical reaction by the equation

$$\boxed{0 = \sum_{i=1}^{s} \nu_i \mathscr{F}_i} \tag{2.7-7}$$

In a mixture of ideal gases, each substance behaves as though the others were absent. If all substances are either pure liquids or solids or ideal gases the enthalpy of the system is a sum of contributions of the separate substances

$$H = \sum_{i=1}^{s} n_i H_{\mathrm{m}}(i) \tag{2.7-8}$$

where $H_{\mathrm{m}}(i)$ is the molar enthalpy (enthalpy per mole) of substance number i and n_i is the amount (in moles) of that substance.

Consider a chemical reaction that begins with reactants in equilibrium or metastable states at some particular temperature and pressure and ends with products in equilibrium states at the same temperature and pressure. The enthalpy change of the reaction is given by

$$\Delta H = H(\text{final}) - H(\text{initial}) = \sum_{i=1}^{s} \Delta n_i H_{\mathrm{m}}(i) \tag{2.7-9}$$

where Δn_i is the change in the amount of substance number i. We say that *one mole of reaction* occurs if

$$\Delta n_i = \nu_i \tag{2.7-10}$$

for each substance. That is, a number of moles of a product appears that is equal to that product's stoichiometric coefficient, and a number of moles of a reactant disappear that are equal to the magnitude of its stoichiometric coefficient. For 1 mol of reaction,

$$\Delta H = \sum_{i=1}^{s} \nu_i H_{\mathrm{m}}(i) \tag{2.7-11}$$

We use dimensionless stoichiometric coefficients. One can think of the units of ν_i as moles of substance i per mole of reaction. The enthalpy change in Eq. (2.7-11) has the units of $\mathrm{J\,mol^{-1}}$ (meaning joules per mole of the reaction as written). If all stoichiometric coefficients are doubled, ΔH for the reaction doubles. When we give a value of ΔH for a reaction, it is always for 1 mol of the reaction as the reaction equation is written.

The molar enthalpy of any substance depends on its state. The *standard state* of a liquid or solid substance is specified to be the pure substance at a fixed pressure of exactly 1 bar (100,000 Pa), which we denote by P°. The standard state for a gas is defined to be the corresponding ideal gas at pressure P°. The difference between the molar enthalpy of a real gas at 1 bar pressure and the corresponding ideal gas at 1 bar is numerically very small, but we will discuss this difference in a later chapter. If substance number i is in its standard state, its molar enthalpy is denoted by $H^\circ_{\mathrm{m}}(i)$. A *standard-state reaction* is one in which all substances are in their standard states before and after the reaction. The enthalpy change for a standard-state reaction is denoted by ΔH°. The standard-state pressure was at one time defined to equal 1 atm (101,325 Pa). The difference in numerical values is small, and the formulas involving P° are the same with either choice. For highly accurate work, one must determine which standard pressure was used for an older set of data.

Actual values for standard-state molar enthalpies are not available because an arbitrary constant can be added to each internal energy without any physical effect. We use the *standard-state enthalpy change of formation* to calculate ΔH° for chemical reactions. The standard-state enthalpy change of formation of substance i is denoted by $\Delta_f H^\circ(i)$ and is defined to be the standard-state enthalpy change of the chemical reaction that forms 1 mol of substance i in the specified phase from the appropriate elements in the standard state in their most stable forms. For example, the most stable form of carbon at 1 bar is graphite, not diamond, so that standard enthalpy changes of formation are relative to graphite, not diamond.[5] Standard-state enthalpy changes of formation for a number of substances are listed in Table A.8 of Appendix A.

The enthalpy change for 1 mol of any standard-state reaction in our restricted class is given by

$$\boxed{\Delta H^\circ = \sum_{i=1}^{s} \nu_i \Delta_f H^\circ(i)} \tag{2.7-12}$$

We can show this equation to be correct from the fact that the enthalpy is a state function. Let process 1 convert the reactants into elements in their most stable form. The standard-state enthalpy change for process 1 is

$$\Delta H_1^\circ = H_{\text{elements}} - H_{\text{reactants}} = \sum_{\substack{i=1 \\ \text{(reactants only)}}}^{s} \nu_i \Delta_f H^\circ(i) \tag{2.7-13}$$

This process is equivalent to the reverse of all of the formation reactions multiplied by the magnitude of the stoichiometric coefficients. The sign in front of the sum in Eq. (2.7-13) is positive because the stoichiometric coefficients are negative.

The products of the reaction must contain the same elements in the same amounts as in the reactants. Let process 2 be the production of the products of the reaction of interest from the elements produced in process 1. The standard-state enthalpy change of process 2 is

$$\Delta H_2^\circ = \sum_{\substack{i=1 \\ \text{(products only)}}}^{s} \nu_i \Delta_f H^\circ(i) \tag{2.7-14}$$

Germain Henri Hess, 1802–1850, was a Swiss-Russian chemist whose law first showed that thermodynamics applies to chemistry.

We now invoke *Hess's law*, which states: *The enthalpy change of any process that is equivalent to successively carrying out two other processes is equal to the sum of the enthalpy changes of those two processes.* This law is a consequence of the fact that enthalpy is a state function, so that its change is path-independent.

Our reaction is equivalent to the sum of processes 1 and 2. By Hess's law,

$$\Delta H^\circ = \sum_{\substack{i=1 \\ \text{(reactants only)}}}^{s} \nu_i \Delta_f H^\circ(i) + \sum_{\substack{i=1 \\ \text{(products only)}}}^{s} \nu_i \Delta_f H^\circ(i) = \sum_{i=1}^{s} \nu_i \Delta_f H^\circ(i) \tag{2.7-15}$$

where the final sum includes all substances involved in the reaction. This equation is the same as Eq. (2.7-12). This equation applies only if the final temperature is equal to the initial temperature.

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[5] An exception is made for phosphorus, which has several solid forms (called allotropes). The less reactive red form is specified instead of the more reactive white form, which is more stable in the absence of other substances.

EXAMPLE 2.29

Find the standard-state enthalpy change of the reaction of Eq. (2.7-6) at 298.15 K, using values of enthalpy changes of formation from Table A.8.

Solution

$$\begin{aligned}\Delta H^\circ &= 2\Delta_f H^\circ(\mathrm{NO_2}) + (-1)\Delta_f H^\circ(\mathrm{N_2O_4}) \\ &= 2(33.095\ \mathrm{kJ\ mol^{-1}}) - (9.079\ \mathrm{kJ\ mol^{-1}}) = 57.11\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

If the formation reaction for a substance cannot actually be carried out, the enthalpy change of formation can be calculated from the enthalpy change of other reactions that can be combined to give the reaction of interest, using Hess's law.

EXAMPLE 2.30

The standard-state enthalpy change of combustion of methane at 298.15 K equals $-890.36\ \mathrm{kJ\ mol^{-1}}$, with liquid water as one of the products. Find the enthalpy change of formation of methane at 298.15 K using the enthalpy changes of formation of H_2O and CO_2.

Solution

The balanced reaction equation is

$$0 = \mathrm{CO_2(g)} + 2\mathrm{H_2O(l)} - \mathrm{CH_4(g)} - 2\mathrm{O_2(g)}$$

so that

$$\begin{aligned}-890.36\ \mathrm{kJ\ mol^{-1}} &= \Delta_f H^\circ(\mathrm{CO_2}) + 2\Delta_f H^\circ(\mathrm{H_2O}) \\ &\quad + (-1)\Delta_f H^\circ(\mathrm{CH_4}) + (-2)\Delta_f H^\circ(\mathrm{O_2})\end{aligned}$$

Because gaseous O_2 is the most stable form of oxygen at 298.15 K, $\Delta_f H^\circ(\mathrm{O_2}) = 0$. Using values of the enthalpy changes of formation of the other substances,

$$\begin{aligned}\Delta_f H^\circ(\mathrm{CH_4}) &= 890.36\ \mathrm{kJ\ mol^{-1}} + (-393.522\ \mathrm{kJ\ mol^{-1}}) \\ &\quad + 2(-285.830\ \mathrm{kJ\ mol^{-1}}) + (-2)(0) \\ &= -74.82\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

This value agrees fairly well with the value in Table A.8, $-74.873\ \mathrm{kJ\ mol^{-1}}$.

Enthalpy Changes at Various Temperatures

An enthalpy change for a reaction at a temperature other than a temperature found in a table can be calculated from heat capacity data. Consider the processes shown in Figure 2.10. The reaction at temperature T_2 is the process whose enthalpy change we want to find. Call it process 2. An alternate pathway with the same initial and final states consists of processes 3, 1, and 4. Process 3 is the change in temperature of the reactants from T_2 to T_1. Process 1 is the chemical reaction at temperature T_1, with a known enthalpy change. Process 4 is the change in temperature of the products from

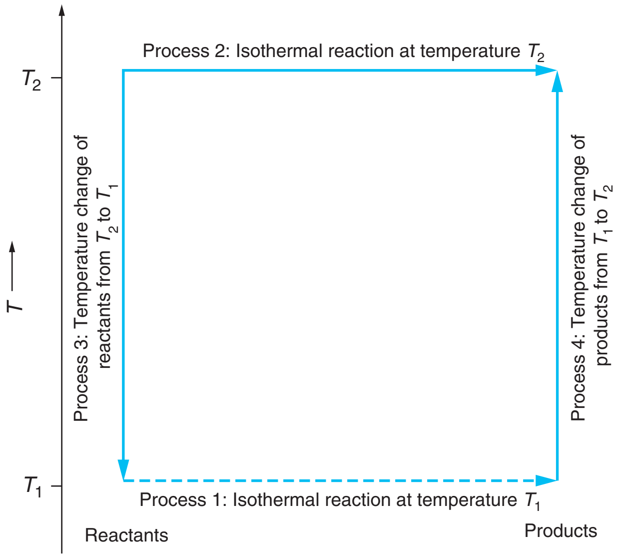

Figure 2.10 The Process to Calculate $\Delta H(T_2)$ from $\Delta H(T_1)$.

T_1 to T_2. According to Hess's law $\Delta H(T_2)$ is equal to the sum of the enthalpy changes of processes 1, 2, and 3:

$$\Delta H(T_2) = \Delta H_3 + \Delta H_1 + \Delta H_4 = \Delta H_3 + \Delta H(T_1) + \Delta H_4 \qquad (2.7\text{-}16)$$

For 1 mol of reaction, process 3 consists of changing the temperature of an amount of each reactant equal to the magnitude of its stoichiometric coefficient, so that

$$\Delta H_3 = \underset{\text{(reactants only in sum)}}{\int_{T_2}^{T_1} \sum_{i=1}^{s} |\nu_i|\, C_{\mathrm{P,m}}(i) dT} = \underset{\text{(reactants only in sum)}}{\int_{T_1}^{T_2} \sum_{i=1}^{s} \nu_i C_{\mathrm{P,m}}(i) dT} \qquad (2.7\text{-}17)$$

where $C_{\mathrm{P,m}}(i)$ is the molar heat capacity of substance i. The second equality comes from interchanging the limits of integration and realizing that the stoichiometric coefficients of reactants are negative. Process 4 is the change in temperature of the products from T_1 to T_2, so that

$$\Delta H_4 = \underset{\text{(products only in sum)}}{\int_{T_1}^{T_2} \sum_{i=1}^{s} \nu_i C_{\mathrm{P,m}}(i) dT} \qquad (2.7\text{-}18)$$

The sums in Eqs. (2.7-17) and (2.7-18) can be combined to give the expression

$$\Delta H(T_2) = \Delta H(T_1) + \int_{T_1}^{T_2} \Delta C_{\mathrm{P}} dT \qquad (2.7\text{-}19)$$

where

$$\Delta C_{\mathrm{P}} = \sum_{i=1}^{s} \nu_i C_{\mathrm{P,m}}(i) \qquad (2.7\text{-}20)$$

All reactants and products are included in this sum. Because reactants have negative stoichiometric coefficients, ΔC_P is the heat capacity of the appropriate numbers of moles of products minus the heat capacity of the appropriate numbers of moles of reactants. If ΔC_P can be assumed to be constant, Eq. (2.7-19) becomes

$$\Delta H(T_2) = \Delta H(T_1) + \Delta C_P(T_2 - T_1) \quad (\Delta C_P \text{ constant}) \tag{2.7-21}$$

Remember that this equation applies only if the reactants and the products are both at temperature T_2.

EXAMPLE 2.31

Using heat capacity data from Table A.8 of Appendix A and assuming the heat capacities to be independent of temperature, find the standard-state enthalpy change at 373.15 K for the reaction of Eq. (2.7-6).

Solution

$$\begin{aligned}\Delta C_P^\circ &= 2C_{P,m}^\circ(NO_2) + (-1)C_{P,m}^\circ(N_2O_4)\\ &= 2(36.874\,\text{J K}^{-1}\,\text{mol}^{-1}) + (-1)\,(77.256\,\text{J K}^{-1}\,\text{mol}^{-1})\\ &= -3.508\,\text{J K}^{-1}\,\text{mol}^{-1} = -0.003508\,\text{kJ K}^{-1}\,\text{mol}^{-1}\end{aligned}$$

Using the value of $\Delta H^\circ(298.15\,\text{K})$ from the previous example,

$$\begin{aligned}\Delta H^\circ(298.15K) &= 57.11\,\text{kJ mol}^{-1} + \left(-0.003508\,\text{kJ K}^{-1}\,\text{mol}^{-1}\right)(75.00\,\text{K})\\ &= 57.11\,\text{kJ mol}^{-1} - 0.263\,\text{kJ mol}^{-1} = 56.85\,\text{kJ mol}^{-1}\end{aligned}$$

Reactions Other Than Standard-State Reactions

If the products and reactants are not at their standard states, the enthalpy change for a reaction can have a different value from that of the standard-state reaction. For the reactions in our present class this difference is small. The enthalpy of an ideal gas does not depend on the pressure, and the enthalpies of real gases are nearly constant for moderate pressure changes. The effect on the enthalpy of pure solids and liquids due to moderate changes in pressures is also small. In a later chapter we will learn how to calculate these effects, but unless there is some need for great accuracy we will use the value of the standard-state enthalpy change at another pressure.

Adiabatic Chemical Reactions

We have discussed reactions in which the final temperature is the same as the initial temperature. The enthalpy change will have a different value if the temperature of the system changes during the reaction. One case of interest is that the chemical reaction takes place adiabatically at constant pressure. In this case the enthalpy change is equal to the heat transferred, which is equal to zero. In order to compute the final temperature

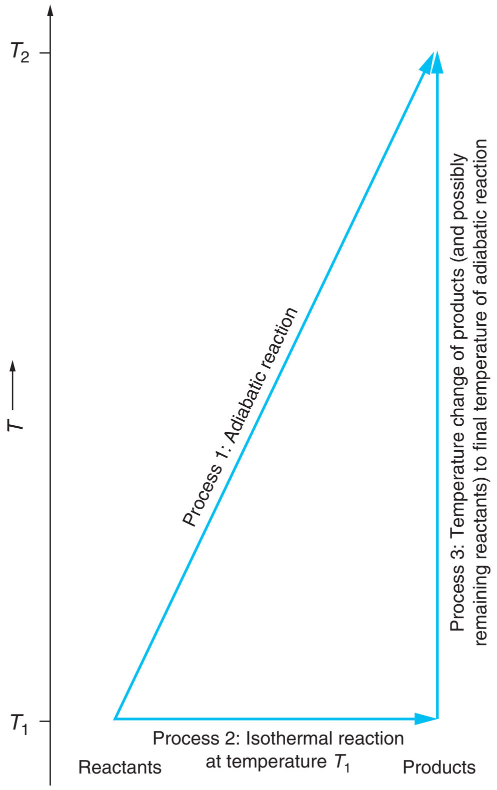

Figure 2.11 The Process to Calculate the Final Temperature of an Adiabatic Reaction.

of a system in which a chemical reaction takes place adiabatically, we consider the processes shown in Figure 2.11. Process 1 is the adiabatic reaction, for which ΔH is equal to zero. Process 2 is the reaction carried out isothermally. Process 3 is the change in temperature of the products plus any remaining reactants to the same final state as process 1. Because enthalpy is a state function, the enthalpy change of process 1 is equal to the sum of the enthalpy changes of processes 2 and 3:

$$\Delta H_1 = \Delta H_2 + \Delta H_3 = 0 \tag{2.7-22}$$

If a stoichiometric mixture is taken and if the reaction proceeds to completion, there are no remaining reactants, and we can write

$$\Delta H_3 = \int_{T_1}^{T_2} \underset{\text{(products only in sum)}}{\sum_{i=1}^{s} \nu_i C_{\mathrm{P,m}}(i)dT} = -\Delta H_2 \tag{2.7-23}$$

This equation can be solved for T_2 if the values of the heat capacities are known as a function of temperature. If there are remaining amounts of some reactants, their heat capacities must be added to the sum in Eq. (2.7-23). If the reaction comes to equilibrium short of completion, the equilibrium can shift as the temperature changes (see Chapter 7). The calculation is more complicated. We will not discuss that case.

EXAMPLE 2.32

Find the final temperature if the reaction of Eq. (2.7-1) is carried out adiabatically at constant pressure beginning at 298.15 K. Assume that a stoichiometric mixture is present before the reaction and that the reaction proceeds to completion. Assume that the heat capacity of water vapor is constant and equal to its value at 2000 K.

Solution

The reaction as written in Eq. (2.7-1) includes liquid water as the product. In our case the water produced will be a vapor, so we calculate ΔH° at 298.15 K for the gaseous product:

$$\Delta H^\circ(298.15\,\mathrm{K}) = 2\Delta_f H^\circ(\mathrm{H_2O(g)}) - 0 - 0$$

$$= 2(-241.818\,\mathrm{kJ\,mol^{-1}}) = -483.636\,\mathrm{kJ\,mol^{-1}} = -483636\,\mathrm{J\,mol^{-1}}$$

$$C_P(\text{products}) = 2(51.18\,\mathrm{J\,K^{-1}\,mol^{-1}}) = 102.36\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

$$\int_{298.15\,\mathrm{K}}^{T_2} \left(102.36\,\mathrm{J\,K^{-1}\,mol^{-1}}\right) dT - 483636\,\mathrm{J\,mol^{-1}} = 0$$

$$\left(102.36\,\mathrm{J\,K^{-1}\,mol^{-1}}\right)(T_2 - 298.15\,\mathrm{K}) = 483636\,\mathrm{J\,mol^{-1}}$$

$$T_2 = 5023\,\mathrm{K} \approx 5000\,\mathrm{K}$$

This result might be inaccurate because of the actual dependence of the heat capacity of water vapor on temperature.

Exercise 2.28

Find the final temperature if a stoichiometric mixture of methane and oxygen is ignited at 298.15 K and allowed to react adiabatically at a constant pressure. Assume that the reaction proceeds to completion and that the heat capacities of the products are constant and equal to their values at 2000 K.

If heat capacities are represented by polynomials as in Table A.6, a more nearly accurate final temperature can be calculated. This leads to a nonlinear equation, which can be solved by trial and error or by other numerical techniques.

Exercise 2.29

Using the parameters from Table A.6, find the final temperature after the adiabatic combustion of the stoichiometric mixture of hydrogen and oxygen in Example 2.32.

PROBLEMS

Section 2.7: Calculation of Enthalpy Changes of a Class of Chemical Reactions

2.48 Calculate $\Delta H°$ and $\Delta U°$ for the reactions at 298.15 K:

a. $C_3H_8(g) + 5\,O_2(g) \longrightarrow 3\,CO_2(g) + 4\,H_2O(l)$

b. $2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g)$

c. $SO_3(g) + H_2O(g) \longrightarrow H_2SO_4(l)$

2.49 Calculate $\Delta H°$ and $\Delta U°$ for the reactions at 298.15 K:

a. $4\,CuO(s) \longrightarrow 2\,Cu_2O(s) + O_2(g)$

b. $2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g)$

c. $C_2H_5OH(l) + 3\,O_2(g) \longrightarrow 2\,CO_2(g) + 3\,H_2O(l)$

2.50 Calculate $\Delta H°$ for the reactions of Problem 2.48 at 75°C.

2.51 Calculate $\Delta H°$ for the reactions of Problem 2.49 at 75°C.

2.52 **a.** Find the values of the enthalpy changes of formation of methane, carbon dioxide, and liquid water at 373.15 K, using heat capacity values from Table A.8.

b. Using the values from part a, find the standard-state enthalpy change for the reaction at 373.15 K:

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

c. Find the standard-state enthalpy change of the reaction of part b, using Eq. (2.7-19). Comment on the comparison of your answer with that of part b.

2.53 **a.** Calculate $\Delta H°$ for the reaction at 298.15 K:

$$2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(l)$$

b. Using the value of $\Delta_{\mathrm{vap}}H_{\mathrm{m}}(H_2O)$ and the result of part a, find $\Delta H°$ of this reaction for the case that the water is vapor.

c. Recalculate this quantity using $\Delta_{\mathrm{f}}H_{\mathrm{m}}(H_2O(g))$ and compare with your result of part a. Comment on any difference.

2.54 The molar enthalpy change of combustion of glycerol at 298.15 K is equal to $-393.73\ \mathrm{kcal\ mol^{-1}}$. Convert this to $\mathrm{kJ\ mol^{-1}}$ and find the value of $\Delta_{\mathrm{f}}H°$ of glycerol at this temperature.

2.55 **a.** The molar enthalpy change of combustion of sucrose, $C_{12}H_{22}O_{11}$, at 298.15 K is equal to $-5640.9\ \mathrm{kJ\ mol^{-1}}$. Calculate its enthalpy change of formation at 298.15 K. Calculate $\Delta U°$ for the combustion reaction.

b. The molar enthalpy change of combustion of stearic acid, $C_{18}H_{36}O_2$, at 298.15 K is equal to $-11280.6\ \mathrm{kJ\ mol^{-1}}$. Calculate its enthalpy change of formation at 298.15 K. Compare its enthalpy change of combustion per gram with that of sucrose.

2.56 Find the value of $\Delta H°$ for the combustion of methane at 125°C. State any assumptions. Assume that the heat capacities are constant between 25°C and 125°C.

2.8 Calculation of Energy Changes of Chemical Reactions

It would be possible to make tables of energy changes of formation and to calculate ΔU values in the same way as ΔH values are calculated from enthalpy changes of formation. However, adequate accuracy can be achieved without constructing a table of $\Delta_{\mathrm{f}}U$ values. From the definition of the enthalpy we can write an expression for ΔU for a chemical reaction:

$$\Delta U = \Delta H - \Delta(PV) \tag{2.8-1}$$

Ordinarily $\Delta(PV)$ is much smaller than ΔH, so that a less accurate calculation of $\Delta(PV)$ might suffice. For example, if ΔH is 1000 times larger than $\Delta(PV)$ and if five significant digits are desired in ΔU, then five significant digits are required in ΔH but only two significant digits are needed in $\Delta(PV)$.

The product PV is given by

$$PV = P(V(\mathrm{s}) + V(\mathrm{l}) + V(\mathrm{g})) \tag{2.8-2}$$

where $V(\mathrm{s})$ is the volume of all of the solid phases, $V(\mathrm{l})$ is the volume of all of the liquid phases, and $V(\mathrm{g})$ is the volume of the gas phase. Under ordinary conditions the molar volume of a gas is several hundred to a thousand times larger than the molar volume of a solid or liquid. If there is at least one gaseous product or reactant we can ignore the volume of the solid and liquid phases to an adequate approximation,

$$PV \approx PV(\mathrm{g})$$

so that

$$\Delta(PV) \approx \Delta PV(\mathrm{g}) \tag{2.8-3}$$

If the products and reactants are at the same temperature and if we use the ideal gas equation as an approximation,

$$\Delta U = \Delta H - \Delta PV(\mathrm{g}) \approx \Delta H - \Delta n(\mathrm{g})RT \tag{2.8-4}$$

where $\Delta n(\mathrm{g})$ is the change in the number of moles of gaseous substances in the reaction equation. If 1 mol of reaction occurs, then

$$\Delta n(\mathrm{g}) = \Delta \nu(\mathrm{g}) = \sum_{\substack{i=1 \\ \text{(gases only)}}}^{s} \nu_i \tag{2.8-5}$$

which defines the quantity $\Delta\nu(\mathrm{g})$, equal to the number of moles of gas in the product side of the balanced chemical equation minus the numbers of moles of gas in the reactant side of the balanced equation.

EXAMPLE 2.33

a. Find $\Delta(PV)$ and ΔU° for the reaction of Eq. (2.7-1) at 298.15 K.

b. Using the fact that the molar volume of liquid water is $18\ \mathrm{cm^3\ mol^{-1}}$ at 298.15 K, make a more accurate calculation of $\Delta(PV)$ for the reaction of the previous example.

Solution

a. The reaction is

$$2\mathrm{H_2(g)} + \mathrm{O_2(g)} \longrightarrow 2\mathrm{H_2O(l)}$$

Since the single product, $\mathrm{H_2O}$, is liquid, $\Delta\nu(\mathrm{g}) = -3$ and $\Delta n(\mathrm{g}) = -3.000$ mol

$$\Delta(PV) = \Delta\nu(\mathrm{g})RT = (-3)(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})$$

$$= -7437\ \mathrm{J\ mol^{-1}} = -7.437\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta H^\circ = 2\Delta_\mathrm{f} H^\circ(\mathrm{H_2O}) - 0 - 0 = -571.660\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta U^\circ = -571.660\ \mathrm{kJ\ mol^{-1}} - (-7.437\ \mathrm{kJ\ mol^{-1}}) = -564.223\ \mathrm{kJ\ mol^{-1}}$$

b.

$$V_2 = (2.000\,\mathrm{mol})(18\,\mathrm{cm^3\,mol^{-1}}) = 36\,\mathrm{cm^3} = 3.6 \times 10^{-5}\,\mathrm{m^3}$$

$$V_1 = \frac{(3.000\,\mathrm{mol})(8.3145\,\mathrm{J\,K^{-1}mol^{-1}})(298.15\,\mathrm{K})}{100000\,\mathrm{Pa}} = 0.0743690\,\mathrm{m^3}$$

$$\Delta V = 3.6 \times 10^{-5}\,\mathrm{m^3} - 0.0743690\,\mathrm{m^3} = -0.07433\,\mathrm{m^3}$$

Since the pressure is constant at $P^\circ = 100000\,\mathrm{Pa}$,

$$\Delta(PV) = P\Delta V = (100000\,\mathrm{Pa})(-0.07340\,\mathrm{m^3}) = -7433\,\mathrm{J\,mol^{-1}}$$

This value compares with the value of $-7437\,\mathrm{J\,mol^{-1}}$ in part a.

Exercise 2.30

Find ΔU° for the reaction of Eq. (2.7-6) at 298.15 K.

Calorimetry

The most common procedure for the determination of enthalpy changes of formation of combustible substances is to carry out combustion reactions in a *bomb calorimeter*. Figure 2.12 depicts such a calorimeter. The reaction is carried out in a rigid container that is called the “bomb.” A pellet of a solid reactant is placed in the bomb along with an excess of oxygen at a pressure of about 25 atm.

The bomb is placed in a bucket containing a measured amount of water, and the water is stirred until a steady or steadily changing temperature is attained, as measured by a thermometer in the water. The sample is ignited electrically, the reaction occurs, and the bomb, water, and bucket are allowed to stabilize. The amount of heat transferred to the calorimeter (bomb, water, and bucket) is calculated from knowledge of the heat capacity of the calorimeter. This heat capacity is very nearly independent of temperature so that

$$q = -q_{\mathrm{cal}} = -C_{\mathrm{cal}}\Delta T \tag{2.8-6}$$

Because the water continues to be stirred and because the water does not attain its final temperature instantaneously, extrapolation techniques are used to determine ΔT.[6] Since the system is at constant volume, $w = 0$ and

$$q = \Delta U \tag{2.8-7}$$

From the amount of solid reactant present, ΔU for 1 mol of reaction is calculated, and then ΔH for 1 mol of reaction is calculated from Eq. (2.8-4). This value of ΔH is not quite equal to ΔH° for the isothermal reaction. Neither the final pressure nor the initial pressure is equal to the standard-state pressure and the gases present are

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[6] C. W. Garland, J. W. Nibler, and D. P. Shoemaker, *Experiments in Physical Chemistry*, 7th ed., McGraw-Hill, Boston, 2003, pp. 145ff.

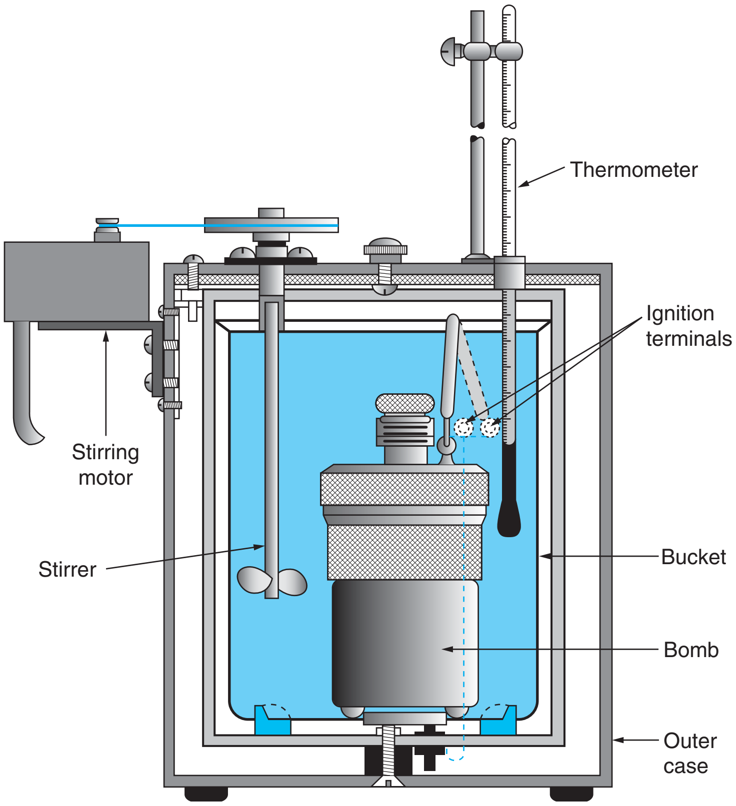

Figure 2.12 **A Bomb Calorimeter.** (Courtesy of the Parr Instrument Co.)

not ideal. We want to find ΔH° for an isothermal reaction, but the final temperature is not equal to the initial temperature. For ordinary work, these differences are negligible compared with the experimental errors, but corrections can be made for highly accurate work. A wire fuse is used to ignite the sample, and the heat of combustion of the wire and the electrical energy needed to ignite the sample can be included in the calculation.

EXAMPLE 2.34

A pellet of naphthalene of mass 1.234 g is burned in a bomb calorimeter with $C_{\text{cal}} = 14225\ \text{J K}^{-1}$. If the initial temperature is 298.150 K and the final temperature is 301.634 K, find ΔU and ΔH for 1 mol of reaction, with liquid water as one of the products. Neglect the heat of combustion of the wire fuse.

Solution

The balanced reaction equation is

$$C_{10}H_8(s) + 12O_2(g) \longrightarrow 10CO_2(g) + 4H_2O(l)$$

$$q = \Delta U = -q_{\text{cal}} = -(14225\ \text{J K}^{-1})(3.484\ \text{K}) = -4.956 \times 10^4\ \text{J}$$

For 1 mol of reaction

$$\Delta U = -\frac{\left(4.956 \times 10^4\,\mathrm{J}\right)}{\left(1.234\,\mathrm{g}\right)}\left(\frac{128.19\,\mathrm{g}}{1\,\mathrm{mol}}\right) = -5.148 \times 10^6\,\mathrm{J\,mol^{-1}}$$

$$\Delta H = -5.148 \times 10^6\,\mathrm{J\,mol^{-1}} + (-2)\left(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}\right)(298.15\,\mathrm{K})$$

$$= -5.153 \times 10^6\,\mathrm{J\,mol^{-1}} = -5153\,\mathrm{kJ\,mol^{-1}}$$

This value compares with the published value, $\Delta H^\circ = -5156.8\,\mathrm{kJ\,mol^{-1}}$, which applies to a constant-temperature reaction at 298.15 K.

The calculation in the previous example ignores the fact that the final temperature is not equal to the initial temperature and that the pressure is not equal to exactly 1 bar. It also neglects the contribution to q from the combustion of part of the wire fuse.

EXAMPLE 2.35

a. Estimate the error due to the inequality of the temperatures of the reactant and products in the previous example.

b. Assume that the mass of iron wire burned in the combustion experiment of the previous example is 8.0 mg. The energy of combustion of iron is $-6.68\,\mathrm{kJ\,g^{-1}}$. Find the percent error in Example 2.34 caused by neglect of the energy of the wire's combustion.

Solution

a. The initial amount of naphthalene was 0.00963 mol, giving 0.0963 mol of CO_2 and 0.0385 mol of H_2O. From the heat capacities in Table A.8, the heat capacity of the products is $6.55\,\mathrm{J\,K^{-1}}$. The heat required to bring the products back to 298.15 K is

$$q_2 = \left(6.55\,\mathrm{J\,K^{-1}}\right)(3.484\,\mathrm{K}) = 22.8\,\mathrm{J} = 0.0228\,\mathrm{kJ}$$

This means that $q_{\mathrm{cal}} = 4.956 \times 10^4\,\mathrm{J} + 22.9\,\mathrm{J} = 4.958 \times 10^4\,\mathrm{J}$ for the reaction with the products at the same temperature as the reactants, for a difference of about .04%.

b. From the example

$$q = -4.956 \times 10^4\,\mathrm{J}$$

The energy of combustion of the iron wire is

$$\Delta U_{\mathrm{wire}} = (0.0080\,\mathrm{g})\left(-6.68\,\mathrm{kJ\,g^{-1}}\right) = 0.0534\,\mathrm{kJ} = 53\,\mathrm{J}$$

The percent error is

$$\%\ \mathrm{error} = \frac{53\,\mathrm{J}}{4.956 \times 10^4\,\mathrm{J}} \times 100\% = 0.11\%$$

Exercise 2.31

What will be the rise in temperature of the calorimeter in the previous example if a pellet of anthracene of mass 1.345 g is burned? The enthalpy change of combustion of anthracene is –7114.5 kJ mol^{-1}.

The calorimetry of substances reacting in solutions can also be carried out at constant pressure. In this case q is equal to ΔH.

Average Bond Energies

If it were possible to determine exactly the energy required to break every type of chemical bond, it would be possible to calculate energy changes of a gaseous chemical reaction from bond energies. However, breaking chemical bonds between the same pair of elements in different compounds requires slightly different amounts of energy, which makes exact tables impractical. Tables of average values have been constructed, from which estimates of energy changes can be made. Table A.9 in Appendix A is a table of such values, given as the energy required to break 1 mol of the given bond. To estimate the energy change for a gas-phase reaction, you can write

$$\begin{aligned}\Delta U = {} & \text{(sum of all bond energies in reactants)} \\ & - \text{(sum of all bond energies in products)}\end{aligned} \tag{2.8-8}$$

The calculation can be simplified if one omits from both sums those bonds that occur in both reactants and products, because their contributions cancel:

$$\begin{aligned}\Delta U = {} & \text{(sum of all bond energies of bonds that are broken)} \\ & - \text{(sum of all bond energies of bonds that are formed)}\end{aligned} \tag{2.8-9}$$

EXAMPLE 2.36

Estimate the energy change of the reaction

$$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$$

Compare with the value obtained from enthalpy changes of formation.

Solution

For 1 mol of reaction, 1 mol of C=C bonds and 1 mol of H–H bonds must be broken, while 1 mol of C–C bonds and 2 mol of C–H bonds must be formed.

$$\begin{aligned}\Delta U &= 613\,\text{kJ mol}^{-1} + 436\,\text{kJ mol}^{-1} - 348\,\text{kJ mol}^{-1} - 2(413\,\text{kJ mol}^{-1}) \\ &= -125\,\text{kJ mol}^{-1}\end{aligned}$$

From enthalpy changes of formation at 298.15 K,

$$\Delta H = \Delta_f H^\circ(C_2H_6) - \Delta_f H^\circ(C_2H_4) - \Delta_f H^\circ(H_2)$$

$$= -84.68\,\text{kJ mol}^{-1} - (52.26\,\text{kJ mol}^{-1}) - 0 = -136.94\,\text{kJ mol}^{-1}$$

$$\Delta U = -136.94\,\text{kJ mol}^{-1} - (-1)\left(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}\right)(298.15\,\text{K})$$

$$= -136.94\,\text{kJ mol}^{-1} + 2.48\,\text{kJ mol}^{-1} = -134.46\,\text{kJ mol}^{-1}$$

The error of 9 kJ mol^{-1} in the previous example is typical. It is larger than the difference between ΔH and ΔU, so that the value of ΔU obtained from average bond energy values is ordinarily used for ΔH without correction for the value of $\Delta(PV)$. Average bond energies are used only if accurate enthalpy changes of formation are not available, since the results are only approximately correct. Average bond energies cannot be used for reactions involving solids or liquids, where intermolecular forces make important contributions. Various schemes have been devised to improve on the simple scheme that we have presented and have produced better results.[7]

Exercise 2.32

Using average bond energy values, estimate ΔH for the reaction:

$$C_2H_2(g) + H_2(g) \longrightarrow C_2H_6(g)$$

Compare your value with the value of ΔH obtained from enthalpy changes of formation.

PROBLEMS

Section 2.8: Calculation of Energy Changes of Chemical Reactions

2.57 **a.** Calculate ΔH° for the reaction at 298.15 K:

$$CH_4(g) + O_2(g) \longrightarrow CO_2(g) + H_2O(l)$$

(Balance the reaction first.)

b. Calculate ΔU°, neglecting the volume of the liquid water.

c. Calculate ΔU° without neglecting the volume of the liquid water, taking $V_m = 18.0\,\text{cm}^3\text{mol}^{-1}$ for liquid water.

2.58 **a.** Calculate the value of $\Delta_f U^\circ$ for carbon dioxide and for carbon monoxide at 298.15 K.

b. Calculate ΔU° for the following reaction at 298.15 K, using the results of part a:

$$2CO(g) + O_2(g) \longrightarrow 2CO_2(g)$$

c. Calculate ΔH° using Eq. (2.8-4) and compare with your result from part a.

2.59 **a.** Estimate the enthalpy change of the following reaction, using average bond energies:

$$2C_2H_6(g) + 7O_2(g) \longrightarrow 4CO_2(g) + 6H_2O(g)$$

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[7] See for example D. W. Smith, *J. Chem. Soc., Faraday Trans.*, **94**, 3087 (1998).

b. Compute the standard-state enthalpy change for this reaction at 298.15 K and at 373.15 K, using enthalpy changes of formation and heat capacity data and compare with your result from part a.

c. Estimate the enthalpy change of the following reaction, using average bond energies:

$$2\,CO(g) + O_2(g) \longrightarrow 2\,CO_2(g)$$

2.60 Estimate the enthalpy changes of the following reactions, using average bond energies. Compare with the value obtained from enthalpy changes of formation if possible.

a. $N_2O_4(g) \longrightarrow 2\,NO_2(g)$

b. $2\,SO_2(g) + O_2(g) \longrightarrow 2\,SO_3(g)$

c. $SO_3(g) + H_2O(g) \longrightarrow H_2SO_4(g)$

2.61 Estimate the enthalpy changes of the following reactions, using average bond energies. Compare with the value obtained from enthalpy changes of formation if possible. The P–Cl bond energy is not included in Table A.9, but you can assume a value of 160 kJ mol^{-1}.

a. $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$

b. $H_2(g) + F_2(g) \longrightarrow 2\,HF(g)$

2.62 **a.** Find $\Delta H°$ for the complete combustion of 1.000 mol of gaseous acetylene (ethyne) in gaseous oxygen to form gaseous carbon dioxide and liquid water at 298.15 K.

b. Find $\Delta H°$ for the complete combustion of 1.000 mol of gaseous acetylene (ethyne) in gaseous oxygen to form gaseous carbon dioxide and gaseous water at 373.15 K.

c. Estimate ΔH for the reaction using average bond energies, assuming gaseous water as one of the products.

2.63 **a.** Calculate $\Delta H°$ for the reaction at 298.15 K:

$$PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$$

b. Calculate ΔU for the reaction at 298.15 K.

c. Use the result from part b to estimate the average bond energy of a P–Cl bond, using the value of 244 kJ mol^{-1} for the CI–CI bond.

2.64 **a.** Find $\Delta H°$ for the reaction at 298.15 K:

$$CH_4(g) + 2\,O_2(g) \longrightarrow CO_2(g) + 2\,H_2O(g)$$

b. Find $\Delta U°$ for the same reaction at 298.15 K.

c. Find $\Delta H°$ and $\Delta U°$ for the same reaction at 373.15 K.

d. Estimate $\Delta U°$ for the same reaction using average bond energies. Comment on the comparison of this value with the correct values.

2.65 For the reaction $C_2H_2(g) + 2\,H_2(g) \longrightarrow C_2H_6(g)$

a. Calculate $\Delta H°$ at 298.15 K.

b. Find $\Delta U°$ for the same reaction at 298.15 K.

c. Estimate ΔU using average bond energies.

d. Calculate $\Delta H°$ at 373.15 K. State any assumptions and approximations.

Summary of the Chapter

The first law of thermodynamics is a form of the law of conservation of energy. This law defines U, the internal energy of a system, through

$$\Delta U = q + w$$

where q is the heat added to the system and w is the work done on the system. The internal energy is a state function of the macroscopic state of the system. Techniques were introduced to carry out several kinds of useful calculations, including work done and heat transferred in various processes, including isothermal and adiabatic processes in ideal gases and real gases.

The enthalpy, H, was defined by

$$H = U + PV$$

where P is the pressure and V is the volume of the system. At constant pressure, ΔH is equal to q for a simple system. Various calculations of ΔH values were carried out, including ΔH values for temperature changes, phase changes, and chemical reactions.

ADDITIONAL PROBLEMS

2.66 **a.** Calculate q, w, ΔU, and ΔH if 100.0 g of water is vaporized at 100.0°C and 1.000 atm. Assume that the water vapor is described by the van der Waals equation of state and that the density of the liquid is $1.00\ \mathrm{g\ cm^{-1}}$.

b. Repeat the calculation assuming gas ideality and neglecting the volume of the liquid compared with that of the vapor. How usable do you think this approximation is?

2.67 It is shown in the theory of hydrodynamics[8] that the speed of sound in a fluid, v_s, is given by

$$v_s^2 = \frac{V_m C_P}{M\kappa_T C_V} = \frac{V_m \gamma}{M\kappa_T}$$

where κ_T is the isothermal compressibility, V_m is the molar volume, and M is the molar mass.

a. Find the speed of sound in air at 298.15 K and 1.000 atm, assuming a mean molar mass of $0.029\ \mathrm{kg\ mol^{-1}}$ and $C_{V,m} = 5R/2$.

b. Find the speed of sound in helium at 298.15 K and 1.000 atm.

c. The speed of sound in ethane at 10°C is equal to $308\ \mathrm{m\ s^{-1}}$. Find the ratio C_P/C_V for ethane at this temperature.

2.68 A sample of 1.000 mol of N_2 gas is expanded adiabatically from a volume of 10.00 L and a temperature of 400.0 K to a volume of 20.00 L. Assume that N_2 is ideal, with $C_{V,m} = 5R/2$.

a. Find the final temperature if the expansion is carried out reversibly.

b. Find the final temperature if the expansion is carried out with a constant external pressure of 1.000 atm.

c. Find the final temperature if the gas expands into a vacuum.

d. Find ΔU and w for each of the processes of parts a, b, and c.

e. For the reversible expansion of part a, show that if the integral

$$w_{rev} = -\int_c P dV$$

is carried out using Eq. (2.4-27) the same value of w is obtained as from

$$w = \Delta U - q = \Delta U$$

2.69 **a.** The pressure on a sample of 1.000 mol of liquid water is increased from 1.00 bar to 100.00 bar at a constant temperature of 20.00°C. Find ΔH, ΔU, q, and w. State any assumptions.

b. The pressure on the same sample of water is increased adiabatically from 1.00 bar to 100.00 bar, beginning at 20.00°C. Find ΔH, ΔU, q, and w. State any assumptions.

2.70 Assume that 1.000 mol of octane, C_8H_{18}, is completely combusted with the stoichiometric amount of oxygen. Assume that the reaction goes to completion.

a. Assume that the reaction takes place at a constant temperature of 298.15 K under standard conditions, with liquid water as one of the products. Find the values of ΔH, ΔU, q, and w.

b. Assume that part of the energy of reaction is used to raise the products of the reaction by 100.0 m near the surface of the earth. Find the values of ΔH, ΔU, q, and w.

c. Assume that the reaction is carried out adiabatically and at constant pressure starting at 298.15 K. Find the final temperature of the products. If the final temperature is above 100°C, the water will be in the form of water vapor.

2.71 Label the following statements as true or false. If a statement is true only under certain conditions, label it as false.

a. If a process is carried out at constant pressure, dq behaves like an exact differential.

b. Although dw is an inexact differential, dw_{rev} is exact.

c. $dw = -PdV$ is correct for all simple systems.

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[8] H. Lamb, *Hydrodynamics*, 6th ed., Cambridge University Press, New York, 1932.

d. The fact that reversible processes cannot occur in the real world makes calculations of reversible processes useless.

e. Because enthalpy is a convenience variable, it would be possible to carry out thermodynamic calculations without using it.

f. ΔH and ΔU values are nearly equal for all processes.

g. ΔH and ΔU values are usually roughly equal to each other for chemical reactions.

h. The difference between C_P and C_V can be neglected in gases.

i. The Joule experiment is a useful way of studying gas nonideality.

j. Calculations of ΔH values from bond energies and from enthalpies of formation are equally accurate.

2.72 **a.** Calculate the enthalpy change of combustion at 25°C of 1.000 mol of each of the following: (1) propane, $C_3H_8(g)$; (2) iso-octane (2,2,4-trimethyl pentane), $C_8H_{18}(l)$; (3) hexadecane (cetane), $C_{16}H_{34}(l)$. Assume that the combustion is complete, forming only CO_2 and H_2O, and that gaseous H_2O is formed. The enthalpy change of formation of liquid hexadecane is equal to $-448\ \mathrm{kJ\ mol^{-1}}$.

b. Liquefied propane is sold as a fuel for various purposes. Iso-octane is a component of gasoline and is the substance used as the reference compound for “octane numbers.” (Its performance is rated as “100 octane.”) Cetane is a component of diesel fuel and is the reference compound for diesel fuel. In order to compare these fuels, compute the enthalpy change of combustion of 1.000 kg of each substance.

2.73 The decrease in air temperature with increasing altitude is partially due to cooling of the air as it expands with decreasing pressure. A typical barometric pressure at the peak of Mount Everest is 251 torr. Find the temperature of a sample of air that is reversibly and adiabatically expanded from a temperature of 298 K and a pressure of 1.00 atm to a pressure of 251 torr. Assume that air is a single ideal gas with $C_{V,m} = 5R/2$.

3

The Second and Third Laws of Thermodynamics: Entropy

PRINCIPAL FACTS AND IDEAS

1. There are two principal physical statements of the second law of thermodynamics: (1) If a system undergoes a cyclic process it cannot turn heat put into the system completely into work done on the surroundings. (2) Heat cannot flow spontaneously from a cooler to a hotter object if nothing else happens.
2. The second law implies that no heat engine can have an efficiency as great as unity.
3. The mathematical statement of the second law establishes a new state function, the entropy, denoted by S and defined through its differential by

$$dS = \frac{dq_{\text{rev}}}{T}$$

4. The mathematical statement of the second law provides a means of calculating the entropy change of any process that begins and ends at equilibrium states.
5. The second law implies that no macroscopic process can decrease the entropy of the universe.
6. Entropy is connected with lack of information through the Boltzmann definition of the statistical entropy:

$$S_{\text{st}} = k_{\text{B}} \ln(\Omega)$$

where k_{B} is Boltzmann's constant and Ω is the number of mechanical states that corresponds to the thermodynamic state of the system, corresponding to a fixed energy.

7. The third law of thermodynamics allows the entropy of any pure perfect crystalline substance consistently to be set equal to zero at absolute zero of temperature.
8. The second and third laws of thermodynamics imply that zero temperature on the Kelvin scale is unattainable.

3.1

The Second Law of Thermodynamics and the Carnot Heat Engine

The statement of the first law of thermodynamics defines the internal energy and asserts as a generalization of experiment fact that it is a state function. The second law of thermodynamics establishes the entropy as a state function, but in a less direct way.

Physical Statements of the Second Law

There are two important physical statements of the second law of thermodynamics. The *Kelvin statement* involves *cyclic processes*, which are processes in which the final state of the system is the same as its initial state: *It is impossible for a system to undergo a cyclic process whose sole effects are the flow of an amount of heat from the surroundings to the system and the performance of an equal amount of work on the surroundings.* In other words, *it is impossible for a system to undergo a cyclic process that turns heat completely into work done on the surroundings.*

The *Clausius statement* is: *It is impossible for a process to occur that has the sole effect of removing a quantity of heat from an object at a lower temperature and transferring this quantity of heat to an object at a higher temperature.* In other words, *heat cannot flow spontaneously from a cooler to a hotter object if nothing else happens.* The Clausius statement of the second law is closely related to ordinary experience. The Kelvin statement is less closely related, and it is remarkable that the statements are equivalent to each other and to the mathematical statement of the second law, which establishes that the entropy is a state function.

The Kelvin statement is named for William Thomson, Lord Kelvin, already mentioned in Chapters 1 and 2.

The Clausius statement is named for Rudolf Julius Emmanuel Clausius, 1822–1888, a German physicist who is generally considered to be the discoverer of the second law of thermodynamics.

No violation of either physical statement of the second law of thermodynamics has ever been observed in a properly done experiment. We regard the second law as a summary and generalization of experimental fact. A machine that would violate the Kelvin statement of the second law and turn heat completely into work in a cyclic process is called *a perpetual motion machine of the second kind*.

The Clausius statement applies only to cyclic processes. Heat can be completely turned into work done on the surroundings without violating the second law if the system undergoes a process that is not cyclic. For example, in an isothermal reversible expansion of an ideal gas $\Delta U = 0$, so that

$$w_{\text{surr}} = -w = \Delta U - q = q \quad \text{(ideal gas, isothermal volume change)} \qquad (3.1\text{-}1)$$

Heat transferred to the system has been completely turned into work done on the surroundings. However, the process is not cyclic and there is no violation of the second law of thermodynamics.

The Carnot Engine

The *Carnot heat engine* is an imaginary model machine that Carnot devised in 1824 to represent a steam engine. A simple *steam engine* is depicted schematically in Figure 3.1a. It has a cylinder with a piston connected to a crankshaft by a connecting rod. There is an intake valve through which a boiler can inject high-pressure steam into the cylinder and an exhaust valve through which spent steam can be exhausted into the atmosphere. This steam engine operates with a two-stroke cycle. The cycle begins with the piston at top dead center (the position of minimum volume in the cylinder) and with the intake

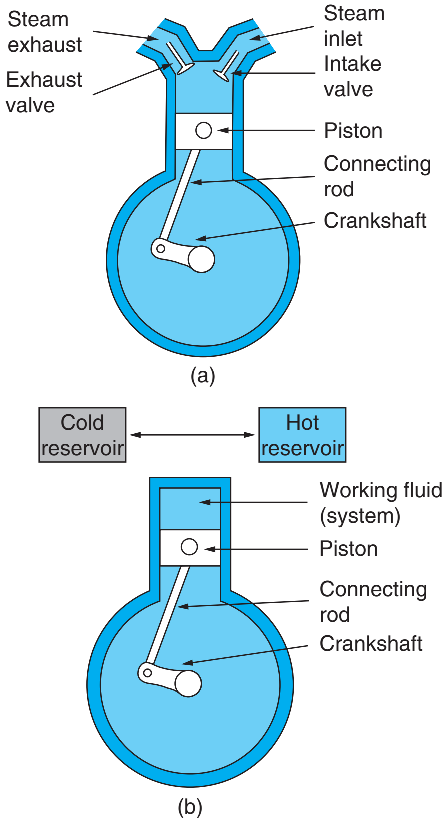


Figure 3.1 Comparison of a Simple Steam Engine and a Carnot Engine (Schematic). (a) A Simple steam engine. (b) A Carnot heat engine.

valve open. High-pressure steam from the boiler enters the cylinder through the intake valve and pushes on the piston, which turns the crankshaft. When the piston reaches bottom dead center (the position of maximum volume in the cylinder) the intake valve closes and the exhaust valve opens. The inertia of the crankshaft and flywheel pushes the piston back toward top dead center, expelling the spent steam through the exhaust valve. The exhaust valve closes and the intake valve opens when top dead center is reached, and the engine is ready to repeat its cycle.

The Carnot engine is depicted in Figure 3.1b. It operates reversibly, so there can be no friction. The cylinder contains a gaseous “working fluid,” which we define to be the system. The Carnot engine has no valves and the system is closed. To simulate passing steam into and out of the cylinder the Carnot engine allows heat to flow from a “hot reservoir” into its working fluid and exhausts heat into a “cold reservoir” by conduction through the cylinder walls or cylinder head.

The Carnot engine operates on a two-stroke cycle that is called the *Carnot cycle*. We begin the cycle with the piston at top dead center and with the hot reservoir in contact with the cylinder. We break the expansion stroke into two steps. The first step is an isothermal reversible expansion of the system at the temperature of the hot reservoir. The final volume of the first step is chosen so that the second step, which is an adiabatic reversible expansion, ends with the system at the temperature of the cold reservoir and with the piston at bottom dead center. The compression stroke is also broken into two steps. The third step of the cyclic process is a reversible isothermal compression with

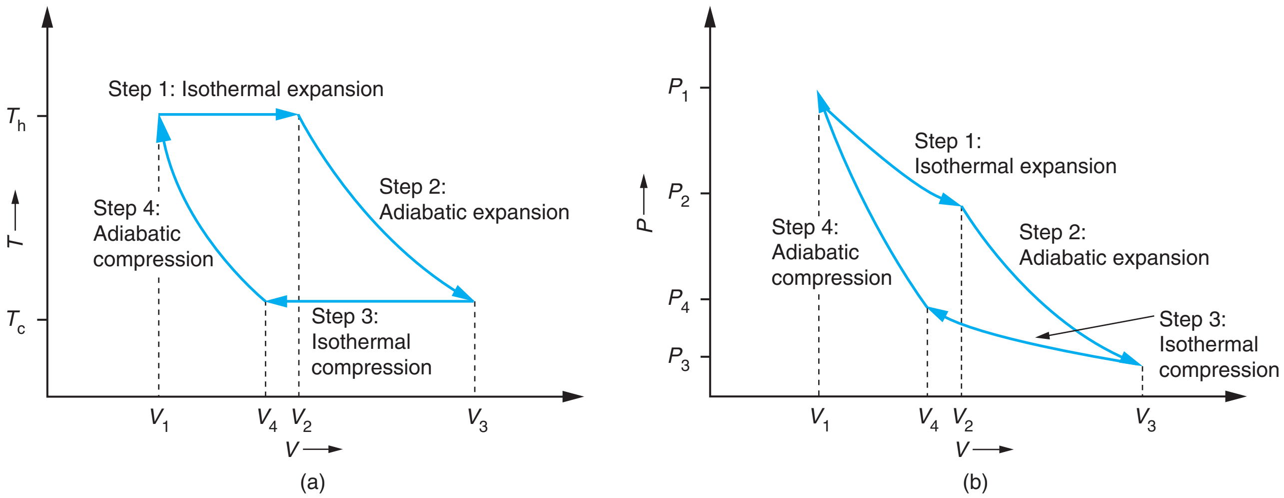


Figure 3.2 The Path of the State Point during a Carnot Cycle. **(a) In the *V*–*T* plane. (b) In the *V*–*P* plane.**

the cylinder in contact with the cold reservoir. This step ends at a volume such that the fourth step, a reversible adiabatic compression, ends with the piston at top dead center and the system at the temperature of the hot reservoir. The engine is now ready to repeat the cycle.

Figure 3.2a shows the path that the state point of the system follows as the engine undergoes one cycle, using V and T as the state variables. The state at the beginning of each step is labeled with the same number as the step. Figure 3.2b shows the same cycle using V and P as the state variables.

Since the second and fourth steps of the Carnot cycle are adiabatic,

$$q_2 = q_4 = 0 \tag{3.1-2}$$

For the entire cycle,

$$q_{\text{cycle}} = q_1 + q_2 + q_3 + q_4 = q_1 + q_3 \tag{3.1-3}$$

Since U is a state function and because the cycle begins and ends at the same state,

$$\Delta U_{\text{cycle}} = 0 \tag{3.1-4}$$

From the first law of thermodynamics,

$$w_{\text{cycle}} = \Delta U_{\text{cycle}} - q_{\text{cycle}} = q_{\text{cycle}} = -q_1 - q_3 \tag{3.1-5}$$

The efficiency, η_{Carnot}, of the Carnot engine is the work done on the surroundings divided by the heat input from the hot reservoir. The heat exhausted at the cold reservoir is wasted and is not included in the efficiency calculation.

$$\eta_{\text{Carnot}} = \frac{w_{\text{surr}}}{q_1} = \frac{-w_{\text{cycle}}}{q_1} = \frac{q_{\text{cycle}}}{q_1} = \frac{q_1 + q_3}{q_1} = 1 + \frac{q_3}{q_1} \tag{3.1-6}$$

From the Kelvin statement of the second law, the efficiency must be less than unity, so that q_3 must be negative. It is not possible to run a Carnot engine without exhausting some heat to a cool reservoir.

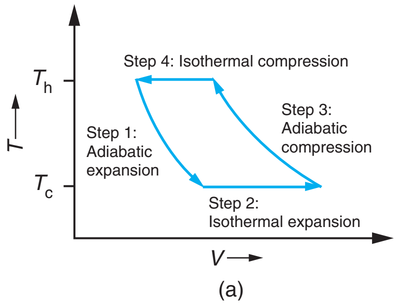


Figure 3.3 The Path of the State Point in the *V–T* Plane during a Carnot Heat Pump Cycle.

A *Carnot heat pump* is a Carnot heat engine that is driven backwards by another engine. It removes heat from the cool reservoir and exhausts heat into the hot reservoir. Figure 3.3 represents a Carnot heat pump cycle, which is the reverse of the cycle of Figure 3.2. The steps are numbered with a prime ($'$) and are numbered in the order in which they occur. Since we are considering the same Carnot engine run backwards,

$$q_4' = -q_1 \tag{3.1-7}$$

and

$$q_2' = -q_3 \tag{3.1-8}$$

Because the cycles are reversible, the amount of work done on the system in the reverse (heat pump) cycle, w', is equal to the amount of work done on the surroundings in the forward (engine) cycle:

$$w'_{\text{cycle}} = -w_{\text{cycle}} = w_{\text{surr}} \tag{3.1-9}$$

For a heat pump, the output is the heat delivered to the hot reservoir and the input is the work put into the heat pump. The ratio of the output to the input is called the *coefficient of performance* of the heat pump and is denoted by η_{hp}. The coefficient of performance equals the reciprocal of the Carnot efficiency, because the input and output are reversed in their roles as well as their signs.

$$\begin{aligned} \eta_{\text{hp}} &= \frac{|q_4'|}{w'_{\text{cycle}}} = -\frac{q_4'}{-q_2' - q_4'} = \frac{q_1}{q_1 + q_3} \\ &= \frac{1}{1 + q_3/q_1} = \frac{1}{\eta_c} \end{aligned} \tag{3.1-10}$$

The Carnot efficiency is always smaller than unity, so the Carnot heat pump coefficient of performance is always greater than unity. The amount of heat delivered to the hot reservoir is always greater than the work put into the heat pump because some heat has been transferred from the cold reservoir to the hot reservoir. There is no violation of the Clausius statement of the second law because the heat pump is driven by another engine. A real heat pump must have a lower coefficient of performance than a reversible heat pump but can easily have a coefficient of performance greater than unity.

No reversible heat engine can have a greater efficiency than the Carnot engine. We prove this by assuming the opposite of what we want to prove and then show that this assumption leads to a contradiction with experimental fact and therefore must be incorrect. Assume that a reversible heat engine does exist with a greater efficiency than a Carnot engine. We call this engine a “superengine” and label its quantities with the letter s and label the quantities for the original Carnot engine by the letter c. By our assumption, $\eta_s > \eta_c$, so that

$$1 + \frac{q_3(\text{s})}{q_1(\text{s})} > 1 + \frac{q_3(\text{c})}{q_1(\text{c})} \tag{3.1-11}$$

Now use the superengine to drive the Carnot engine as a heat pump between the same two heat reservoirs that are used by the superengine. If there is no friction all of the work done by the engine is transmitted to the heat pump:

$$w(\text{s}) = -w'(\text{c}) \tag{3.1-12}$$

From Eq. (3.1-10) the amount of heat put into the hot reservoir by the Carnot heat pump is equal to

$$-q'_4(\mathrm{c}) = \frac{w'(\mathrm{c})}{1 + q_3(\mathrm{c})/q_1(\mathrm{c})}$$

The amount of heat removed from the hot reservoir by the superengine is

$$q_1(\mathrm{s}) = -\frac{w(\mathrm{s})}{1 + q_3(\mathrm{s})/q_1(\mathrm{s})} < \frac{w'(\mathrm{c})}{1 + q_3(\mathrm{c})/q_1(\mathrm{c})}$$

Therefore

$$q_1(\mathrm{s}) < -q'_4(\mathrm{c})$$

A greater amount of heat has been put into the hot reservoir by the Carnot heat pump than was removed from this reservoir by the superengine. This conclusion is contrary to the Clausius statement of the second law. The only source of this contradiction is our assumption that a superengine exists with a greater efficiency than that of a Carnot engine, so the efficiency of the second reversible engine cannot be larger than that of a Carnot engine.

The second reversible heat engine also cannot have a smaller efficiency than the first Carnot engine. If it did its coefficient of performance as a heat pump, which is the reciprocal of its efficiency as a heat engine, would be larger than that of a Carnot heat pump, and the second law could be violated by using the first engine to drive the second engine as a heat pump. We have shown that *the efficiency of a reversible heat engine operating with two heat reservoirs does not depend on the nature of the working fluid or on the details of its design, but depends only on the temperatures of the heat reservoirs.*

Exercise 3.1

Carry out the proof that a reversible engine cannot have a smaller efficiency than a Carnot engine if it uses the same heat reservoirs.

A heat engine operating irreversibly can have a lower efficiency than a Carnot engine. If a heat engine operates irreversibly its coefficient of performance as a heat pump will not necessarily be the reciprocal of its engine efficiency since each step cannot necessarily be reversed. Therefore, driving the irreversible engine backward as a heat pump by a Carnot engine would not necessarily violate the second law if it has a lower efficiency than a Carnot engine.

The Thermodynamic Temperature and the Zeroth Law of Thermodynamics

The zeroth law of thermodynamics states a fact that many had tacitly accepted during the development of thermodynamics, and it gradually became apparent that it required a formal statement. It is stated: *If two objects, A and B, are at thermal equilibrium with each other and if B is at thermal equilibrium with a third object, C, then A is also at thermal equilibrium with C.* This law is considered to be basic to the other laws of thermodynamics, so it is called the zeroth law of thermodynamics, although it was announced after the other laws. The order of announcement was as follows: the second law, followed by the first law, the third law, and the zeroth law. The name "zeroth law" was coined by Ralph H. Fowler.

Ralph H. Fowler, 1889–1945, was a prominent professor of physics at Cambridge University.

Any other reservoir at the same temperature could be substituted for one of the reservoirs of our Carnot engine without any change in our analysis. The value of the ratio q_3/q_1 in a Carnot cycle therefore depends only on the temperatures of the reservoirs and not on their composition. The *thermodynamic temperature*, θ, is defined by

$$\boxed{\frac{\theta_c}{\theta_h} = \left|\frac{q_3}{q_1}\right| \quad \text{(definition of } \theta\text{)}} \tag{3.1-13}$$

where θ_c is the thermodynamic temperature of the cold reservoir and θ_h is the thermodynamic temperature of the hot reservoir. We require the thermodynamic temperature to be positive. The Carnot efficiency is now given by

$$\eta_{\text{Carnot}} = 1 - \frac{\theta_c}{\theta_h} \tag{3.1-14}$$

The thermodynamic temperature scale is not related to any particular kind of substance and is therefore more fundamental than the ideal gas temperature scale. We now show that the thermodynamic temperature scale can coincide with the ideal gas temperature scale. Assume that the working fluid of a Carnot engine is an ideal gas with a constant heat capacity. For the first step of the Carnot cycle, from Eq. (2.4-10)

$$q_1 = nRT_h \ln(V_2/V_1) \tag{3.1-15}$$

For the third step,

$$q_3 = nRT_c \ln(V_4/V_3) \tag{3.1-16}$$

We can now locate the states at which steps 1 and 3 terminate by using Eq. (2.4-21) twice:

$$\frac{T_c}{T_h} = \left(\frac{V_2}{V_3}\right)^{nR/C_{V,m}} \tag{3.1-17}$$

and

$$\frac{T_c}{T_h} = \left(\frac{V_1}{V_4}\right)^{nR/C_{V,m}} \tag{3.1-18}$$

These two equations imply that

$$\frac{V_1}{V_2} = \frac{V_4}{V_3} \tag{3.1-19}$$

When this relation is substituted into Eq. (3.1-16),

$$q_3 = nRT_c \ln(V_4/V_3) = nRT_c \ln(V_1/V_2) = -nRT_c \ln(V_2/V_1) \tag{3.1-20}$$

Equation (3.1-20) and Eq. (3.1-15) are substituted into Eq. (3.1-5) to give

$$w_{\text{cycle}} = -q_{\text{cycle}} = -q_1 - q_3 = nR(-T_h + T_c)\ln(V_2/V_1) \tag{3.1-21}$$

and

$$\eta_{\text{Carnot}} = \frac{w_{\text{surr}}}{q_1} = \frac{T_{\text{h}} - T_{\text{c}}}{T_{\text{h}}} = 1 - \frac{T_{\text{c}}}{T_{\text{h}}} \tag{3.1-22}$$

By comparison of Eqs. (3.1-14) and (3.1-22),

$$\frac{\theta_{\text{c}}}{\theta_{\text{h}}} = \frac{T_{\text{c}}}{T_{\text{h}}} \tag{3.1-23}$$

The thermodynamic temperature and ideal gas temperature are proportional to each other and Eq. (3.1-22) can be used for any Carnot engine. We choose the kelvin as the unit for both scales so that the two scales coincide. We will use the symbol T from now on to stand for the temperature on both the thermodynamic scale and the ideal gas scale. We call both scales the *absolute temperature scale* or the *Kelvin temperature scale*.

Exercise 3.2

Calculate the efficiency of a Carnot heat engine that represents a steam engine with its boiler at 600.0 K and its exhaust at 373.15 K.

The Carnot heat pump coefficient of performance is now

$$\eta_{\text{hp}} = \frac{1}{\eta_{\text{Carnot}}} = \frac{1}{1 - T_{\text{c}}/T_{\text{h}}} \tag{3.1-24}$$

If a heat pump functions as a refrigerator (or air conditioner), the *coefficient of performance* is defined to be the heat removed from the cold reservoir divided by the work put into the refrigerator:

$$\eta_{\text{r}} = \frac{q_2'}{w_{\text{cycle}}} = \frac{q_2'}{-q_2' - q_4'} = -\frac{q_3}{q_1 + q_3}$$

$$\eta_{\text{r}} = \frac{1}{-q_1/q_3 - 1} = \frac{1}{T_{\text{h}}/T_{\text{c}} - 1} \tag{3.1-25}$$

For Carnot heat pumps the coefficient of performance is always greater than unity, and for Carnot refrigerators the coefficient of performance exceeds unity if $T_{\text{h}}/T_{\text{c}} < 2$.

EXAMPLE 3.1

Calculate the coefficient of performance of a Carnot heat pump operating between a high temperature of 70.0°F and a low temperature of 40.0°F.

Solution

$$T_{\text{c}} = 273.15\,\text{K} + (40°\text{F} - 32°\text{F})\left(\frac{5\,\text{K}}{9°\text{F}}\right) = 277.59\,\text{K}$$

$$T_h = 273.15\,\mathrm{K} + (40^\circ\mathrm{F} - 32^\circ\mathrm{F})\left(\frac{5\,\mathrm{K}}{9^\circ\mathrm{F}}\right) = 294.26\,\mathrm{K}$$

$$\eta_{hp} = \frac{1}{1 - \dfrac{T_c}{T_h}} = \frac{1}{1 - \dfrac{277.59\,\mathrm{K}}{294.26\,\mathrm{K}}} = 17.6$$

Exercise 3.3

a. Calculate the coefficient of performance of a reversible refrigerator operating between an interior temperature of 4.0°C and an exterior temperature of 22.0°C.

b. Assume that a house is heated by a heat pump that has a coefficient of performance equal to 50.0% of that of a reversible heat pump. If the interior temperature is 22.0°C and the exterior temperature is 4.0°C, find the cost per joule of heating the house if electrical energy costs \$0.13 per kilowatt-hour.

c. If a real heat pump has an efficiency that is 50.0% of that of the reversible heat pump of part a, find the cost per joule of heating a house in the United States if electrical energy costs \$0.13 per kilowatt-hour and if the temperatures are as in part b.

PROBLEMS

Section 3.1: The Second Law of Thermodynamics and the Carnot Heat Engine

3.1 **a.** A Carnot engine contains 0.250 mol of a monatomic ideal gas as its working fluid. Assume C_V to be constant and equal to $3nR/2$. If $T_h = 473$ K, $T_c = 373$ K, $V_1 = 0.600$ L, and if the compression ratio (the ratio V_3/V_1) equals 6.00, find the efficiency and the values of V_2 and V_4.

b. Calculate w for each of the steps in the cycle of part a.

3.2 A Carnot engine contains as working fluid 0.150 mol of neon (assume ideal) with $C_{V,m} = 3R/2$. If $T_h = 600$ K and $T_c = 373$ K, find the values of V_1, V_2, V_3, P_3, P_4, and V_4 if $P_1 = 20.00$ atm and $P_2 = 5.00$ atm.

3.3 Carbon monoxide is used as the fuel for a Carnot engine with a high temperature of 450°C and a cool temperature of 100°C. Determine how high the combustion of 1.000 mol of CO could lift a 1.00 kg mass near the surface of the earth. Assume that all of the heat from the combustion is transferred to the engine and assume that the combustion takes place at 450°C.

3.4 A Carnot engine is operated by burning 1.00 mol of methane at a temperature of 1000 K. The cool reservoir is at 373 K.

a. Find the enthalpy change of the combustion reaction at 1000 K.

b. Find the amount of work that can be done by the engine when it burns this much fuel. Assume that no heat is lost.

3.5 **a.** A steam engine operates with its boiler at 200°C and a pressure of 15.34 atm, and with its exhaust at a temperature of 100°C and a pressure of 1.000 atm. Find the Carnot efficiency for these temperatures. What can you say about the efficiency of the steam engine?

b. The boiler is reinforced to operate at 360°C and a pressure of 184 atm. If the exhaust remains at 100°C, find the percentage improvement in the Carnot efficiency.

c. If the coal that the steam engine in part b burns is assumed to be pure graphite (not a good assumption) find the mass of coal required to produce 10.00 horsepower for 1.000 hour, assuming the Carnot efficiency. 1 horsepower = 746 watt = 746 J s^{-1}.

3.6 Assume gasoline to be pure n-octane and assume that its enthalpy change of combustion is approximately independent of temperature. Calculate the height to which combustion of 1.000 kg of gasoline can lift an automobile with a mass of 1500 kg. Assume that the automobile engine has a combustion temperature of 2000°F and an exhaust temperature of 1100°F and that the engine has an efficient 75% as large as that of a Carnot engine operating between these temperatures.

3.7 **a.** Assume that natural gas is pure methane (it is actually 90–95% methane). Find the amount of heat put into a house by the combustion of 100 cubic feet of natural gas at 20.0°C and 1.00 atm if 20.0% of the heat is wasted (hot gases go up the flue).

b. Find the amount of heat put into a house if 100.0 cubic feet of natural gas at 20.0°C and 1.00 atm is burned in an electric generating plant that is 80.0% as efficient as a Carnot engine operating between 2000°C and 800°C and if 90% of this energy is delivered to a heat pump operating between 20.0°C and 0.00°C. Assume that this heat pump has a coefficient of performance that is 80.0% of that of a Carnot heat pump.

c. Find the amount of heat put into a house if 100.0 cubic feet of natural gas is burned in an electric generating plant that is 80.0% as efficient as a Carnot engine operating between 2000°C and 800°C and if 90% of this energy is delivered to a resistance heater that has 100% efficiency.

3.8 **a.** Calculate the coefficient of performance of a Carnot food freezer with an interior temperature of -18°C and an exterior temperature of 25°C. 1 watt $= 1\ \mathrm{J\ s^{-1}}$.

b. Calculate the amount of electrical energy in kilowatt-hours necessary to freeze 1.000 kg of water in the Carnot freezer of part a.

3.9 A reversible heat engine accepts heat from a hot reservoir at temperature T_1 but exhausts part of the heat $(-q_2)$ at temperature T_2 and part $(-q_3)$ of it at temperature T_3, where $T_2 > T_3$. Find the efficiency if $q_3 = \frac{T_2}{T_3} q_2$.

3.10 **a.** Assume that the human body has the same efficiency in doing mechanical work as a Carnot engine with an upper temperature equal to human body temperature, 37°C, and a lower temperature equal to 25°C. Find the efficiency.

b. The actual efficiency of the human body is approximately equal to 20%. How can you explain this, since no heat engine can be more efficient than a Carnot engine?

3.11 It has been proposed that a heat engine might economically operate using the temperature difference between sea water near the surface and at a depth of several hundred feet.

a. Assume that such a heat engine has 50% of the efficiency of a Carnot engine and operates between 30°C and 20°C. Find the efficiency of the engine.

b. Assume that the heat engine drives an electric generator that produces 100 Mwatt (100 megawatts). Find the volume of sea water that must pass through the high-temperature heat exchanger per second if the heat exchanger lowers the temperature of the sea water from 30°C to 20°C. Assume that the sea water has the same heat capacity as pure water at 298.15 K, $75.351\ \mathrm{J\ K^{-1}\ mol^{-1}}$, and density equal to $1.00 \times 10^3\ \mathrm{kg\ m^{-3}}$.

3.2 The Mathematical Statement of the Second Law: Entropy

The second law of thermodynamics can be stated mathematically in a way that defines a new state function: *If the differential* dS *is defined by*

$$dS = \frac{dq_{\mathrm{rev}}}{T} \quad \text{(definition of the entropy } S\text{)} \tag{3.2-1}$$

then dS *is an exact differential and* S *is a state function called the entropy.* We now show that dq_{rev}/T is an exact differential. The integral of an exact differential is path-independent, so that its integral around a closed path (a path that starts and ends at the same point) vanishes. The converse is also true: If the integral around an arbitrary closed path vanishes, the differential is exact. We need to show that

$$\oint \frac{dq_{\mathrm{rev}}}{T_{\mathrm{surr}}} = 0 \tag{3.2-2}$$

for all reversible cyclic processes in a closed system. The symbol $\oint$ represents a line integral around a closed curve in the state space (beginning and ending at the same state).

We begin with a Carnot cycle. From Eqs. (3.1-13) and (3.1-23)

$$\frac{q_1}{T_\mathrm{h}} = -\frac{q_3}{T_\mathrm{c}} \tag{3.2-3}$$

Since T is constant on the isothermal segments and since $dq_\mathrm{rev} = 0$ on the adiabatic segments, the line integral for a Carnot cycle is

$$\oint \frac{dq_\mathrm{rev}}{T} = \frac{1}{T_\mathrm{h}}\int_{V_1}^{V_2} dq_\mathrm{rev} + 0 + \frac{1}{T_\mathrm{c}}\int_{V_3}^{V_4} dq_\mathrm{rev} + 0 = \frac{q_1}{T_\mathrm{h}} + \frac{q_3}{T_\mathrm{c}} = 0 \tag{3.2-4}$$

so that Eq. (3.2-2) is established for any Carnot cycle.

We now show that Eq. (3.2-2) is valid for the reversible cyclic process of Figure 3.4a. Steps 1, 3, and 5 are isothermal steps, and steps 2, 4, and 6 are adiabatic steps. Let point 7 lie on the curve from state 6 to state 1, at the same temperature as states 3 and 4, as shown in Figure 3.4b. We now carry out the reversible cyclic process 1 → 2 → 3 → 7 → 1, which is a Carnot cycle and for which the line integral vanishes. We next carry out the cycle 7 → 4 → 5 → 6 → 7. This is also a Carnot cycle, so the line integral around this cycle vanishes. During the second cycle the path from state 7 to state 3 was traversed from left to right. During the first cycle, the path from state 3 to state 7 was traversed from right to left. When the two cyclic line integrals are added, the integrals on these two paths cancel each other, and if we leave them both out the sum of the two line integrals is unchanged. The sum of the two line integrals is now a vanishing line integral for the cyclic process 1 → 2 → 3 → 4 → 5 → 6 → 7→ 1, which is the cycle of Figure 3.4a.

We now show that Eq. (3.2-2) holds for any cyclic process made up of isothermal and adiabatic reversible steps. Consider the process of Figure 3.5a, which can be divided into three Carnot cycles, just as that of Figure 3.4a was divided into two Carnot cycles. We can do the same division into Carnot cycles for any cycle that is made up of reversible isothermal and adiabatic steps. If each Carnot cycle is traversed once, the integrals on all of the paths in the interior of the original cycle are traversed twice, once in each direction, and therefore cancel out when all of the line integrals are added together. The exterior curve is traversed once, and the integral of Eq. (3.2-2) is shown to vanish around the cycle. For example, Figure 3.5b shows a cycle equivalent to eight

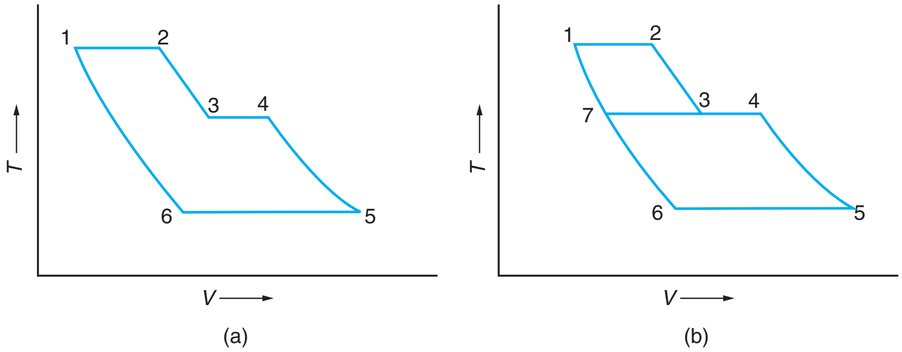
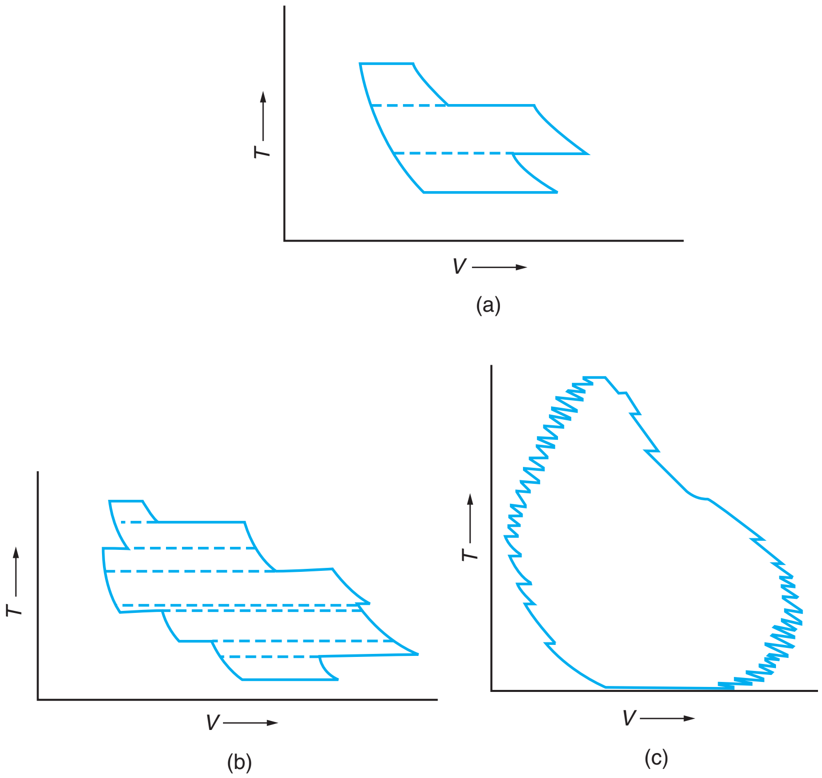


Figure 3.4 A Reversible Cycle of Isotherms and Adiabats. (a) The original cycle. (b) The cycle with an added process.



(a)

(b)

(c)

Figure 3.5 Reversible Cycles of Isotherms and Adiabats. (a) A cycle equivalent to three Carnot cycles. (b) A cycle equivalent to eight Carnot cycles. (c) A cycle equivalent to a large number of Carnot cycles.

Carnot cycles, and Figure 3.5c shows a more complicated cycle that can be divided into a large number of Carnot cycles. We conclude that the line integral of dq_{rev}/T around any path consisting of reversible isotherms and adiabats vanishes.

In order to represent an arbitrary cycle we construct reversible isothermal and adiabatic steps that are smaller and smaller in size, until the curve of the arbitrary cycle is more and more closely approximated by isothermal and adiabatic steps. In the limit that the sizes of the steps approach zero, any curve is exactly represented and the line integral of dq_{rev}/T vanishes for any cycle. The differential $dS = dq_{\mathrm{rev}}/T$ is therefore exact and S is a state function. For a simple system containing one substance and one phase, S must be a function of three state variables. We can write

$$S = S(T, V, n) \tag{3.2-5}$$

or

$$S = S(U, V, n) \tag{3.2-6}$$

and so on. Because we have defined only the differential of the entropy, any constant can be added to the value of the entropy without any significant change, just as a constant can be added to the value of U without any significant change.

Constantin Caratheodory, 1872–1950, was a Greek-German mathematician who made many contributions in mathematics in addition to his work in thermodynamics.

Caratheodory[1] showed that dq_{rev}/T is an exact differential by a more formal mathematical procedure. His argument is sketched briefly in Appendix D. It begins with the fact that two reversible adiabats cannot cross. We now show that this is a fact. We have already seen an example of it in the previous chapter when we derived a formula for the reversible adiabat for an ideal gas with a constant heat capacity. Equation (3.4-21b) is

$$T = T_1\left(\frac{V_1}{V}\right)^{nR/C_V} \tag{3.2-7}$$

This equation represents a family of functions of T as a function of V, one for each initial state:

$$T = T(V) \tag{3.2-8}$$

No two curves in this family can intersect.

To show that two reversible adiabats cannot cross for other systems we assume the opposite of what we want to prove and then show that this assumption leads to a contradiction with fact and therefore must be false. Assume that there are two different reversible adiabats in the state space of a closed simple system and that the curves coincide at state number 1, as depicted in Figure 3.6. We choose a state on each reversible adiabat, labeled state number 2 and state number 3 such that the reversible process leading from state 2 to state 3 has $q > 0$. Now consider a reversible cyclic process $1 \to 2 \to 3 \to 1$. Since steps 1 and 3 are adiabatic,

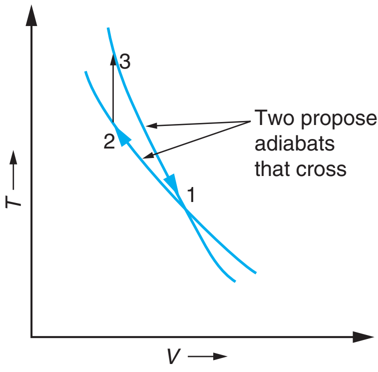


Figure 3.6 Two Reversible Adiabats That Cross (Assumption to Be Proved False).

$$q_{\text{cycle}} = q_2 > 0 \tag{3.2-9}$$

Since $\Delta U = 0$ in any cyclic process,

$$w_{\text{surr}} = -w_{\text{cycle}} = q_{\text{cycle}} = q_2 \tag{3.2-10}$$

Heat transferred to a system undergoing a cyclic process has been converted completely to work done on the surroundings, violating the second law of thermodynamics. The source of this violation is the assumption that two reversible adiabats can cross. Therefore, only one reversible adiabat passes through any given state point. The rest of Caratheodory's argument is summarized in Appendix D.

Entropy Changes for Adiabatic Processes

Consider a reversible adiabatic process for any kind of a system. We integrate Eq. (3.2-1) along the curve representing the process. Since $dq_{\text{rev}} = 0$ for every step of the process,

$$\boxed{\Delta S_{\text{rev}} = \int \frac{dq_{\text{rev}}}{T} = 0 \quad \text{(reversible adiabatic process)}} \tag{3.2-11}$$

A reversible adiabatic process does not change the entropy of the system. We next show that if a system undergoes an irreversible adiabatic process its entropy increases.

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[1] C. Caratheodory, *Math. Ann.*, **67**, 335 (1909); J. G. Kirkwood and I. Oppenheim, *Chemical Thermodynamics*, McGraw-Hill, New York, 1961, p. 31ff; J. deHeer, *Phenomenological Thermodynamics*, Prentice Hall, Englewood Cliffs, NJ, 1986, p. 123ff.

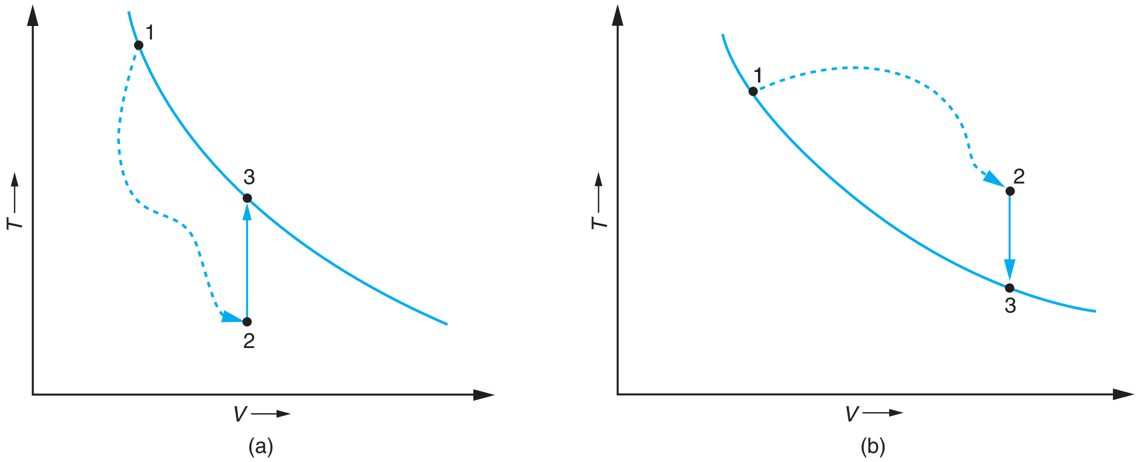

Figure 3.7 Reversible and Irreversible Adiabats. (a) Impossible case. An irreversible adiabatic process cannot lead to the low-temperature side of the reversible adiabat. (b) Possible case. The irreversible adiabatic process can lead to the high-temperature side of the reversible adiabat.

Figure 3.7 shows schematically two possibilities for an irreversible adiabatic process of a closed simple system in which the initial state (state 1) and the final state (state 2) are equilibrium states. During the process, the state of the system is not an equilibrium state and cannot be represented by a point in the V–T plane. The broken curve in the figure indicates that the state point leaves the V–T plane and then returns to the V–T plane at the end of the process.

We now show that an irreversible adiabatic process must lead to a higher temperature than the reversible adiabatic process starting at the same initial state (state 1). The solid curve in Figure 3.7a represents the reversible adiabat passing through state 1. We first assume that state 2 lies below this curve (an assertion that we want to disprove). Let state 3 be the state on the reversible adiabat that has the same volume as state 2. After the irreversible step 1 has occurred, we carry out a reversible constant-volume step from state 2 to state 3 (step 2). For a constant-volume process,

$$q_2 = \int_c dq = \int_c C_V dT \tag{3.2-12}$$

It is an experimental fact that the heat capacity of any system is positive. Therefore, $q_2 > 0$, since the temperature of state 2 is lower than that of state 3. After step 2, we carry out a reversible adiabatic step from state 3 to state 1 (step 3). Step 1 and step 3 are both adiabatic, so that

$$q_{\text{cycle}} = q_2 > 0 \tag{3.2-13}$$

Since U is a state function,

$$\Delta U_{\text{cycle}} = 0 \tag{3.2-14}$$

The work done on the surroundings in the cycle is

$$w_{\text{surr}} = -w_{\text{cycle}} = -\Delta U_{\text{cycle}} + q_{\text{cycle}} = -\Delta U_{\text{cycle}} + q_2 = q_2 \tag{3.2-15}$$

Heat transferred to the system in a cyclic process has been completely turned into work done on the surroundings, which is a violation of the second law. An irreversible adiabatic process cannot lead to a state that is lower in temperature than the reversible adiabat.

If state 2 is above the reversible adiabatic curve as in Figure 3.7b, we carry out a constant-volume reversible step (step 2) from state 2 to state 3, and an adiabatic reversible step from state 3 to state 1. This time, because state 2 is at a higher temperature than state 3 and because the capacity of the system must be positive,

$$q_{\text{cycle}} = q_2 < 0 \tag{3.2-16}$$

so that

$$w_{\text{surr}} = -w_{\text{cycle}} = -\Delta U_{\text{cycle}} + q_{\text{cycle}} = -\Delta U_{\text{cycle}} + q_2 = q_2 < 0 \tag{3.2-17}$$

In this case, heat transferred to the surroundings has been turned completely into work done on the system. This does not violate the second law of thermodynamics because the surroundings do not undergo a cyclic process. The final temperature for an irreversible adiabatic process cannot be lower than for a reversible adiabatic process with the same final volume, but it can be higher.

Now consider the entropy change for the irreversible adiabatic process that was depicted in Figure 3.7b. Because S is a state function,

$$\Delta S_{\text{cycle}} = \Delta S_1 + \Delta S_2 + \Delta S_3 = 0 \tag{3.2-18}$$

Because step 3 is reversible and adiabatic, $\Delta S_3 = 0$, and

$$\Delta S_1 = -\Delta S_2 \tag{3.2-19}$$

Because step 2 is reversible, we can integrate Eq. (3.2-1) for this step:

$$\Delta S_2 = \int_{T_2}^{T_3} \frac{dq_{\text{rev}}}{T} = \int_{T_2}^{T_3} \frac{C_{\text{V}}}{T} dT < 0 \tag{3.2-20}$$

The inequality comes from the fact that the temperature and the heat capacity are both positive and the fact that the temperature of state 2 must be greater than that of state 3. Because $\Delta S_1 = -\Delta S_2$, ΔS_1 must be positive. Therefore,

$$\boxed{\Delta S_{\text{irrev}} = \Delta S_1 > 0 \quad \text{(irreversible adiabatic process)}} \tag{3.2-21}$$

Combining Eqs. (3.2-11) and (3.2-21),

$$\boxed{\Delta S \geq 0 \quad \text{(any adiabatic process)}} \tag{3.2-22}$$

where the equality holds for reversible processes. *For any adiabatic process, the entropy of the system cannot decrease*. This is the most important consequence of the second law of thermodynamics. Because we define the universe to include all objects that interact with each other, the universe can undergo only adiabatic processes. *In any reversible process, the entropy of the universe remains constant. In any irreversible process, the entropy of the universe increases.*

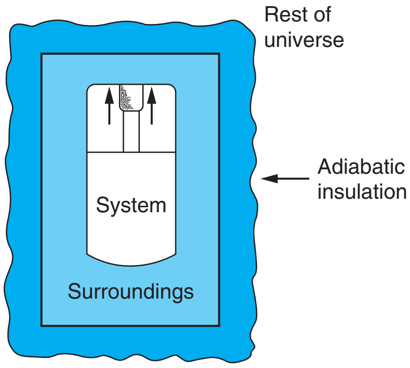

Figure 3.8 A System and Its Surroundings (a "Combination") Adiabatically Insulated from the Rest of the Universe.

Entropy Changes for Nonadiabatic Processes

Consider a closed system and its surroundings arranged as in Figure 3.8. We call the system plus its surroundings the "combination" and assume that the combination is isolated from the rest of the universe and can undergo only adiabatic processes. The entropy of the combination is the sum of the entropy of the system and the entropy of the surroundings:

$$S_{\text{com}} = S + S_{\text{surr}} \tag{3.2-23a}$$

$$dS_{\text{com}} = dS + dS_{\text{surr}} \tag{3.2-23b}$$

where a symbol without a subscript refers to the system. Since the combination can undergo only adiabatic processes,

$$dS_{\text{com}} = dS + dS_{\text{surr}} \geq 0 \tag{3.2-24}$$

In order to focus on the system, we rewrite Eq. (3.2-24) in the form

$$dS \geq -dS_{\text{surr}} \tag{3.2-25}$$

It is not necessary that dS be positive. However, if dS is negative, then dS_{surr} must be positive and large enough that the sum $dS + dS_{\text{surr}}$ is not negative. Since we wish to focus our attention on the system, we make the simplest possible assumption about the surroundings. We assume that the heat capacity and thermal conductivity of the surroundings are so large that all processes in the surroundings can be considered to be reversible. This means that

$$dS_{\text{surr}} = \frac{dq_{\text{surr}}}{T_{\text{surr}}} = -\frac{dq}{T_{\text{surr}}} \tag{3.2-26}$$

The second equality comes from the fact that any heat transferred to the surroundings must come from the system. Equation (3.2-25) is now

$$\boxed{dS \geq \frac{dq}{T_{\text{surr}}}} \tag{3.2-27}$$

where the equality applies to reversible processes and the inequality applies to irreversible processes. The temperature of the surroundings, not the temperature of the system, occurs in Eq. (3.2-27). This equation is the complete mathematical statement of the second law and has been derived from a physical statement of the second law. It is also possible to take the mathematical statement as a postulate and to derive the physical statements from it.[2]

Exercise 3.4

Show from the mathematical statement of the second law that heat cannot flow from a cooler object to a hotter object if nothing else happens. *Hint*: Consider two objects that form a combination that is isolated from the rest of the universe and are at different temperatures.

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[2] Kirkwood and Oppenheim, *op. cit.*

No violations of the second law of thermodynamics have ever been observed in a properly done experiment, so there is no reason to doubt its applicability. If it is universally applicable, the ultimate fate of the universe will be to approach a state of thermodynamic equilibrium in which every object in the universe will be at the same temperature. There will be no energy flow from stars to planets, and no life or any other macroscopic processes will be possible. This *"heat death" of the universe* will of course not occur for a very long time, but is unavoidable if the second law is universally valid.

Some people have speculated that the second law might not be universally valid, but might just be a statement of what nearly always occurs. If so, perhaps under some circumstances violations of the second law could be observed (possibly if the universe begins to contract instead of expand). This idea is unsupported speculation, and we have every reason to apply the second law of thermodynamics to any process in any macroscopic system.[3]

PROBLEMS

Section 3.2: The Mathematical Statement of the Second Law: Entropy

3.12 Calculate the entropy change for each of the four steps in the Carnot cycle of Problem 3.2, and show that these entropy changes sum to zero.

3.3 The Calculation of Entropy Changes

For a process in a closed system that begins at an equilibrium or metastable state and ends at an equilibrium state, the entropy change of the process is given by the line integral on a reversible path from the initial state to the final state.

$$\Delta S = S_{\text{final}} - S_{\text{initial}} = \int_c dS = \int_c \frac{dq_{\text{rev}}}{T} \tag{3.3-1}$$

Since entropy is a state function, we can calculate ΔS for a process that is not reversible so long as it has equilibrium or metastable initial and final states by calculating on a reversible path with the same initial and final states.

Entropy Changes of Isothermal Reversible Processes in Closed Systems

Since the process is reversible we integrate along the actual path of the process, and since T is constant we can factor $1/T$ out of the integral:

$$\Delta S = \int_c \frac{dq_{\text{rev}}}{T} = \frac{1}{T}\int_c dq_{\text{rev}} = \frac{q_{\text{rev}}}{T} \quad \text{(reversible isothermal process, closed system)} \tag{3.3-2}$$

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[3] See S. Frautschi, "Entropy in an Expanding Universe," *Science*, **217**, 592 (1982).

For isothermal reversible volume changes in a system consisting of an ideal gas, q_{rev} is given by Eq. (2.4-10), so that

$$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right) \quad \text{(ideal gas, reversible isothermal process)} \tag{3.3-3}$$

EXAMPLE 3.2

Find ΔS, ΔS_{surr}, q, w, and ΔU for the reversible isothermal expansion of 3.000 mol of argon (assumed ideal) from a volume of 100.0 L to a volume of 500.0 L at 298.15 K.

Solution

$$\Delta S = (3.000\ \text{mol})(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\ln\left(\frac{500.0\ \text{L}}{100.0\ \text{L}}\right) = 40.14\ \text{J K}^{-1}$$

Since the process is reversible,

$$\Delta S_{\text{universe}} = \Delta S + \Delta S_{\text{surr}} = 0$$

$$\Delta S_{\text{surr}} = -\Delta S = -40.14\ \text{J K}^{-1}$$

Since the system is an ideal gas, $\Delta U = 0$.

$$q = (3.000\ \text{mol})\,(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\,(298.15\ \text{K})\ln\left(\frac{500.0\ \text{L}}{100.0\ \text{L}}\right)$$

$$= 11{,}970\ \text{J}$$

$$w = -q = -11{,}970\ \text{J}$$

Exercise 3.5

Find ΔS, ΔS_{surr}, q, w, and ΔU if 3.000 mol of argon (assumed to be ideal) expands reversibly and isothermally from a volume of 50.0 L to a volume of 250.0 L at 298.15 K. Compare your answers with those of the previous example and explain any difference.

For a nonideal gas, the entropy change of a reversible isothermal volume change can be calculated from Eq. (3.3-2) if an expression for q_{rev} is obtained.

EXAMPLE 3.3

Find ΔS and ΔS_{surr} for the reversible expansion of 1.000 mol of argon from 2.000 L to 20.00 L at a constant temperature of 298.15 K as in Example 2.15. Argon is represented by the truncated virial equation of state as in that example.

Solution

Using the result of Example 2.15a for q_{rev}

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{5757\ \text{J}}{298.15\ \text{K}} = 19.31\ \text{J K}^{-1}$$

Entropy Changes for Processes That Begin and End at the Same Temperature

If a process is not isothermal but has a final temperature that is equal to its initial temperature, we can calculate ΔS for the process by integrating dq_{rev}/T on a reversible isothermal path. The actual process does not have to be reversible or isothermal, but the initial and final states must be equilibrium or metastable states at the same temperature.

EXAMPLE 3.4

Calculate the entropy change for the following process: A sample containing 2.000 mol of helium gas originally at 298.15 K and 1.000 bar is cooled to its normal boiling temperature of 4.00 K, condensed to a liquid, and then cooled further to 2.00 K, where it undergoes another phase transition to a second liquid form, called liquid helium II. This liquid phase is suddenly vaporized by a beam of laser light, and the helium is brought to a temperature of 298.15 K and a pressure of 0.500 bar.

Solution

Since entropy is a state function the entropy change is the same as for an isothermal reversible expansion from 1.000 bar to 0.500 bar:

$$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right) = nR\ln\left(\frac{P_1}{P_2}\right)$$

where we have used Boyle's law, $PV =$ constant at constant temperature.

$$\Delta S = (2.000\,\text{mol})(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\ln\left(\frac{1.000\,\text{bar}}{0.500\,\text{bar}}\right) = 11.5\,\text{J K}^{-1}$$

Entropy Changes for Reversible Phase Changes

Two phases of a single substance can be at equilibrium with each other at a fixed temperature that depends on the pressure. For example, liquid and gaseous water can be at equilibrium with each other at 100.00°C if the pressure is 1.000 atm (760.0 torr), and can be at equilibrium with each other at 25.00°C if the pressure is 23.756 torr. If an equilibrium phase change is carried out at constant pressure and temperature Eq. (3.3-2) applies. Since the pressure is constant, q is equal to ΔH, and

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{\Delta H}{T} \quad \text{(reversible phase change at constant pressure)} \tag{3.3-4}$$

EXAMPLE 3.5

Find the entropy change of the system and of the surroundings if 3.000 mol of water freezes reversibly at 1.000 atm. The freezing temperature is 0.00°C at this pressure, and the specific enthalpy change of fusion is equal to 79.7 cal g^{-1} at this temperature.

Solution

$$\Delta S=\frac{(3.000\,\text{mol})(18.02\,\text{g mol}^{-1})(79.7\,\text{cal g}^{-1})(4.184\,\text{J cal}^{-1})}{273.15\,\text{K}}=-66.0\,\text{J K}^{-1}$$

Since the process is reversible, $\Delta S_{\text{univ}}=0$ and

$$\Delta S_{\text{surr}}=-\Delta S=66.0\ \text{J K}^{-1}$$

Exercise 3.6

Calculate ΔH, q, and ΔS for the reversible vaporization of 50.0 g of ethanol at 1.000 atm. The molar enthalpy change of vaporization is equal to 40.48 k J mol^{-1} and the boiling temperature at 1.000 atm is 78.5°C.

Entropy Changes for Reversible Temperature Changes

Another simple class of processes consists of temperature changes in closed systems without phase change or chemical reaction. If the pressure is constant, the relations of Eqs. (2.5-6) and (2.5-8) give

$$dq=dH=C_{\text{P}}dT\quad\text{(closed system, constant pressure)}\tag{3.3-5}$$

so that Eq. (3.3-2) becomes

$$\Delta S=\int_{T_1}^{T_2}\frac{C_{\text{P}}}{T}dT\quad\text{(closed system, constant pressure process)}\tag{3.3-6}$$

where T_1 is the initial temperature and T_2 is the final temperature.

EXAMPLE 3.6

Calculate ΔS and ΔS_{surr} for reversibly heating 2.000 mol of liquid water from 0.00°C to 100.00°C at a constant pressure of 1.00 atm.

Solution

The specific heat capacity of liquid water is nearly constant and equal to 1.00 cal K^{-1}g^{-1} or 4.18 J K^{-1}g^{-1}.

$$\Delta S=\int_{273.15\,\text{K}}^{373.15\,\text{K}}\frac{C_{\text{P}}}{T}dT=C_{\text{P}}\int_{273.15\,\text{K}}^{373.15\,\text{K}}\frac{1}{T}dT=C_{\text{P}}\ln\left(\frac{373.15\,\text{K}}{273.15\,\text{K}}\right)$$

$$=(2.000\,\text{mol}^{-1})(18.02\,\text{g mol}^{-1})(4.18\,\text{J K}^{-1}\,\text{g}^{-1})\ln\left(\frac{373.15\,\text{K}}{273.15\,\text{K}}\right)=47.0\,\text{J K}^{-1}$$

$$\Delta S_{\text{surr}}=-\Delta S=-47.0\,\text{J K}^{-1}$$

EXAMPLE 3.7

For a gas whose molar constant-pressure heat capacity is represented by

$$C_P = a + bT + cT^{-2}$$

derive a formula for ΔS if the temperature is changed reversibly from T_1 to T_2 at constant pressure.

Solution

$$\Delta S = n\int_{T_1}^{T_2} \frac{C_{P,m}}{T}dT = n\int_{T_1}^{T_2} \frac{a + bT + cT^{-2}}{T}dT$$

$$= na\ln\left(\frac{T_2}{T_1}\right) + nb(T_2 - T_1) - \frac{nc}{2}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Exercise 3.7

Calculate the entropy change for heating 2.000 mol of CO_2 gas from −20.00°C to 100.00°C at a constant pressure of 1.000 atm using the formula from the previous example and data from Table A.6 of Appendix A.

For temperature changes at constant volume, Eq. (2.4-3) gives

$$dq = dU = C_V dT \quad \text{(closed system, constant volume)} \tag{3.3-7}$$

so that Eq. (3.3-2) becomes

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V}{T}dT \quad \text{(closed system, constant volume)} \tag{3.3-8a}$$

If the heat capacity is constant

$$\Delta S = C_V \ln\left(\frac{T_2}{T_1}\right) \tag{3.3-8b}$$

EXAMPLE 3.8

Calculate q, w, ΔU, and ΔS if 1.000 mol of helium gas is heated reversibly from 25.0°C to 50.0°C at a constant volume. Assume that $C_{V,m}$ is equal to $3R/2$ and is constant.

Solution

$$w = 0$$

$$q = C_V\Delta T = (1.000\,\text{mol})\left(\frac{3}{2}\right)(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(25.0\,\text{K}) = 311.8\,\text{J}$$

$$\Delta U = q = 311.8\,\text{J}$$

$$\Delta S = (1.000\,\text{mol})\left(\frac{3}{2}\right)(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\ln\left(\frac{323.15\,\text{K}}{298.15\,\text{K}}\right) = 1.004\,\text{J K}^{-1}$$

Notice that the volume does not matter so long as it is constant.

Exercise 3.8

a. Calculate ΔS if 2.500 mol of neon gas is heated reversibly from 80.0°C to 250.0°C at a constant volume of 100.0 L.
b. Calculate ΔS_{surr}.

Entropy Changes for Irreversible Processes

If a system undergoes any irreversible process with equilibrium initial and final states, we can calculate the entropy change of the system using a reversible process that has the same initial and final states as the irreversible process. A separate calculation is necessary for the entropy change of the surroundings, since the final state of the surroundings will not necessarily be the same for the reversible process as for the irreversible process.

EXAMPLE 3.9

Calculate ΔS, ΔS_{surr}, and ΔS_{univ} if 2.000 mol of argon (assume ideal) expands isothermally and irreversibly at 298.15 K from a volume of 10.00 L to a volume of 40.00 L at a constant external pressure of 1.000 atm. Assume that $P(\text{transferred}) = P_{\text{ext}}$ and that the surroundings remain at equilibrium at 298.15 K.

Solution

The initial and final states of the system are the same as for a reversible isothermal expansion, so that

$$\Delta S = \frac{q_{\text{rev}}}{T} = nR\ln\left(\frac{V_2}{V_1}\right)$$

$$= (2.000\,\text{mol})(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\ln\left(\frac{40.00\,\text{L}}{10.00\,\text{L}}\right) = 23.05\,\text{J K}^{-1}$$

In the ΔS calculation we have used q_{rev}, not the actual value of q, since we must integrate on a reversible path. In the calculation of ΔS_{surr} we must use the actual value of the heat transferred to the surroundings. We assume that P_{ext} is equal to $P(\text{transferred})$. Since $\Delta U = 0$ for an isothermal process in an ideal gas,

$$q_{\text{surr}} = -q = -\Delta U + w = w = -P_{\text{ext}}\Delta V = -\left(101325\ \text{N m}^{-2}\right)\left(0.030\ \text{m}^3\right)$$

$$= -3040\ \text{J}$$

$$\Delta S_{\text{surr}} = -\frac{3040\,\text{J}}{298.15\,\text{K}} = -10.20\,\text{J K}^{-1}$$

$$\Delta S_{\text{univ}} = 23.05\,\text{J K}^{-1} - 10.20\,\text{J K}^{-1} = 12.85\,\text{J K}^{-1}$$

Exercise 3.9

Calculate ΔS_{surr} if 2.500 mol of neon gas is heated irreversibly from 80.0°C to 250.0°C at a constant volume of 100.0 L with the surroundings remaining at equilibrium at 265.0°C.

Exercise 3.10

Find ΔS, ΔS_{surr}, and ΔS_{univ} if 3.000 mol of argon (assumed ideal) expand isothermally into a vacuum at 298.15 K, expanding from a volume of 15.00 L to a volume of 40.00 L.

EXAMPLE 3.10

Calculate ΔS, ΔS_{surr}, and ΔS_{univ} for the irreversible heating of 2.000 mol of liquid water from 0.00°C to 100.00°C at a constant pressure of 1.000 atm. Assume that the surroundings remain at equilibrium at 101°C as the system warms up.

Solution

Since entropy is a state function, ΔS is the same as in Example 3.6:

$$\Delta S = 47.0\,\text{J K}^{-1}$$

Since the process was carried out at constant pressure, $q = \Delta H$, and is the same as for the reversible process in Example 3.6.

$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T_{\text{surr}}} = -\frac{q}{T_{\text{surr}}} = -\frac{(2.000\,\text{mol})(18.01\,\text{g mol}^{-1})(4.184\,\text{J K}^{-1}\,\text{g}^{-1})(100.00\,\text{K})}{374.15\,\text{K}}$$

$$= -40.28\,\text{J K}^{-1}$$

$$\Delta S_{\text{univ}} = \Delta S + \Delta S_{\text{surr}} = 47.0\,\text{J K}^{-1} - 40.28\,\text{J K}^{-1} = 6.73\,\text{J K}^{-1}$$

Exercise 3.11

Find ΔS and ΔS_{surr} for the irreversible heating of 2.000 mol of gaseous neon from 0.00°C to 100.00°C at constant pressure, assuming that the surroundings remain at a constant temperature of 100.00°C.

Metastable supercooled or superheated systems can undergo irreversible phase changes at constant pressure, and their entropy changes can be calculated by considering reversible processes with the same initial and final states.

EXAMPLE 3.11

Calculate the entropy change of the system, the surroundings, and the universe for the process of Example 2.28. Assume that the surroundings remain at equilibrium at −15.00°C.

Solution

We use the same reversible path as in Example 2.28:

$$\Delta S_1 = \int_{258.15\text{K}}^{273.15\text{K}} \frac{C_P(\text{l})}{T}\,dT = C_P(\text{l})\ln\left(\frac{273.15\,\text{K}}{258.15\,\text{K}}\right)$$

$$= (2.000\,\text{mol})(75.48\,\text{J K mol}^{-1})\ln(1.0581) = 8.526\,\text{J K}^{-1}$$

$$\Delta S_2 = \frac{\Delta H_2}{T} = \frac{-1.202 \times 10^4\,\mathrm{J}}{273.15\,\mathrm{K}} = -44.00\,\mathrm{J\,K^{-1}}$$

$$\Delta S_3 = \int_{273.15\,\mathrm{K}}^{258.15\,\mathrm{K}} \frac{C_P(\mathrm{s})}{T}dT = C_P(\mathrm{s})\ln\left(\frac{258.15\,\mathrm{K}}{273.15\,\mathrm{K}}\right)$$

$$= (2.000\,\mathrm{mol})(37.15\,\mathrm{J\,K^{-1}\,mol^{-1}})\ln(0.9451) = -4.20\,\mathrm{J\,K^{-1}}$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = -39.68\,\mathrm{J\,K^{-1}}$$

From Example 2.28, $\Delta H = -10870\,\mathrm{J}$.

$$\Delta S_{\mathrm{surr}} = \frac{q_{\mathrm{surr}}}{T_{\mathrm{sun}}} = -\frac{q}{T_{\mathrm{surr}}} = -\frac{\Delta H}{T_{\mathrm{surr}}} = \frac{10870\,\mathrm{J}}{258.15\,\mathrm{K}} = 42.09\,\mathrm{J\,K^{-1}}$$

$$\Delta S_{\mathrm{univ}} = \Delta S + \Delta S_{\mathrm{surr}} = -39.69\,\mathrm{J\,K^{-1}} + 42.09\,\mathrm{J\,K^{-1}} = 2.40\,\mathrm{J\,K^{-1}}$$

Nonequilibrium Steady States

In some cases a system undergoes an irreversible process in such a way that the nonequilibrium state of the system does not change during the process. We say that the system is in a *steady state.* We cannot calculate the entropy of the system since it is not in an equilibrium state, but we can conclude that its entropy does not change during the process. Any entropy changes occur in the surroundings.

The system depicted in Figure 3.9a provides an example of such a situation. The surroundings consist of one large object at temperature T_1 and another large object at a higher temperature T_2. These objects are insulated from the rest of the universe and from each other except for a thin bar (our system) connecting the objects. If the objects are very large compared with the system and if they have large thermal conductivities, they will have nearly uniform and constant temperatures, and we can treat them as though they operate reversibly. After an induction period the system will come to a steady state with a temperature that depends on position but not on time, as depicted in Figure 3.9b. Consider a period of time Δt during which a quantity of heat q passes through the bar. Since the bar is in a steady state the amount of heat entering one end of the bar is equal to the amount of heat leaving the other end.

The entropy change of object 1 is

$$\Delta S_{\mathrm{surr},1} = \int \frac{dq_1}{T_1} = \frac{q_1}{T_1} = \frac{q}{T_1} \tag{3.3-9}$$

The entropy change of object 2 is

$$\Delta S_2 = \frac{q_2}{T_2} = -\frac{q}{T_2} \tag{3.3-10}$$

The entropy change of the surroundings is

$$\Delta S = q_1\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{3.3-11}$$

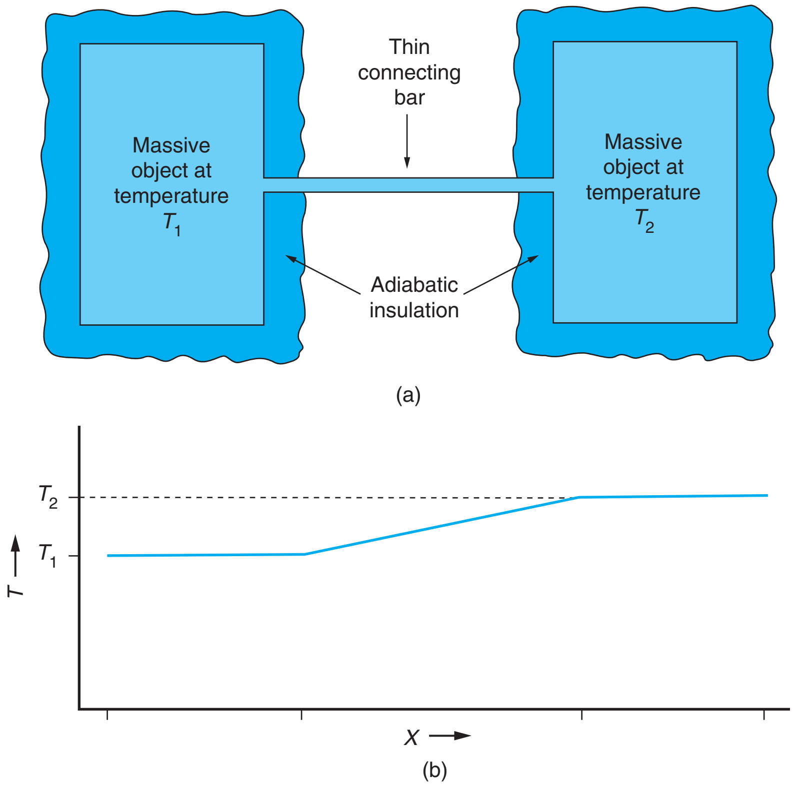

Figure 3.9 **An Example Irreversible Process.** (a) The system. (b) The temperature distribution in the system.

The state of the system does not change during the process. The entropy change of the universe is

$$\Delta S_{\mathrm{univ}} = \Delta S_{\mathrm{surr}}$$

The time rate of change of the entropy of the universe is called the *entropy production.* Think of it as the rate at which new entropy is being generated. For our steady-state process, the entropy production is

$$\frac{dS_{\mathrm{univ}}}{dt} = \left(\frac{dq}{dt}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \left(\frac{dq}{dt}\right)\left(\frac{\Delta T}{T_1 T_2}\right) \tag{3.3-12}$$

where dq/dt is the rate at which heat is transferred and where $\Delta T = T_2 - T_1$. The entropy production is the product of two factors. The first factor, dq/dt, represents the rate of the process, and the second factor, $\Delta T/(T_1 T_2)$, represents the driving force of the process.

Exercise 3.12

For the system of Figure 3.9, calculate the rate of entropy production if the first object is at 325 K and the second object is at 375 K, and if 200.0 J of heat flows in 30.0 s.

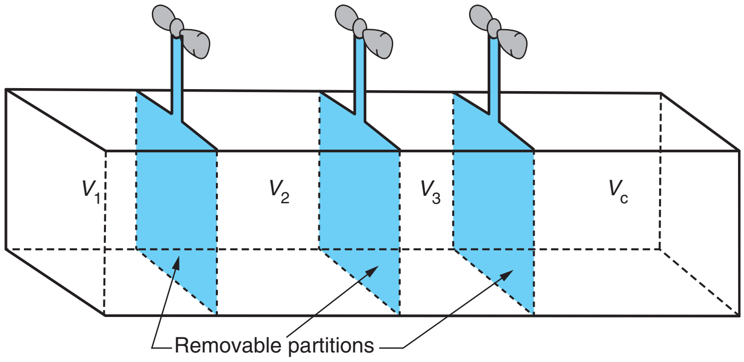

Figure 3.10 A System for Carrying Out the Irreversible Mixing of Gases.

The Entropy Change of Mixing Ideal Gases

The *entropy change of mixing* is the entropy change for producing a mixture from the pure components. Consider a mixture of several ideal gases in which n_1 is the amount of substance 1, n_2 is the amount of substance 2, and so on. The number of substances is denoted by s. We imagine an initial state with each substance confined in a separate compartment of a container, as shown in Figure 3.10. We arrange the system so that each gas is at the temperature and the pressure of the final mixture by letting

$$V_i = \frac{n_i RT}{P} \quad (i = 1, 2, 3, \ldots, s) \tag{3.3-13}$$

where V_i is the volume of compartment number i, n_i is the amount of substance number i in compartment number i, and T and P are the temperature and pressure of the final mixture. The total volume of the container is denoted by V:

$$V = \sum_{i=1}^{s} V_i \tag{3.3-14}$$

The gases are mixed by withdrawing the partitions between compartments, so that each gas mixes irreversibly with the others and fills the entire volume. According to Dalton's law of partial pressures each gas in a mixture of ideal gases acts as though it were alone in the container. Gas number i undergoes a process with the same initial and final states as an isothermal reversible expansion from volume V_i to volume V. The entropy changes of the individual gases are given by Eq. (3.3-3):

$$\Delta S_i = n_i R \ln\left(\frac{V}{V_i}\right) \quad (i = 1, 2, 3, \ldots, s) \tag{3.3-15}$$

The entropy change of the system is the sum of these quantities:

$$\Delta S = \sum_{i=1}^{s} n_i R \ln\left(\frac{V}{V_i}\right) \tag{3.3-16}$$

We now express ΔS in terms of the mole fractions. The *mole fraction* of substance number i is defined by

$$x_i = \frac{n_i}{n} \quad \text{(definition of the mole fraction } x_i\text{)} \tag{3.3-17}$$

where n is the total amount of all gases,

$$n = \sum_{j=1}^{s} n_j \tag{3.3-18}$$

From Eq. (3.3-13) we have

$$x_i = \frac{n_i}{n} = \frac{PV_i/RT}{PV/RT} = \frac{V}{V_i} \tag{3.3-19}$$

so that the entropy change on mixing the ideal gases is

$$\boxed{\Delta S_{\text{mix}} = R\sum_{i=1}^{s} n_i \ln(1/x_i) = -R\sum_{i=1}^{s} n_i \ln(x_i)} \tag{3.3-20}$$

This equation applies to the mixing of substances in other kinds of systems besides ideal gases, if the mixing is random. It can be used to calculate the entropy change of mixing of isotopes of a single element. In a later chapter we will show that it can also be used for the entropy of change of mixing of a class of liquid or solid solutions called ideal solutions.

EXAMPLE 3.12

Assume that 1.000 mol of dry air consists of 0.780 mol of nitrogen, 0.210 mol of oxygen, and 0.010 mol of argon. Find the entropy change of mixing of 1.000 mol of dry air. Disregard the fact that each substance has more than one isotope.

Solution

$$\begin{aligned}\Delta S &= -(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\big[(0.780\,\text{mol})\ln(0.780)\\ &\quad + (0.21\,\text{mol})\ln(0.210) + (0.01\,\text{mol})\ln(0.01)\big]\\ &= 4.72\,\text{J K}^{-1}\end{aligned}$$

Exercise 3.13

a. Find the entropy change of mixing for 1.000 mol of the normal mixture of bromine atoms, with 50.69% ^{79}Br and 49.31% ^{81}Br.

b. Find the entropy change of mixing in 0.500 mol of naturally occurring Br_2. Note that there are three kinds of Br_2 molecules if there are two isotopes.

PROBLEMS

Section 3.3: The Calculation of Entropy Changes

3.13 **a.** Calculate ΔS for each step of the following cycle and sum the results to obtain ΔS for the cycle: Step 1: 1.000 mol of helium is expanded reversibly and isothermally at 298.15 K from 10.00 L to 20.00 L. Step 2: The gas is heated reversibly at a constant volume from 298.15 K and 20.00 L to a temperature of 473.15 K. Step 3: The gas is compressed reversibly and isothermally at 473.15 K from 20.00 L to 15.00 L.

Step 4: The gas is cooled reversibly at a constant volume of 15.00 L from 473.15 K to 373.15 K. Step 5: The gas is compressed reversibly and isothermally at 373.15 K from a volume of 15.00 L to a volume of 10.00 L. Step 6: The gas is cooled reversibly at a constant volume of 10.00 L from 373.15 K to 298.15 K.

b. Repeat the calculation with all steps the same as in part a except that step 1 is carried out isothermally and irreversibly with a constant external pressure of 1.000 atm.

3.14 A sample of 2.000 mol of nitrogen gas (assume ideal with $C_{V,m} = 5R/2$) expands adiabatically and irreversibly from a volume of 8.000 L and a temperature of 500.0 K to a volume of 16.000 L against an external pressure of 1.000 atm. Find the final temperature, ΔU, q, w, and ΔS for this process. Find the initial and final pressures.

3.15 A sample of 1.000 mol of helium gas (assumed ideal with $C_{V,m} = 3R/2$) expands adiabatically and irreversibly from a volume of 3.000 L and a temperature of 500. K to a volume of 10.00 L against a constant external pressure of 1.000 atm. Find the final temperature, ΔU, q, w, and ΔS for this process. Compare each quantity with the corresponding quantity for a reversible adiabatic expansion to the same final volume.

3.16 The normal boiling temperature of ammonia is −33°C, and its enthalpy change of vaporization is 24.65 kJ mol^{-1}. The density of the liquid is 0.7710 g mL^{-1}.

a. Calculate q, w, ΔU, ΔH, ΔS, and ΔS_{surr} if 1.000 mol of ammonia is vaporized at −33°C. Use the ideal gas equation of state to estimate the volume of the gas and neglect the volume of the liquid.

b. Repeat the calculations of part a, using the van der Waals equation of state to find the molar volume of the gas under these conditions (use successive approximations or other numerical procedure to solve the cubic equation) and without neglecting the volume of the liquid.

3.17 **a.** Find the change in entropy for the vaporization of 2.000 mol of liquid water at 100°C and a constant pressure of 1.000 atm.

b. Find the entropy change for the heating of 2.000 mol of water vapor at a constant pressure of 1.000 atm from 100°C to 200°C. Use the polynomial representation in Table A.6 for the heat capacity of water vapor.

3.18 **a.** Calculate the entropy change for the isothermal expansion of 1.000 mol of argon gas (assume ideal) from a volume of 5.000 L to a volume of 10.000 L.

b. Calculate the entropy change for the isothermal expansion of 1.000 mol of argon gas (assume ideal) from a volume of 10.000 L to a volume of 15.000 L.

c. Explain in words why your answer in part b is not the same as that of part a, although the increase in volume is the same.

3.19 **a.** 1.000 mol of helium is compressed reversibly and isothermally from a volume of 100.00 L and a temperature of 298.15 K to a volume of 50.00 L. Calculate ΔS, q, w, and ΔU for the process. Calculate ΔS_{surr} and ΔS_{univ}.

b. Calculate the final temperature, ΔS, q, w, ΔU, ΔS_{surr}, and ΔS_{univ} if the gas is compressed adiabatically and reversibly from the same initial state to a final volume of 50.00 L.

c. The gas is compressed adiabatically and irreversibly from the same initial state to the same final volume with $P_{\text{ext}} = 1.000$ atm. What can you say about the final temperature, ΔS, q, w, ΔU, ΔS_{surr}, and ΔS_{univ}?

d. The gas is compressed isothermally and irreversibly from the same initial state to the same final volume with $P_{\text{ext}} = 1.000$ atm. What can you say about ΔS, q, w, ΔU, ΔS_{surr}, and ΔS_{univ}?

3.20 2.000 mol of helium is expanded adiabatically and irreversibly at a constant external pressure of 1.000 atm from a volume of 5.000 L and a temperature of 273.15 K to a volume of 25.000 L. Calculate ΔS, ΔS_{surr}, and ΔS_{univ}. State any approximations or assumptions.

3.21 **a.** Calculate the entropy change for the following reversible process: 2.000 mol of neon (assume ideal with $C_{V,m} = 3R/2$) is expanded isothermally at 298.15 K from 2.000 atm pressure to 1.000 atm pressure and is then heated from 298.15 K to 398.15 K at a constant pressure of 1.000 atm. Integrate on the path representing the actual process.

b. Calculate the entropy change for the reversible process with the same initial and final states as in part a, but in which the gas is first heated at constant pressure and then expanded isothermally. Again, integrate on the path representing the actual process. Compare your result with that of part a.

c. Calculate the entropy change of the surroundings in each of the parts a and b.

d. Calculate the entropy changes of the system and the surroundings if the initial and final states are the same as in parts a and b, but if the gas is expanded irreversibly and isothermally against an external pressure of 1.000 atm and then heated irreversibly with the surroundings remaining essentially at equilibrium at 400 K.

3.22 Find ΔH, ΔS, and q for the reversible heating of 0.500 mol of benzene from 25°C to 100°C at a constant pressure of 1.000 atm. The normal boiling temperature of benzene is 80.1°C and the enthalpy change of vaporization is $30.8\ \mathrm{kJ\ mol^{-1}}$.

3.23 **a.** A sample of 2.000 mol of neon is expanded reversibly and adiabatically from a volume of 10.00 L and a temperature of 500.0 K to a volume of 25.00 L. Find the final temperature, q, w, ΔU, ΔS, and ΔS_{univ} for the process. State any assumptions or approximations.

b. The same sample is restored to its original state and is first expanded adiabatically and irreversibly at a constant external pressure of 1.000 atm to a volume of 25.00 L, then cooled reversibly to the same final temperature as in part a at a constant volume of 25.00 L. Find the final temperature for the irreversible step, and find q, w, ΔU, and ΔS for this entire two-step process. What can you say about ΔS_{univ} for each step of this two-step process?

3.24 1.000 mol of carbon tetrafluoride is vaporized at the normal boiling point of −128°C and 1.000 atm (both P and T held constant). The molar volume of the liquid is $44.9\ \mathrm{cm\ mol^{-1}}$. The enthalpy change of vaporization is $12.62\ \mathrm{kJ\ mol^{-1}}$. Find q, w, ΔS, and ΔH for this process.

3.25 A sample of 2.000 mol of a monatomic ideal gas is expanded and heated. Its initial temperature is 300.0 K and its final temperature is 400.0 K. Its initial volume is 20.00 L and its final volume is 40.00 L. Calculate ΔS. Does the choice of path between the initial and final states affect the result?

3.26 The molar heat capacity of water vapor is represented by

$$C_{P,\mathrm{m}} = 30.54\ \mathrm{J\ K^{-1}\ mol^{-1}} + (0.01029\ \mathrm{J\ K^{-2}\ mol^{-1}})T$$

where T is the absolute temperature.

a. Find ΔH for heating 2.000 mol of water vapor at a constant pressure of 1.000 atm from 100°C to 500°C.

b. Find q, w, and ΔU for the process.

c. Find ΔS for the process.

3.4 Statistical Entropy

Since molecules can occupy various states without changing the macroscopic state of the system of which they are a part, it is apparent that many microstates of a macroscopic system correspond to one macroscopic state. We denote the number of microstates corresponding to a given macrostate by Ω. The quantity Ω is sometimes called the *thermodynamic probability* of the macrostate. The thermodynamic probability is a measure of lack of information about the microstate of the system for a particular macrostate. A large value corresponds to a small amount of information, and a value of unity corresponds to knowledge that the system is in a specific microstate.

For a macrostate specified by values of U, V, and n, Boltzmann defined a *statistical entropy*:

$$S_{\mathrm{st}} = k_{\mathrm{B}} \ln(\Omega) + S_0 \quad \text{(definition of statistical entropy)} \qquad (3.4\text{-}1)$$

where k_{B} is Boltzmann's constant, equal to R/N_{Av}. The constant S_0 is a constant that we usually set equal to zero. The task of this section is to show that the statistical entropy can be equivalent to the thermodynamic entropy for a model system that is called a *lattice gas*. This system contains a number N of noninteracting point-mass molecules confined in a container with volume V. We assume that the particles obey classical mechanics. The lattice gas is in an equilibrium macrostate specified by values of U, V and N. The microstate of the lattice gas is specified by the positions and velocities of all of the particles.

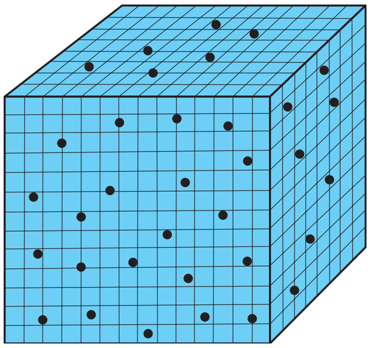

Figure 3.11 The Lattice Gas.

We now specify the positions of the particles in a new way. We mentally divide the volume of the box into a number M of rectangular cells of equal size stacked in a three-dimensional array (lattice) as shown schematically in Figure 3.11. Since the cell boundaries are imaginary the molecules pass freely through them. Instead of giving the values of three coordinates to specify the location of one particle we specify which cell it occupies. This *"coarse-grained" description* gives less precise information about the location of the particles than specifying exact coordinate values, but we can increase the precision by making the cells smaller. We continue to specify the velocity of each particle by specifying the values of three velocity components.

We assume that the probability that a randomly chosen molecule has a particular velocity is independent of the probability that it has a particular position. It is a fact of probability theory that the number of ways of accomplishing two independent events is the product of the number of ways of accomplishing each event. The thermodynamic probability is therefore the product of two factors, one for the coordinates and one for the velocities:

$$\Omega = \Omega_{\text{coord}}\Omega_{\text{vel}} \tag{3.4-2}$$

We now seek a formula to represent Ω_{coord} for our lattice gas. The number of possible coordinate states for a single molecule is equal to the number of cells, M. Since the molecules are mass points, the presence of one molecule in a cell does not keep other molecules from occupying the same cell. Any state of a second molecule can occur with any state of the first molecule, so the number of possible coordinate states for two molecules is M^2. Any state of a third molecule can occur with any state of the first pair of molecules, so the number of possible states for three particles is M^3. For a system of N molecules,

$$\Omega_{\text{coord}} = M^N \tag{3.4-3}$$

EXAMPLE 3.13

Calculate the value of Ω_{coord} and $\ln(\Omega_{\text{coord}})$ for 1.000 mol of an ideal gas in a volume of 24.4 L if cells of 0.500 nm on a side are taken.

Solution

$$V_{\text{cell}} = (0.500 \times 10^{-9}\ \text{m})^3 = 1.25 \times 10^{-28}\ \text{m}^3$$

$$M = \frac{V}{V_{\text{cell}}} = \frac{0.0244\ \text{m}^3}{1.25 \times 10^{-28}\ \text{m}^3} = 1.95 \times 10^{26}$$

$$\Omega_{\text{coord}} = M^N = (1.95 \times 10^{26})^{6.02\times 10^{23}} = 10^{1.58\times 10^{25}}$$

This is such a large number that we are not able to give any significant digits.

$$\ln(\Omega_{\text{coord}}) = 6.02 \times 10^{23} \ln(1.95 \times 10^{26}) = 3.65 \times 10^{25}$$

The value of Ω_{coord} in Example 3.10 is calculated on the assumption that the particles are distinguishable from each other. When quantum mechanics is studied, it is found that identical particles must be treated as inherently indistinguishable from each other. The number of ways of rearranging N distinguishable objects is $N!$ (N factorial), which is defined as the product of all of the integers starting with N and ranging down to unity:

$$N! = N(N-1)(N-2)(N-3)\ldots(2)(1) \quad \text{(definition)} \tag{3.4-4}$$

If the particles are actually indistinguishable, we have overcounted the value of Ω by this factor. We should replace the expression in Eq. (3.4-3) by

$$\Omega_{\text{coor}} = \frac{M^N}{N!} \tag{3.4-5}$$

so that

$$\ln(\Omega_{\text{coor}}) = N\ln(M) - \ln(N!) \tag{3.4-6}$$

For very large values of N the use of the exact expression for $N!$ is inconvenient. For fairly large values of N we can apply *Stirling's approximation*:

$$N! \approx (2\pi N)^{1/2} N^N e^{-N} \tag{3.4-7}$$

$$\ln(N!) \approx \frac{1}{2}\ln(2\pi N) + N\ln(N) - N \tag{3.4-8}$$

For very large values of N we can neglect the first term on the right-hand side of this equation:

$$\ln(N!) \approx N\ln(N) - N \tag{3.4-9}$$

With this approximation

$$\ln(\Omega) \approx N\ln(M) - N\ln(N) + N \tag{3.4-10}$$

EXAMPLE 3.14

Find the value of $\ln(\Omega_{\text{coord}})$ in Example 3.13 using Eq. (3.4-8).

Solution

$$\ln(\Omega_{\text{coord}}) = 3.64 \times 10^{25} - (6.022 \times 10^{23})\ln(6.022 \times 10^{23}) + 6.022 \times 10^{23}$$

$$= 4.03 \times 10^{24}$$

$$\Omega_{\text{coord}} = e^{4.03\times 10^{24}} = 10^{1.75\times 10^{24}}$$

Exercise 3.14

a. List the 36 possible states of two dice and give the probability for each sum of the two numbers showing in the upper faces of the dice.

b. Determine how many possible states occur for four dice.

c. Determine how many possible states occur for two "indistinguishable" dice, which means that there is no difference between a four on the first die and a five on the second die, or between a five on the first die and a four on the second, etc. Explain why the correct answer is not equal to 18.

The Statistical Entropy and the Thermodynamic Entropy

We now show that the change in the statistical entropy of our lattice gas for an isothermal volume change is equal to the change in the thermodynamic entropy for an ideal gas for the same volume change. Equation (3.3-3) gives the change in the thermodynamic entropy for an isothermal volume change in an ideal gas:

$$\Delta S = nR\ln(V_2/V_1) \tag{3.4-11}$$

where V_2 is the final volume and V_1 is the initial volume. The change in the statistical entropy for any process is

$$\Delta S_{\mathrm{st}} = k_{\mathrm{B}}\ln(\Omega_2) - k_{\mathrm{B}}\ln(\Omega_1) = k_{\mathrm{B}}\ln(\Omega_2/\Omega_1) = k_{\mathrm{B}}\ln\left(\frac{\Omega_{\mathrm{coord(2)}}\Omega_{\mathrm{vel(2)}}}{\Omega_{\mathrm{coord(1)}}\Omega_{\mathrm{vel(1)}}}\right) \tag{3.4-12}$$

The velocity of a molecule is independent of its position, so we assert that the velocity factor Ω_{vel} will not change in an isothermal change of volume. The velocity factors in Eq. (3.4-11) cancel, and

$$\Delta S_{\mathrm{st}} = k_{\mathrm{B}}\ln\left(\frac{\Omega_{\mathrm{coord(2)}}}{\Omega_{\mathrm{coord(1)}}}\right) \tag{3.4-13}$$

Using Eq. (3.4-6) and the fact that N is fixed,

$$\Delta S_{\mathrm{st}} = k_{\mathrm{B}}\ln\left(\frac{M_2^N}{M_1^N}\right) = k_{\mathrm{B}}\ln\left(\left(\frac{M_2}{M_1}\right)^N\right) = Nk_{\mathrm{B}}\ln\left(\frac{M_2}{M_1}\right) \tag{3.4-14}$$

The correction for indistinguishability does not affect ΔS_{st} for our process since the two divisors of N cancel.

In order to maintain a given precision of position specification, the size of the cells must be kept constant, so that the number of cells is proportional to the volume of the system:

$$M_2/M_1 = V_2/V_1 \tag{3.4-15}$$

Therefore,

$$\Delta S_{\mathrm{st}} = Nk_{\mathrm{B}}\ln(V_2/V_1) \tag{3.4-16}$$

The change in the statistical entropy is identical to the change in thermodynamic entropy given in Eq. (3.4-11) if we let

$$Nk_{\mathrm{B}} = nR \tag{3.4-17}$$

which assigns the value to Boltzmann's constant that we have already used:

$$k_{\mathrm{B}} = \frac{nR}{N} = \frac{R}{N_{\mathrm{Av}}} = \frac{8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}}{6.0221\times 10^{23}\ \mathrm{mol^{-1}}} = 1.3807\times 10^{-23}\ \mathrm{J\,K^{-1}} \tag{3.4-18}$$

We assert without further discussion that the equivalence between the statistical and thermodynamic entropies for isothermal expansions in a lattice gas is typical of all systems and all processes and write the general relation

$$S = S_{\text{st}} = k_{\text{B}} \ln(\Omega) + S_0 \quad \text{(general relation)} \tag{3.4-19}$$

where S is the thermodynamic entropy and where S_0 is a constant that can be taken equal to zero if that is convenient.

EXAMPLE 3.15

a. Find the coordinate contribution to the statistical entropy corresponding to the value of $\ln(\Omega_{\text{coord}})$ in Example 3.13.
b. Find the coordinate contribution to the statistical entropy corresponding to the value of $\ln(\Omega_{\text{coord}})$ corrected for indistinguishability in Example 3.14.

Solution

a.
$$S_{\text{coor}} = k_{\text{B}} \ln(\Omega_{\text{coord}}) = \left(1.3807 \times 10^{-23}\,\text{J K}^{-1}\right)(3.64 \times 10^{25})$$
$$= 503\,\text{J K}^{-1}$$

b.
$$S_{\text{coor}} = k_{\text{B}} \ln(\Omega_{\text{coord}}) = (1.3807 \times 10^{-23}\,\text{J K}^{-1})(4.03 \times 10^{24})$$
$$= 55.6\,\text{J K}^{-1}$$

The value in part a is much larger than the total entropy of a monatomic gas near room temperature. For example $S_m^\circ = 146.327\,\text{J K}^{-1}\,\text{mol}^{-1}$ at 298.15 K. The correction for indistinguishability in part b is obviously needed.

Exercise 3.15

Find the value of Ω for a system if its entropy is equal to $210\,\text{J K}^{-1}$.

The Interpretation of Entropy

Entropy has both macroscopic and molecular aspects, as we have seen. The thermodynamic entropy is defined in terms of heat transferred in a reversible process. When heat is transferred from a higher to a lower temperature, the entropy of the universe increases. Heat at a lower temperature is less efficient in driving a Carnot engine, so entropy has some connection with the efficiency with which heat can be turned into work. In a later chapter we will discuss free energy, which is closely associated with the thermodynamic entropy.

On the microscopic level, the statistical entropy is a measure of lack of information about the mechanical state of a system. It is commonly said that entropy is a measure of "randomness" with larger values corresponding to greater randomness. This statement is an imprecise and possibly misleading way of stating the connection between entropy and lack of information about the mechanical state. A room in a state of disarray is sometimes said to have a higher entropy than a room that has been organized. This is correct only if we have no information about the disorder in the room. If the disordered room can be viewed so that it is in a known state of disorder, its statistical entropy is no greater than that of the room if it is in a known state of order. However, disorder or randomness generally corresponds to greater lack of information about the mechanical state of the system, and the statement has some validity. The fact that a liquid has greater entropy than a solid corresponds not to the fact that a liquid has a more irregular structure, but to the fact that we do not know which disordered state it is in.

The connection between the statistical entropy and lack of information about the microstate can be illustrated by an example. Assume that a deck of 52 playing cards can be shuffled randomly in some way so that the order of the cards is completely unknown. (Note that a perfect shuffle, in which the deck is divided exactly in half and the cards are shuffled one card at a time from each half, results in an order that is known if the order was known prior to the shuffle. It is said that a sequence of a certain number of perfect shuffles restores the original order of the cards.) Lay the cards out face down on a table in four rows of 13 cards without looking at them. The statistical entropy of the cards is now

$$\begin{aligned} S_{\text{st}} &= k_{\text{B}} \ln(52!) = (1.3807 \times 10^{-23}\ \text{J K}^{-1}) \ln(8.0658 \times 10^{67}) \\ &= 2.1588 \times 10^{-21}\ \text{J K}^{-1} \end{aligned}$$

Now turn each card over without changing its position. The cards are still in an arrangement without any regular pattern, but we can now see which card is in each position. Ω is now equal to 1 and the statistical entropy is 0, even though the cards are still in the same disordered arrangement as when they were lying face down. It is not the lack of an ordered arrangement (the "randomness") that corresponds to an increase in entropy. It is the lack of information.

PROBLEMS

Section 3.4: Statistical Entropy

3.27 Assume that you have 1.00 mol of normal six-sided dice.

- **a.** If nothing is known about the orientation of the dice, what is the statistical entropy?
- **b.** If it is somehow known that every die is oriented with six spots on the top face, what is the statistical entropy?

3.28 Assume that a card game uses a deck of 96 unique cards. Calculate the change in statistical entropy of a deck of 96 cards if it is randomly shuffled. That is, it goes from a state in which the order of the cards is known to a completely unknown ordering.

3.29 Assume that a card game uses a deck of 96 cards, consisting of 24 sets of cards such that each set of four cards consists of four identical cards. Calculate the change in statistical entropy of a deck of 96 cards if it is randomly shuffled. That is, it goes from a state in which the order of the cards is known to a completely unknown ordering.

3.30 Assume that you have 100 coins, each of which can lie on a table with "heads" up or "tails" up.

- **a.** How many different arrangements are there for the coins?
- **b.** If you can turn one coin over per second, how long would it take you to go through all of the possible conformations of the coins?

3.31 Assume that an element exists that has two isotopes, and that each isotope has an abundance of 50.00%. Using the formula for the entropy of mixing for an ideal gas, calculate ΔS_{mix} for a sample of 1.000 mol of this element.

3.32 Tell whether the thermodynamic entropy of the system increases or decreases in each of the following processes, and tell why it behaves as it does. Do the same for the statistical entropy in each process.

- **a.** A sample of a gas is heated at constant volume.
- **b.** A sample of gas is expanded at constant temperature.
- **c.** A sample of liquid water is heated.
- **d.** A sample of liquid water is frozen.
- **e.** A sample of liquid water is vaporized.

3.5 The Third Law of Thermodynamics and Absolute Entropies

Walther Hermann Nernst, 1864–1941, was a German physical chemist who received the 1920 Nobel Prize in chemistry for his work on the third law of thermodynamics. He made numerous other contributions, including the Nernst equation of electrochemistry.

Theodor William Richards, 1868–1928, was an American chemist who won the 1914 Nobel Prize in chemistry for his accurate chemical determinations of atomic masses.

Max Karl Ernst Ludwig Planck, 1858–1947, was a German physicist who won the 1918 Nobel Prize in physics for his pioneering work in quantum theory.

Gilbert Newton Lewis, 1875–1946, was an American chemist who made a number of important contributions. Prior to the development of quantum mechanics, Lewis proposed that covalent chemical bonds arise from sharing of electrons according to the octet rule. He also proposed in 1926 that the name "photon" be applied to quanta of light.

Franz Eugen (Sir Francis) Simon, 1893–1956, was a German-British physicist who, independently of Giauque, developed the method of adiabatic demagnetization to reach low temperatures.

William Francis Giauque, 1895–1982, was an American chemist who discovered that ordinary oxygen consists of three isotopes. He received the 1949 Nobel Prize in chemistry for pioneering the process of adiabatic demagnetization to attain low temperatures.

The third law of thermodynamics was first stated by Nernst: *For certain isothermal chemical reactions between solids, the entropy changes approach zero as the thermodynamic temperature approaches zero*. Nernst based this statement on his analysis of experimental data obtained by T. W. Richards, who studied the entropy changes of chemical reactions between solids as the temperature was made lower and lower. The statement of Nernst was sometimes called *Nernst's heat theorem*, although it is a statement of experimental fact and not a mathematical theorem.

In 1911 Planck proposed extending Nernst's statement to assert that the entropies of individual substances actually approach zero as the temperature approaches zero. However, there is no experimental justification for this assertion. In 1923 Lewis proposed the following statement of the third law: "*If the entropy of each element in some crystalline state be taken as zero at the absolute zero of temperature, every substance has a finite positive entropy—but at the absolute zero of temperature the entropy may become zero, and does so become in the case of perfect crystalline substances.*"[4] We base our entropy calculations on this statement.

The restriction to perfect crystals was made necessary by the discoveries of Simon and Giauque, who found that substances such as CO and NO fail to obey the third law in their ordinary solid forms. These substances easily form metastable crystals with some molecules in positions that are the reverse of the equilibrium positions, and ordinary crystals are in metastable states such that their entropies do not approach zero at 0 K. We will return to this topic later in this section.

Exercise 3.16

Show that if the entropies of pure perfect crystalline elements are taken equal to nonzero constants at zero temperature, the molar entropy of a pure perfect crystalline compound at zero temperature is equal to the sum of the entropies of the appropriate numbers of moles of the elements at zero temperature.

The Unattainability of Absolute Zero

In Section 3.2, we showed that two reversible adiabats cannot cross. Since a reversible adiabat corresponds to constant entropy, the curve representing $T = 0$ is a reversible adiabat as well as an isotherm (curve of constant temperature). This is depicted in Figure 3.12, in which the variable X represents an independent variable specifying the state of the system, such as the volume or the magnetization. A reversible adiabat gives the temperature as a function of X. Since two reversible adiabats cannot intersect, no other reversible adiabat can cross or meet the $T = 0$ isotherm. Therefore, no reversible adiabatic process can reduce the temperature of the system to zero temperature. Furthermore, since we found in Section 3.2 that irreversible adiabatic processes lead to higher temperatures than a reversible adiabat, no adiabatic process, reversible or irreversible, can lead to zero temperature.

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[4] G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, 1st ed., McGraw-Hill, New York, 1923, p. 448.

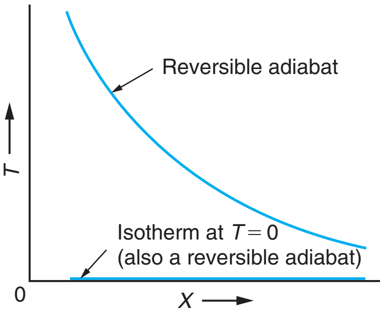

Figure 3.12 Reversible Adiabats Showing the Unattainability of Zero Temperature.

If no adiabatic process can lead to zero temperature, one might ask if some other kind of process might lead to zero temperature. Unless a heat reservoir already exists at zero temperature, conduction of heat away from an object cannot do the job, since heat flows from a hotter to a cooler object. A refrigerator cannot do the job, since its coefficient of performance must be less than that of a Carnot refrigerator, which approaches zero as the lower temperature approaches zero. We therefore conclude that no process can cause a system to attain 0 K, which is therefore called *absolute zero*. The unattainability of absolute zero is a consequence of both the second and third laws.

Very low temperatures have been attained by adiabatic demagnetization. The first step of this process, invented by Giauque, consists of magnetizing an object isothermally. The magnetization process decreases the entropy, since it aligns magnetic dipoles in the material and reduces the randomness of the system. Heat flows from the object to a heat reservoir during the magnetization. Once the object is magnetized, it is adiabatically insulated and then removed from the magnetic field that has magnetized it. During the adiabatic demagnetization, which approximates a reversible process, the entropy remains nearly constant and the temperature drops. Carrying out this process repeatedly has achieved temperatures of less than 0.000001 K (1 μK) in the nuclear spins of a magnetizable system. Recent studies of ultralow temperatures have involved opposing laser beams that effectively stop the translational motion of atoms, thus lowering their temperature so far as this motion is concerned. Saubamea and coworkers have achieved an effective temperature of 3×10^{-9} K (3 nK).[5]

Absolute Entropies

According to the third law as stated by Lewis, we can consistently set the entropy of any pure perfect crystalline substance equal to zero at zero temperature. The entropy change to bring a sample of a pure substance from zero temperature in a perfect crystalline form to some specified state is called the *absolute entropy* of that substance at that state. For any substance

$$S(T_1) = \int_0^{T_1} \frac{dq_{\text{rev}}}{T} \tag{3.5-1}$$

where $S(T_1)$ is the absolute entropy of the substance at temperature T_1. If there is no solid-solid phase transition between $T = 0$ and $T = T_1$ and if the final and initial states are at the same pressure, we can write for a solid substance

$$S_{\text{m}}(T_1) = -\int_0^{T_1} \frac{C_{\text{P,m}}}{T} dT \quad \text{(solid substance)} \tag{3.5-2}$$

Inspection of Eq. (3.5-2) shows that the heat capacity must approach zero as the temperature approaches zero in order to prevent divergence of the integral. Heat capacity data are difficult to obtain at very low temperatures, but all experimentally determined heat capacities tend toward zero as the temperature approaches zero. If no data are available

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[5] See for example J. Lawall, S. Kulin, B. Saubamea, N. Bigelow, M. Leduc, and C. Cohen-Tannoudji, *Phys. Rev. Lett.*, **75**, 4194 (1995).

Peter J. W. Debye, 1884–1966, was a Dutch-American physicist and chemist who received the Nobel Prize in chemistry in 1936 for his work on the dipole moments of molecules and who made numerous other important contributions.

for low temperatures, an approximate theory of Debye[6] can be used in lieu of data. According to this theory, the vibrations of a crystal of a monatomic substance produce a contribution to C_V at low temperatures that is proportional to T^3. An approximate theory for the motion of mobile electrons in metals gives a contribution proportional to T,[7] so that for sufficiently low temperature

$$C_{V,m} = aT^3 + bT \quad \text{(valid at low temperature)} \tag{3.5-3}$$

where a and b are parameters that can be determined from experimental data. For electrical insulators the parameter b is equal to zero. Equation (3.5-3) is quite reliable up to temperatures of about 15 K. Above this temperature data are usually available. Since the difference between C_P and C_V is numerically small for solids, Eq. (3.5-3) is usually used for C_P as well as for C_V.

Exercise 3.17

a. Show that if Eq. (3.5-3) is valid between zero temperature and some temperature T_1 and if $b = 0$, the value of the molar entropy at T_1 is given by

$$S_m(T_1) = \frac{aT_1^3}{3} = \frac{C_{V,m}(T_1)}{3} \tag{3.5-4}$$

b. Find the expression for $S_m(T_1)$ if b is not equal to zero.

If a phase transition occurs between zero temperature and the temperature of interest, Eq. (3.5-2) must be modified to include the entropy change of the phase transition. If the substance is a liquid at temperature T_1, the analogue of Eq. (3.5-2) is

$$S_m(T_1) = -\int_0^{T_f} \frac{C_{P,m}(s)}{T} dT + \frac{\Delta_{fus} H_m}{T_f} + \int_{T_f}^{T_1} \frac{C_{P,m}(l)}{T} dT \quad \text{(liquid system)} \tag{3.5-5}$$

where T_f is the reversible melting (fusion) temperature, $\Delta_{fus} H_m$ is the molar enthalpy change of fusion (melting), $C_{P,m}(s)$ is the molar heat capacity of the solid, and $C_{P,m}(l)$ is the molar heat capacity of the liquid.

Exercise 3.18

Write the equation analogous to Eq. (3.5-5) that applies to a gaseous substance.

Calculation of Entropy Changes for Chemical Reactions

Since absolute (third-law) entropies can be calculated from experimental data, tables of their values have been created. Some values for substances in their standard states

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[6] P. Debye, *Ann. Physik*, **17**(4), 817 (1911). See Section 22.3.

[7] J. S. Blakemore, *Solid State Physics*, 2nd ed., Saunders, Philadelphia, 1974, p. 176ff.

are included in Table A.8 of Appendix A. These values can be used to calculate entropy changes for chemical reactions. Consider a chemical reaction with a reaction equation written as in Chapter 2:

$$0 = \sum_{i=1}^{s} \nu_i \mathscr{F}_i \tag{3.5-6}$$

where ν_i is the stoichiometric coefficient of substance i and $\mathscr{F}_i$ is an abbreviation for its chemical formula. Since entropy is a state function, ΔS for a reaction at temperature T_1 must be equal to the sum of the entropy changes of the three processes: (1) The reactants are cooled to 0 K; (2) the chemical reaction is carried out at 0 K; and (3) the products are heated to temperature T_1. The entropy change for process (1) is equal to the negative of the sum of the absolute entropies of the reactants. The entropy change for process (2) equals zero according to the third law. The entropy change for process (3) is equal to the sum of the absolute entropies of the products. Therefore, ΔS for the reaction at temperature T_1 is given by

$$\boxed{\Delta S(T_1) = \sum_{i=1}^{s} \nu_i S_{\mathrm{m},i}(T_1)} \tag{3.5-7}$$

where s is the number of substances involved in the reaction and where $S_{\mathrm{m},i}(T_1)$ stands for the absolute molar entropy of substance number i at temperature T_1. Remember that the stoichiometric coefficients for products are positive and those for reactants are negative, so that equation represents the absolute entropies of the products minus those of the reactants. Compare this equation with Eq. (2.7-12), which contains enthalpy changes of formation. In Eq. (2.7-12) elements in their most stable form can be omitted from the formula for $\Delta H°$, since their enthalpies of formation are equal to zero. The formula for ΔS must include all substances since $S_{\mathrm{m},i}(T_1)$ does not vanish for elements at nonzero temperature.

The Standard State for the Entropy

For a solid or liquid, the standard state is the actual substance at pressure $P°$ (exactly 1 bar). For a gas, the standard state is a hypothetical ideal gas state at the standard pressure $P°$ (1 bar). That is, a correction must be made for the difference between the entropy of the real gas at pressure $P°$ and the corresponding ideal gas at pressure $P°$. We will discuss how to make this correction in Chapter 4, but the correction is small for ordinary pressures, and we can usually neglect it. These standard states are the same as for the enthalpy.

EXAMPLE 3.16

Compute the standard-state entropy change for 1 mol of the reaction

$$0 = 2\,\mathrm{CO_2(g)} - 2\,\mathrm{CO(g)} - \mathrm{O_2(g)}$$

if the product and reactants are at 298.15 K.

Solution

Using values from Table A.8,

$$\begin{aligned}\Delta S^{\circ} &= (2)(213.64\,\mathrm{J\,K^{-1}\,mol^{-1}}) + (-2)(197.564\,\mathrm{J\,K^{-1}\,mol^{-1}})\\ &\quad + (-1)(205.029\,\mathrm{J\,K^{-1}\,mol^{-1}})\\ &= -172.88\,\mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned}$$

Exercise 3.19

a. Explain in molecular terms why ΔS of the reaction in Example 3.16 is negative.
b. Calculate ΔH° for this reaction.
c. Without doing any calculation make a prediction about the entropy change of the surroundings for this reaction.
d. Assuming that the surroundings remain at equilibrium at 298.15 K, calculate the entropy change of the surroundings and of the universe for 1 mol of the reaction in Example 3.16.

Entropy Changes of Chemical Reactions at Various Temperatures

If you desire an entropy change for a chemical reaction at some temperature not found in a table, you can calculate it by using the fact that entropy is a state function. The procedure is analogous to that used with the enthalpy in Chapter 2. Assume that the entropy change at temperature T_1 is known and its value at temperature T_2 is desired. The entropy change at temperature T_2 is equal to the entropy change to bring the reactants from temperature T_2 to temperature T_1 plus the entropy change of the reaction at temperature T_1 plus the entropy change to bring the products from temperature T_1 to temperature T_2. If there are no phase changes between T_2 and T_1, the result is analogous to Eq. (2.7-19),

$$\Delta S(T_2) = \Delta S(T_1) + \int_{T_1}^{T_2} \frac{\Delta C_P}{T}\,dT \qquad (3.5\text{-}8)$$

where ΔC_P is defined in Eq. (2.7-20). If ΔC_P is temperature-independent,

$$\Delta S\,(T_2) = \Delta S\,(T_1) + \Delta C_P \ln\left(\frac{T_2}{T_1}\right) \quad (\Delta C_P\ \text{constant}) \qquad (3.5\text{-}9)$$

EXAMPLE 3.17

Calculate ΔS° for the reaction of the previous example at 373.15 K. Assume that the heat capacities are temperature-independent.

Solution

Using values from the appendix for 298.15 K,

$$\begin{aligned}\Delta C_P &= 2(37.129\,\mathrm{J\,K^{-1}\,mol^{-1}}) - 2(29.142\,\mathrm{J\,K^{-1}\,mol^{-1}}) - 29.376\,\mathrm{J\,K^{-1}\,mol^{-1}}\\ &= -13.402\,\mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta S^{\circ}(373.15\,\mathrm{K}) &= -172.88\,\mathrm{J\,K^{-1}\,mol^{-1}} + (-13.402\,\mathrm{J\,K^{-1}\,mol^{-1}})\ln\left(\frac{373.15\,\mathrm{K}}{298.15\,\mathrm{K}}\right)\\ &= -172.88\,\mathrm{J\,K^{-1}\,mol^{-1}} - 3.007\,\mathrm{J\,K^{-1}\,mol^{-1}} = 175.89\,\mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned}$$

Exercise 3.20

a. Calculate the entropy change at 298.15 K for the reaction

$$2\,H_2(g) + O_2(g) \rightarrow 2\,H_2O(l)$$

b. Calculate the entropy change at 400.0 K for the same reaction except that $H_2O(g)$ is the product.

Chapter 2 presented the approximate calculation of energy changes of chemical reactions, using average bond energies. There is an analogous estimation scheme for the entropy changes of chemical reactions, in which contributions from bonds and contributions from groups of atoms are included.[8] We do not discuss this scheme, but the interested student can read the article by Benson and Buss.

Statistical Entropy and the Third Law of Thermodynamics

As mentioned earlier, there are some substances such as carbon monoxide that do not obey the third law of thermodynamics in their ordinary forms. The absolute entropy of these substances determined by an integration such as in Eq. (3.5-1) turned out to be too small to agree with values inferred from entropy changes of chemical reactions and absolute entropies of other substances. Carbon monoxide molecules have only a small dipole moment (small partial charges at the ends of the molecule) and the two ends of the molecule are nearly the same size, so a carbon monoxide molecule fits into the crystal lattice almost as well with its ends reversed as in its equilibrium position. Metastable crystals can easily form with part of the molecules in the reversed position. If we assume that the occurrence of reversed molecules is independent of the rest of the state of the crystal, we can write

$$\Omega = \Omega_{\mathrm{orient}}\Omega_{\mathrm{rest}} \tag{3.5-10}$$

where Ω_{orient} is the number of ways of orienting the molecules in ways compatible with our knowledge of the state of the system, and Ω_{rest} is the number of possible states of the crystal if the orientation of the molecules is ignored.

Statistical mechanics predicts that at absolute zero the various vibrations of a crystal lattice all fall into a single lowest-energy state, as do the electronic motions. If there is no entropy of isotopic mixing,

$$\lim_{T\to 0} \Omega_{\mathrm{rest}} = 1 \quad \text{(equilibrium crystal)} \tag{3.5-11}$$

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[8] S. W. Benson and J. H. Buss, *J. Chem. Phys.*, **29**, 546 (1958); S. W. Benson *et al., Chem. Rev.*, **69**, 279 (1969).

If a metastable crystal exists in which each molecule can occur with equal probability in either the equilibrium state or the reversed state, then

$$\Omega_{\text{orient}} = 2^N \qquad \text{(metastable CO crystal)} \qquad (3.5\text{-}12)$$

where N is the number of molecules in the crystal. The molar statistical entropy of the metastable crystal near zero temperature is

$$S_{\text{st, m}} = k_B \ln(2^{N_{\text{Av}}}) = N_{\text{Av}} k_B \ln(2) = R\ln(2) = 5.76\,\text{J K}^{-1}\,\text{mol}^{-1} \qquad (3.5\text{-}13)$$

This value agrees with the amount by which carbon monoxide appeared to deviate from the third law.

Exercise 3.21

Pretend that you have synthesized 1.00 mol of $CaCO_3$ in which each carbonate ion has one ^{16}O atom, one ^{17}O atom, and one ^{18}O atom. Assume that every calcium atom is the same isotope and that every carbon atom is the same isotope. Calculate the entropy of the metastable crystal near zero temperature, if nothing is known about the orientations of the carbonate ions except that each equilibrium oxygen position is occupied by an oxygen atom of some isotope.

Trouton's Rule

Trouton's rule is an empirical rule for estimating entropy changes of vaporization. It states that for "normal" liquids the molar entropy change of vaporization, $\Delta_{\text{vap}} S_{\text{m}}$, at the normal boiling temperature (at 1.000 atm) is roughly equal to $10.5R \approx 88\,\text{J K}^{-1}\,\text{mol}^{-1}$. If you need a value for $\Delta_{\text{vap}} S_{\text{m}}$ or $\Delta_{\text{vap}} H_{\text{m}}$ and do not have data, you can use Trouton's rule to obtain an estimate. Trouton's rule underestimates the entropy change of vaporization for liquids such as ethanol and water, in which there is considerable molecular association. Trouton's rule also badly overestimates the entropy change of vaporization for hydrogen and helium. Modifications of Trouton's rule have been proposed, including a version that uses entropy changes of vaporization to form gases with the same value of the molar volume instead of whatever molar volume corresponds to 1 atm pressure at the normal boiling temperature. This modified rule seems to be more closely related to the formula for ΔS_{st} in Eq. (3.4-19) than the original version. The values for hydrogen and helium fall closer to those of other substances if this modified rule is used. There is also a method in which contributions for different groups of atoms in the molecule are considered.[9]

EXAMPLE 3.18

Use Trouton's rule to estimate $\Delta_{\text{vap}} H$ for methane from its normal boiling temperature, $-164°\text{C}$. Compare with the correct value in Table A.7 of the Appendix.

Solution

$$\Delta_{\text{vap}} H_{\text{m}} \approx (109\,\text{K})(88\,\text{J K}^{-1}\,\text{mol}^{-1}) = 9600\,\text{J mol}^{-1}$$

The value in Table A.7 is

$$\Delta_{\text{vap}} H_{\text{m}} = (555.19\,\text{J g}^{-1})(16.043\,\text{g mol}^{-1}) = 8907\,\text{J mol}^{-1}$$

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[9] D. Hoshino, K. Nagahama, and M. Hirata, *Ind. Eng. Chem. Fundam.*, **22**, 430 (1983).

Exercise 3.22

Use Trouton's rule to estimate $\Delta_{\text{vap}}H$ for ethane from its normal boiling temperature, $-88.6°\text{C}$. Compare with the correct value in Table A.7 of the Appendix.

PROBLEMS

Section 3.5: The Third Law of Thermodynamics and Absolute Entropies

3.33 Assign the following nonzero constant values for the standard-state molar entropies at 0 K:

$$\text{C(s)}\ 10.00\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$$

$$\text{O}_2\text{(s)}\ 20.00\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$$

$$\text{H}_2\text{(s)}\ 30.00\,\text{J}\,\text{K}^{-1}\,\text{mol}^{-1}$$

Accepting as experimental fact that the entropy changes of all reactions between pure solids at 0 K are equal to zero, assign values for the standard-state molar entropies of $CO_2(s)$ and $H_2O(s)$ at 0 K.

3.34 Calculate $\Delta S°$ at 298.15 K for each of the following reactions:

a. $2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$

b. $2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$

c. $CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$

d. $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$

3.35 Calculate $\Delta S°$ at 298.15 K for each of the following reactions:

a. $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$

b. $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$

c. $C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$

d. $2n\text{-}C_8H_{18}(g) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(g)$

3.36 Using absolute entropy values from Table A.8 and heat-capacity values from Table A.6 or Table A.8, calculate S_m° values for the substances at the indicated temperatures. If no polynomial representations are available, assume constant heat capacities.

a. $H_2(g)$ at 100.0°C

b. $O_2(g)$ at 100.0°C

c. $H_2O(l)$ at 100.0°C

d. $H_2O(g)$ at 100.0°C

3.37 Using absolute entropy values from Table A.8 and heat-capacity values from Table A.6 or Table A.8, calculate S_m° values for the substances at the indicated temperatures. If no polynomial representations are available, assume constant heat capacities.

a. $CH_4(g)$ at 200.0°C

b. $H_2O(g)$ at 200.0°C

3.38 **a.** Using absolute entropy values calculated in Problem 3.36, calculate $\Delta_{\text{vap}}S_\text{m}^\circ$, the standard molar enthalpy of vaporization for H_2O at 100.0°C.

b. Calculate $\Delta_{\text{vap}}S_\text{m}^\circ$ for H_2O at 25°C.

c. Calculate $\Delta_{\text{vap}}S_\text{m}^\circ$ at 100.0°C from data in Table A.7.

d. Comment on your values in light of Trouton's rule.

3.39 Tabulated entropy changes of formation could be used to calculate entropy changes of chemical reactions instead of absolute entropies.

a. Using absolute entropies, calculate the standard-state entropy change of formation at 298.15 K for $CO(g)$, $O_2(g)$, and $CO_2(g)$.

b. Calculate the standard-state entropy change at 298.15 K for the reaction:

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

using your values of entropy changes of formation from part a. Compare your result with that of Example 3.16.

3.40 Using S_m° values calculated in Problem 3.36, calculate $\Delta S°$ at 100°C for the reaction:

$$0 = 2\,H_2O(g) - O_2(g) - 2\,H_2(g)$$

3.41 Find the value of S°_{m} for solid silver at 270.0 K from the following data:

T/K	$C_{P,\mathrm{m}}$/J K^{-1} mol^{-1}	T/K	$C_{P,\mathrm{m}}$/J K^{-1} mol^{-1}
30	4.77	170	23.61
50	11.65	190	24.09
70	16.33	210	24.42
90	19.13	230	24.73
110	20.96	250	25.03
130	22.13	270	25.31
150	22.97		

Assume that the Debye formula can be used from 0 K to 30.0 K. Since there are an odd number of data points that are equally spaced, you can use Simpson's rule.

3.42 The following are heat capacity data for pyridine.[10]

T/K	$C_{P,\mathrm{m}}$(s)/ J K^{-1} mol^{-1}	T/K	$C_{P,\mathrm{m}}$(s)/ J K^{-1} mol^{-1}	T/K	$C_{P,\mathrm{m}}$(l)/ J K^{-1} mol^{-1}
13.08	4.448	151.57	63.434	231.49	120.67
21.26	12.083	167.60	68.053	239.70	122.23
28.53	19.288	179.44	71.756	254.41	124.54
35.36	25.309	193.02	76.467	273.75	127.93
48.14	33.723	201.61	79.835	293.96	131.88
64.01	40.748	212.16	84.446	298.15	132.74
82.91	46.413	223.74	94.328	307.16	134.55
101.39	50.861	231.49	101.25		
132.32	58.325				

A value of 8278.5 J mol^{-1} is reported for the enthalpy change of fusion at the normal melting temperature of 231.49 K.

a. Assuming that the Debye formula can be used between 0 K and 13.08 K, find the absolute entropy of solid pyridine at 231.49 K.

b. Find the absolute entropy of liquid pyridine at 231.49 K and at 298.15 K. Use a numerical technique to approximate the integrals needed.

3.43 For each of the substances in Table A.7, calculate the entropy change of vaporization at the normal boiling temperature and compare your result with Trouton's rule. Which of the substances qualify as "normal" liquids?

3.44 For each of the following substances, calculate the entropy change of vaporization at the normal boiling temperature and compare your result with Trouton's rule. Which of the substances qualify as "normal" liquids?

Substance	Boiling temperature/K	$\Delta_{\mathrm{vap}}H_{\mathrm{m}}$/kJ mol^{-1}
propane	231.0	20.133
n-butane	272.6	24.272
n-pentane	309.2	27.594
2-methyl butane	301.0	27.074
2,2-dimethyl propane	282.6	23.634
hexane	342.2	31.912
2-methyl pentane	333.4	32.119
3-methyl pentane	336.4	32.400
2,2-dimethyl butane	322.8	30.422
2,3-dimethyl butane	331	29.790

Summary of the Chapter

Kelvin's statement of the second law of thermodynamics is that heat put into a system that undergoes a cyclic process cannot be completely converted into work done on the surroundings. Clausius' statement of this law is that heat cannot flow from a cooler to a hotter body if nothing else happens. The mathematical statement of the second law was shown to be a consequence of the Kelvin statement. It asserts that S, the entropy, is a state function if we define

$$dS = \frac{dq_{\mathrm{rev}}}{T}$$

It was shown from the second law that in any reversible process the entropy of the universe remains constant, whereas in any irreversible process the entropy of the universe must increase.

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[10] F. T. Gucker and R. L. Seifert, *Physical Chemistry*, W. W. Norton, New York, 1966, p. 445.

A general procedure for the calculation of an entropy change in a closed system without phase change or chemical reaction is to carry out the line integral

$$\Delta S = \int_c \frac{dq_{\text{rev}}}{T}$$

over a curve in state space corresponding to a reversible path.

The statistical entropy is defined by

$$S_{\text{st}} = k_{\text{B}} \ln(\Omega) + S_0$$

where k_{B} is Boltzmann's constant and where Ω is the thermodynamic probability, equal to the number of mechanical states that might be occupied by the system given its macroscopic state. The quantity S_0 is an arbitrary constant whose value we can take to equal zero. We showed that for an isothermal expansion of a model system the change in the statistical entropy and the change in the thermodynamic entropy are equal.

The third law of thermodynamics asserts that if the entropies of all samples of pure perfect crystalline elements are taken as zero, the entropies of all samples of pure perfect crystalline compounds can also consistently be taken as zero. Entropies relative to the entropy at zero temperature are called absolute entropies. The values of these absolute entropies can be used to calculate entropy changes of chemical reactions.

A consequence of the second and third laws of thermodynamics is that no finite number of operations, either reversible or irreversible, can bring an object to zero temperature.

ADDITIONAL PROBLEMS

3.45 **a.** Sketch a diagram representing the Carnot cycle in a state space with S on the horizontal axis and T on the vertical axis.

b. Show that the work done on the surroundings in one cycle is equal to the area enclosed in this diagram.

3.46 Assume that a substance A can react without any energy change to an isomer C (as in a racemization reaction).

a. Assume that 1.000 mol of substance A is placed in a container that is adiabatically isolated from any surroundings and is allowed to equilibrate. Write an expression for the entropy change of the system as a function of x, the amount of A that has reacted.

b. Find the value of x at which the entropy of the system is at a maximum.

c. Find the value of the equilibrium constant for the reaction.

3.47 Supercooled (metastable) water vapor commonly occurs in the atmosphere if dust particles are not present to begin condensation to the liquid. Sometimes small particles, such as tiny crystals of silver iodide, are released from airplanes in an attempt to begin condensation. This process is called "cloud seeding." At a certain location, water vapor at 25°C has a metastable partial pressure of 32.0 torr. The equilibrium value at this temperature is 23.756 torr. Consider the air that is present to be the surroundings, and assume it to remain at equilibrium at 25°C. A tiny particle is added to begin condensation. Calculate ΔS, ΔH, and ΔS_{surr} per mole of water that condenses. State any assumptions.

3.48 Without doing any detailed calculations, specify for each process whether each of the following quantities is positive, negative, or equal to zero: q, w, ΔU, ΔS, and ΔS_{surr}.

a. The system consisting of two large objects and a small bar between them is allowed to come to equilibrium from an initial state in which the two objects are at different temperatures. Assume that the objects have fixed volume.

b. A sample of water is boiled at 100°C and 1.00 atm.

c. A sample of supercooled liquid water at −10°C is allowed to equilibrate adiabatically at constant pressure after a tiny crystal of ice is dropped into it.

d. A sample of an ideal gas expands irreversibly and adiabatically into a vacuum, as in the Joule experiment.

e. A sample of gas is heated at constant volume.

f. A sample of gas is heated at constant pressure.

g. A sample of gas expands reversibly at constant temperature.

h. A sample of gas expands reversibly and adiabatically.

3.49 Assume that an automobile engine burns 2,2,4-trimethyl pentane (iso-octane), forming only $CO_2(g)$ and $H_2O(g)$. The density of iso-octane is $0.6909\ \mathrm{g\ mL^{-1}}$, and 1.00 gallon is approximately equal to 3.76 L.

a. Find the amount of heat that can be obtained from combustion of 1.000 gallon of iso-octane. Ignore the temperature dependence of ΔH of the combustion reaction.

b. If the combustion temperature is 2200°C and the exhaust temperature is 800°C, find the maximum height to which an automobile of 1000.0 kg can be lifted by combustion of 1.000 gallon of iso-octane. Ignore all forms of friction. State any assumptions.

c. In some countries, antipollution laws require that the combustion temperature of automobile engines be lowered by exhaust gas recirculation, in an attempt to reduce the amount of nitrogen oxides produced. Repeat part b with a combustion temperature of 1800°C.

3.50 Construct an accurate graph of each of the following:

a. $S^\circ_\mathrm{m}(T) - S^\circ_\mathrm{m}(100\ \mathrm{K})$ for a monatomic ideal gas with $C_{V,\mathrm{m}} = 3R/2$ as a function of temperature from 100 K to 300 K.

b. $S_\mathrm{m}(V_\mathrm{m}) - S_\mathrm{m}(1.000\ \mathrm{L})$ of an ideal gas as a function of V_m from $1.000\ \mathrm{L\ mol^{-1}}$ to $10.00\ \mathrm{L\ mol^{-1}}$ at a constant temperature of 300 K.

c. $S^\circ_\mathrm{m}(T) - S^\circ_\mathrm{m}(223.15\ \mathrm{K})$ for water as a function of temperature from 223.15 K to 323.15 K.

3.51 Label each of the following statements as true or false. If a statement is true only under certain conditions, label it as false.

a. The entropy of any system must increase when an irreversible process occurs.

b. The entropy of the surroundings must increase when an irreversible process occurs.

c. The entropy of the universe must increase when an irreversible process occurs.

d. The entropy of any system remains constant when a reversible process occurs.

e. The entropy of the surroundings remains constant when a reversible process occurs.

f. The entropy of the universe remains constant when a reversible process occurs.

g. The energy of an isolated system remains constant when a reversible process occurs in the system.

h. The energy of an isolated system decreases when a reversible process occurs in the system.

3.52 A steam engine has an efficiency that is 55% as large as that of a Carnot engine. If its boiler is at 250°C and its exhaust is at 100°C, calculate the height to which it can lift a 1000 kg mass near the earth's surface if it burns 5.00 kg of coal. Pretend that the coal is pure graphite and that its enthalpy change of combustion is equal to that at 25°C.

3.53 Assume that naturally occurring chlorine is 75% ^{35}Cl and 25% ^{37}Cl.

a. Calculate the entropy of mixing in 1.00 mol of atomic chlorine.

b. Assume that you have 1.00 mol of carbon tetrachloride in which the chlorine isotopes are randomly mixed. Assume that all of the carbon atoms are ^{12}C. How many different kinds of molecules are there, and what is the amount in moles of each kind of molecule?

c. Find the entropy of mixing of the 1.00 mol of carbon tetrachloride.

3.54 The calculation of the statistical entropy of a metastable disordered ice crystal is a famous problem that has not yet been solved exactly. Each water molecule has an oxygen atom with two hydrogens covalently bonded (at a smaller distance) and two hydrogens on other molecules hydrogen bonded to it (at a larger distance). A large number of coordinate states can be generated by moving the hydrogens around. For example, if one of the hydrogen-bonded hydrogens is brought closer to a given oxygen and covalently bonded to it, one of the covalently bonded hydrogens must move farther away and become hydrogen bonded. Make a crude first estimate of the statistical entropy of a disordered ice crystal containing 1.000 mol of water molecules by pretending that each oxygen can have its four hydrogens move independently of the others, so long as two hydrogens are close to it and two are farther from it.

3.55 Pretend that you can synthesize 1.000 mol of carbon tetrachloride in which every molecule contains four different isotopes of chlorine. Assume that in the crystal at a very low temperature any one of the molecules can occupy any one of the possible orientations such that each equilibrium location of a chlorine atom is occupied by one of the four isotopes but that the crystal is otherwise in its equilibrium state.

a. How many different orientations are there for each molecule?

b. What is the statistical entropy of the crystal?

4

The Thermodynamics of Real Systems

PRINCIPAL FACTS AND IDEAS

1. The second law of thermodynamics provides the general criterion for possible processes: The entropy of the universe cannot decrease.
2. This general criterion can be used to derive criteria for spontaneous processes in a system under various circumstances.
3. The Gibbs and Helmholtz energies provide information about the maximum amount of work that can be done by a system.
4. General equations for the differentials of various thermodynamic functions can be written from the first and second laws.
5. Thermodynamic equations for practical applications can be obtained from these general equations.
6. The methods of calculus can provide useful thermodynamic relations, such as the Maxwell relations.
7. The chemical potential is an important variable in describing multicomponent systems.
8. Euler's theorem and the Gibbs–Duhem relation are useful in making calculations.

4.1

Criteria for Spontaneous Processes and for Equilibrium: The Gibbs and Helmholtz Energies

In Chapters 2 and 3 we presented the fundamental principles of thermodynamics. In this chapter we use these principles to construct thermodynamic tools with which to analyze real systems. Learning to use these tools allows you to apply thermodynamics in a useful way. Someone has facetiously said that the practice of thermodynamics is like finding the right wrench with which to pound on the right screw.

Criteria for Spontaneous Processes in Closed Systems

The general criterion for spontaneous processes is that the entropy of the universe must increase. We now express this criterion in terms of the properties of a closed system that can exchange heat and work with its surroundings. We make the simplest possible assumption about the surroundings: that the surroundings have a very large thermal conductivity and a very large heat capacity so that all processes in the surroundings are reversible. Equation (3.2-27) asserts that under these conditions all processes must obey

$$dS \geq \frac{dq}{T_{\text{surr}}} = \frac{(dU - dw)}{T_{\text{surr}}} \tag{4.1-1}$$

where T_{surr} is the temperature of the surroundings and where we have used the first law to write the second equality. Since T_{surr} must be positive, we can multiply by T_{surr} without changing the direction of the inequality, obtaining

$$\boxed{dU - dw - T_{\text{surr}}\,dS \leq 0} \tag{4.1-2}$$

We now consider several special cases.

The first case is that of an *isolated system*, which is a closed system that cannot exchange either heat or work with its surroundings. In this case $dq = 0$ and $dw = 0$ so that $dU = 0$ and

$$\boxed{dS \geq 0 \quad \text{(isolated system)}} \tag{4.1-3}$$

An isolated system is an *adiabatic system* with the additional requirement that $dw = 0$, so Eq. (4.1-3) is a special case of Eq. (3.2-22) for an adiabatic system.

The second case is that $dS = 0$ and $dw = 0$,

$$\boxed{dU \leq 0 \quad (S \text{ constant}, dw = 0)} \tag{4.1-4}$$

This is a case that is not likely to be encountered in thermodynamics since there is no convenient way to keep the entropy of a system constant while a process occurs.

The third case is that of an *isothermal system* (constant-temperature system). If the system is maintained at the constant temperature of the surroundings ($T = T_{\text{surr}}$), Eq. (4.1-2) becomes

$$dU - TdS - dw \leq 0 \quad (T = T_{\text{surr}} = \text{constant}) \tag{4.1-5}$$

If our system is simple, $dw = -P(\text{transmitted})\,dV$, and

$$dU - TdS + P(\text{transmitted})\,dV \leq 0 \quad \text{(simple system, } T \text{ constant)} \tag{4.1-6}$$

There are two important cases for isothermal closed simple systems. The first case is that of a constant volume, so that $dV = 0$:

$$dU - TdS \leq 0 \quad \text{(simple system, } T \text{ and } V \text{ constant)} \tag{4.1-7}$$

The *Helmholtz energy* is denoted by A and is defined by

$$\boxed{A = U - TS \quad \text{(definition)}} \tag{4.1-8}$$

The Helmholtz energy is named for Hermann Ludwig von Helmholtz, 1821–1894, already mentioned in Chapter 2 as the first person to announce the first law of thermodynamics.

The Helmholtz energy has been known to physicists as the "free energy" and as the "Helmholtz function." It has been known to chemists as the "work function" and as the "Helmholtz free energy." The differential of the Helmholtz energy is

$$dA = dU - TdS - SdT \tag{4.1-9}$$

so that if T is constant

$$dA = dU - TdS \quad \text{(constant } T) \tag{4.1-10}$$

Equation (4.1-7) is the same as

$$\boxed{dA \leq 0 \quad \text{(simple system, } T \text{ and } V \text{ constant)}} \tag{4.1-11}$$

The second important isothermal case is the case that the pressure of the system is constant and equal to P_{ext} and to P (transmitted). We refer to this case simply as "constant pressure." In this case,

$$\boxed{dU + PdV - TdS \leq 0 \quad \begin{array}{l}\text{(simple system,}\\ T \text{ and } P \text{ constant)}\end{array}} \tag{4.1-12}$$

The *Gibbs energy* is defined by

$$\boxed{G = U + PV - TS \quad \text{(definition)}} \tag{4.1-13}$$

The Gibbs energy is named for Josiah Willard Gibbs, 1839–1903, an American physicist who made fundamental contributions to thermodynamics and statistical mechanics and who was the first American scientist after Benjamin Franklin to gain an international scientific reputation.

The Gibbs energy is related to the enthalpy and the Helmholtz energy by the relations

$$\boxed{G = H - TS = A + PV} \tag{4.1-14}$$

The Gibbs energy has been called the "free energy," the "Gibbs free energy," the "Gibbs function," and the "free enthalpy." The symbol F has been used in the past for both the Helmholtz energy and the Gibbs energy. To avoid confusion, the symbol F should not be used for either of these functions and the term "free energy" should not be used.

The differential of the Gibbs energy is

$$dG = dU + PdV + VdP - TdS - SdT \tag{4.1-15}$$

If T and P are constant, this equation becomes

$$dG = dU + PdV - TdS \quad (T \text{ and } P \text{ constant}) \tag{4.1-16}$$

The relation in Eq. (4.1-12) is the same as

$$dG \le 0 \quad (\text{simple system, } T \text{ and } P \text{ constant}) \tag{4.1-17}$$

The criteria for finite processes are completely analogous to those for infinitesimal processes. For example, for a simple system at constant pressure and temperature, a finite spontaneous process must obey

$$\Delta G \le 0 \quad (\text{simple system, } T \text{ and } P \text{ constant}) \tag{4.1-18}$$

Constant temperature and pressure are the most common circumstances in the laboratory, so Eq. (4.1-18) is the most useful criterion for the spontaneity of chemical reactions. Thermodynamics does not distinguish between chemical and physical processes, and Eq. (4.1-17) is valid for physical processes such as phase transitions as well as for chemical reactions.

Pierre Eugene Marcelin Berthelot, 1827–1907, was a French chemist who synthesized many useful compounds, but who argued against Dalton's atomic theory of matter.

Pierre-Maurice-Marie Duhem, 1861–1916, was a French physicist whose doctoral dissertation showing Berthelot's conjecture to be false was initially rejected because of Berthelot's objection.

In the 19th century, Berthelot incorrectly maintained that all spontaneous chemical reactions must be *exothermic* ($\Delta H < 0$). The incorrectness of Berthelot's conjecture was shown by Duhem, who established Eq. (4.1-18), which can be written in the form

$$\Delta H - T\Delta S \le 0 \quad \begin{array}{l}(\text{simple system,} \\ T \text{ and } P \text{ constant})\end{array} \tag{4.1-19}$$

The ΔH term dominates at sufficiently low temperature, but the $T\Delta S$ term becomes important and can dominate at sufficiently high temperature. In many chemical reactions near room temperature the $T\Delta S$ term is numerically less important than the ΔH term, and most spontaneous chemical reactions are exothermic, a fact that presumably led Bertholet to his thermodynamically incorrect assertion.

We can illustrate the interplay of ΔH and ΔS with the vaporization of a liquid, for which ΔH and ΔS are both positive. At a given pressure there is some temperature at which the vaporization is a reversible process so that $\Delta G = 0$ and $\Delta H = T\Delta S$. When T is smaller than this equilibrium temperature, the ΔH term dominates and $\Delta G > 0$ for the vaporization process. That is, condensation is spontaneous and the equilibrium phase is the liquid phase. At a higher temperature the $T\Delta S$ term dominates and $\Delta G < 0$ for the vaporization process, which is spontaneous. The gas phase is the equilibrium phase.

Some people say that there are two tendencies: (1) that of the enthalpy or energy of a system tends to decrease, and (2) that the entropy of the system tends to increase. In fact, there is only one fundamental tendency, that of the entropy of the universe to increase. We can separately focus on the two terms in Eq. (4.1-19), but you should remember that the lowering of the enthalpy corresponds to an increase in the entropy of the surroundings.

We summarize our results for the cases considered:

1. *If a system is isolated, its entropy cannot decrease.*
2. *If* S *of a closed system is fixed and no work is done,* U *cannot increase.*
3. *If a simple closed system is at constant* T *and* V, A *cannot increase.*
4. *If a simple closed system is at constant* T *and* P, G *cannot increase.*

The Equilibrium State of a Closed Simple System

For a system to be at macroscopic equilibrium, every process must have proceeded to the state at which the appropriate criterion for spontaneity has been satisfied. For example, when a closed simple system at constant temperature and pressure reaches equilibrium, the Gibbs energy must have reached the minimum value possible at that pressure and temperature. In Figure 4.1 the variable x schematically represents the extent to which a chemical reaction or some other process has occurred. We assume that a state variable such as the Gibbs energy is a differentiable function of its independent variables, so that there is a smooth minimum as shown in Figure 4.1a, not a cusp as shown in Figure 4.1b. The value of x at the minimum in the curve corresponds to the equilibrium state for the particular constant values of P and T and conforms to

$$\left(\frac{\partial G}{\partial x}\right)_{T,P} = 0 \quad \text{(closed simple system at macroscopic equilibrium with } T \text{ and } P \text{ constant)} \tag{4.1-20}$$

If the temperature and pressure are constant, an infinitesimal change in a simple system at equilibrium must obey

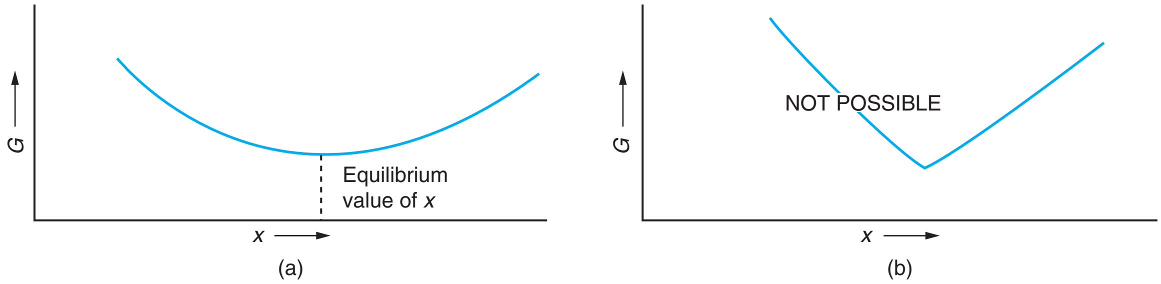
$$dG = 0 \quad \text{(closed simple system at macroscopic equilibrium with } T \text{ and } P \text{ constant)} \tag{4.1-21}$$

For a closed simple system at constant temperature and volume, the value of x at equilibrium corresponds to a minimum in A:

$$\left(\frac{\partial A}{\partial x}\right)_{T,P} = 0 \quad \text{(closed simple system at macroscopic equilibrium with } T \text{ and } V \text{ constant)} \tag{4.1-22}$$

An infinitesimal change at equilibrium at constant T and V must obey

$$dA = 0 \quad \text{(closed simple system at macroscopic equilibrium } T \text{ and } V \text{ constant)} \tag{4.1-23}$$



(a) (b)

Figure 4.1 The Gibbs Energy as a Function of the Extent of a Process. (a) As it actually is assumed to be (schematic). (b) As it is assumed not to be (schematic).

Once a system has reached equilibrium, its state is independent of how that state was reached. The Gibbs energy is at a minimum if processes at constant T and P are considered. The Helmholtz energy is at a minimum if processes at constant T and V are considered. If a simple closed system is at constant T and P but not yet at equilibrium, a spontaneous process could possibly increase the value of A, but must decrease the value of G. If a simple closed system is at constant T and V but is not yet at equilibrium, a spontaneous process could possibly increase the value of G, but must decrease the value of A.

Maximum Work

We now seek criteria for the maximum work that can be done on the surroundings by a closed system. For a system at constant temperature, Eq. (4.1-5) is

$$dU - TdS - dw = dA - dw \leq 0 \quad (T \text{ constant}) \tag{4.1-24}$$

This is the same as

$$dA \leq dw \quad (T \text{ constant}) \tag{4.1-25}$$

For a finite process at constant temperature

$$\Delta A \leq w \quad (T \text{ constant}) \tag{4.1-26}$$

At constant temperature, the Helmholtz energy of a system can be increased by doing work on the system, but ΔA cannot exceed w. Alternatively, the system can do work on the surroundings by lowering its Helmholtz energy, but the work done on the surroundings is limited by

$$dw_{\text{surr}} \leq -dA \quad (T \text{ constant}) \tag{4.1-27}$$

For a finite process at constant temperature

$$w_{\text{surr}} \leq -\Delta A \quad (T \text{ constant}) \tag{4.1-28}$$

A system that is not a simple system can exchange work with the surroundings in different ways. We write

$$dw = -P(\text{transmitted})\, dV + dw_{\text{net}} \tag{4.1-29}$$

The term $-P(\text{transmitted})\, dV$ represents the work that can be done on the system by changing its volume. We now call this term *compression work* or *P–V work*. The term dw_{net} represents any work in addition to compression work that can be done on a nonsimple system. We call it the *net work*. Two examples of net work are electrical work and stress-strain work (stretching a spring or a rubber band). If the volume of a system is constant, $dw = dw_{\text{net}}$ and we can write

$$w_{\text{net,surr}} \leq -\Delta A \quad (T \text{ and } V \text{ constant}) \tag{4.1-30}$$

In the case of constant temperature and constant pressure with P equal to P(transmitted), Eq. (4.1-24) is

$$dU - TdS + PdV - dw_{\text{net}} = dG - dw_{\text{net}} \leq 0 \quad (T \text{ and } P \text{ constant})$$

$$dG \leq dw_{\text{net}} \quad (T \text{ and } P \text{ constant}) \tag{4.1-31}$$

For a finite process

$$\Delta G \leq w_{\text{net}} \quad (T \text{ and } P \text{ constant}) \tag{4.1-32}$$

It is possible to increase the Gibbs energy of a nonsimple system at constant T and P by doing net work on the system, but the increase in the Gibbs energy cannot be greater than the net work done on the system. In electrolysis or charging a battery, a chemical reaction is caused to proceed in the nonspontaneous direction (the direction of increase of the Gibbs energy) by passing an electric current through an electrochemical cell, performing net work.

A nonsimple system can do work on the surroundings by lowering its Gibbs energy, but Eq. (4.1-31) provides a limit to the net work that can be done on the surroundings:

$$dw_{\text{net,surr}} \leq -dG \quad (T \text{ and } P \text{ constant}) \tag{4.1-33}$$

For a finite process,

$$w_{\text{net,surr}} \leq -\Delta G \quad (T \text{ and } P \text{ constant}) \tag{4.1-34}$$

To do net work on the surroundings at constant T and P, a process with a negative value of ΔG must be found.

Equilibrium Criteria for Nonsimple Systems

If a system at equilibrium undergoes an infinitesimal change at constant T and V,

$$dA - dw_{\text{net}} = 0 \quad \begin{pmatrix}\text{equilibrium,} \\ \text{constant } T \text{ and } V\end{pmatrix} \tag{4.1-35}$$

In the case of constant T and P,

$$dG - dw_{\text{net}} = 0 \quad \begin{pmatrix}\text{equilibrium,} \\ \text{constant } T \text{ and } P\end{pmatrix} \tag{4.1-36}$$

The equilibrium state of a nonsimple system is affected by the agent that can do net work on it. For example, a galvanic cell such as a lead storage battery has an equilibrium state that depends on the external voltage applied to it. With an external voltage you can charge a lead storage battery to an equilibrium state with large amounts of reactants (Pb, PbO_2, and H_2SO_4). If you remove the external voltage and attach a short circuit, the battery will tend toward an equilibrium state in which the battery is fully discharged and the reactants are depleted, leaving a large amount of products ($PbSO_4$).

PROBLEMS

Section 4.1: Criteria for Spontaneous Processes and for Equilibrium: The Gibbs and Helmholtz Energies

4.1 If a simple system is somehow maintained at constant S and P, show that its enthalpy cannot increase.

4.2 **a.** Calculate $\Delta S°$ and $\Delta H°$ for the vaporization of 1.000 mol of water at 298.15 K from the data in Table A.8 in the appendix.

b. Calculate $\Delta G°$ for the vaporization of 1.000 mol of water at 298.15 K.

c. Assume that both $\Delta S°$ and $\Delta H°$ for the vaporization of water are temperature-independent. Find the temperature at which $\Delta G° = \Delta H° - T\Delta S°$ vanishes. If your assumption were correct, this should be the temperature at which liquid water and water vapor are at equilibrium if the pressure is 1.000 bar.

d. Assume that $C_{P,m}$ is temperature-independent for both the solid and the liquid and find the temperature at which $\Delta G° = \Delta H° - T\Delta S°$ vanishes.

4.3 Consider the reaction at 298.15 K:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

a. Calculate the value of $\Delta H°$ for this reaction.

b. Assume that $\Delta H°$ is temperature-independent. If the heat from this reaction is used to power a steam turbine with an efficiency that is 60.0% as great as that of a Carnot engine operating between 200.0°C and 400.0°C, find the maximum amount of work that can be done by the combustion of 2.000 mol of hydrogen gas.

c. Calculate $\Delta G°$ for this reaction at 298.15 K from $\Delta H°$ and $\Delta S°$.

d. This reaction is carried out in fuel cells in spacecraft. Calculate the maximum amount of net work that can be done on the surroundings by the reaction of 2.000 mol of hydrogen gas at 298.15 K. Calculate the total amount of work that can be done on the surroundings. Comment on the comparison between your results from parts b and d.

4.2 Fundamental Relations for Closed Simple Systems

Thermodynamics includes a number of useful relations that allow one variable to be replaced by another to which it is equal but which can be more easily evaluated. In this section we obtain several such relations based on expressions for the differentials of state functions. For a closed simple system and for reversible processes the first law of thermodynamics is

$$dU = dq_{\text{rev}} - PdV \quad \text{(closed simple system)} \tag{4.2-1}$$

and the second law is

$$dS = \frac{dq_{\text{rev}}}{T} \quad \text{(closed simple system)} \tag{4.2-2}$$

Combination of these equations using the fact that T cannot be negative gives an important relation for dU for reversible processes in a simple closed system:

$$\boxed{dU = TdS - PdV \quad \text{(simple closed system; reversible processes)}} \tag{4.2-3}$$

This equation is restricted to reversible changes of state because dq_{rev} was used in its derivation and because $P = P(\text{transmitted})$ was assumed.

Irreversible thermodynamics or *nonequilibrium thermodynamics* is an extended version of thermodynamics that deals with rates of entropy production and with rates of processes and their driving forces. In irreversible thermodynamics, Eq. (4.2-3) is assumed to be valid for nonequilibrium changes if the deviation from equilibrium is not too large. This assumption is an additional hypothesis and does not follow from thermodynamics. See the Additional Reading section for further information on irreversible thermodynamics.

The equilibrium macroscopic state of a one-phase simple system is specified by $c + 2$ independent variables, where c is the number of independent substances (components) in the system. If the system is closed, the amounts of the substances are fixed and only two variables can be varied independently. We take U to be a function of S and V for a simple closed system. An infinitesimal change in U that corresponds to a reversible process is given by the fundamental relation of differential calculus:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n} dV \quad \text{(simple closed system; reversible processes)} \tag{4.2-4}$$

where the single subscript n means that the amounts of all substances present are fixed. Comparison of Eqs. (4.2-3) and (4.2-4) gives us two important relations:

$$\boxed{\left(\frac{\partial U}{\partial S}\right)_{V,n} = T} \tag{4.2-5}$$

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_{S,n} = -P} \tag{4.2-6}$$

Maxwell Relations

From the *Euler reciprocity relation* shown in Eq. (B-13) of Appendix B, we can write

$$\left(\frac{\partial^2 U}{\partial S \partial V}\right)_n = \left(\frac{\partial^2 U}{\partial V \partial S}\right)_n \tag{4.2-7}$$

A second derivative is the derivative of a first derivative,

$$\left(\frac{\partial^2 U}{\partial V \partial S}\right)_n = \left(\frac{\partial T}{\partial V}\right)_{S,n} \tag{4.2-8}$$

$$\left(\frac{\partial^2 U}{\partial S \partial V}\right)_n = -\left(\frac{\partial P}{\partial S}\right)_{V,n} \tag{4.2-9}$$

Therefore

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_{S,n} = -\left(\frac{\partial P}{\partial S}\right)_{V,n} \quad \text{(a Maxwell relation)}} \tag{4.2-10}$$

The Maxwell relations are named for James Clerk Maxwell, 1831–1879, a great British physicist who made fundamental contributions to electromagnetic theory, gas kinetic theory, and thermodynamics.

Equation (4.2-10) is one of a class of equations called *Maxwell relations*. A common use of these relations is to replace a partial derivative that is hard to measure with one that can more easily be measured. For example, it would be difficult to measure $(\partial P/\partial S)_{V,n}$, but much easier to measure $(\partial T/\partial V)_{S,n}$.

EXAMPLE 4.1

From the relation in Eq. (4.2-10), find an expression for $(\partial P/\partial S)_{V,n}$ for an ideal gas with constant heat capacity.

Solution

Equation (2.4-21) gives for a reversible adiabatic process in an ideal gas with constant heat capacity

$$T = T_1\left(\frac{V_1}{V}\right)^{nR/C_\mathrm{V}}$$

where we omit the subscripts on the final values of T and V. Since a reversible adiabatic process corresponds to constant entropy, differentiation of this formula with respect to V corresponds to constant S:

$$\begin{aligned}\left(\frac{\partial P}{\partial S}\right)_{V,n_n} &= -\left(\frac{\partial T}{\partial V}\right)_{S,n}\\ &= -T_1\,(V_1)^{nR/C_\mathrm{V}}\left(\frac{nR}{C_\mathrm{V}}\right)V^{-(nR/C_\mathrm{V})-1}\\ &= \frac{nRT_1}{C_\mathrm{V}V}\left(\frac{V_1}{V}\right)V^{nR/C_\mathrm{V}}\end{aligned}$$

To complete the solution, we replace $T_1{V_1}^{nR/C_\mathrm{V}}$ by TV^{nR/C_V}:

$$\left(\frac{\partial P}{\partial S}\right)_{V,n} = -\frac{nRT}{C_\mathrm{V}V} = -\frac{RT}{C_{\mathrm{V,m}}V}$$

Exercise 4.1

a. Find the value of $(\partial P/\partial S)_{V,n}$ for 1.000 mol of helium at 1.000 atm (101325 Pa) and 298.15 K. Assume that helium is ideal with $C_\mathrm{V} = 3nR/2$.

b. Find the value of $(\partial P/\partial S)_{V,n}$ for 2.000 mol of helium at 1.000 atm (101325 Pa) and 298.15 K. Explain the dependence on the amount of substance.

c. Find the value of $(\partial P/\partial S)_{V,n}$ for 1.000 mol of helium at 2.000 atm (202650 Pa) and 298.15 K. Explain the dependence on the pressure.

We now write the differential dH for a closed system from the definition of H:

$$\begin{aligned}dH &= dU + PdV + VdP = TdS - PdV + PdV + VdP \qquad (4.2\text{-}11)\\ &= TdS + VdP \quad \text{(closed system)}\end{aligned}$$

Therefore

$$\boxed{\left(\frac{\partial H}{\partial S}\right)_{P,n} = T} \tag{4.2-12}$$

and

$$\boxed{\left(\frac{\partial H}{\partial P}\right)_{S,n} = V} \tag{4.2-13}$$

Using the Euler reciprocity relation, we obtain a second Maxwell relation:

$$\boxed{\left(\frac{\partial T}{\partial P}\right)_{S,n} = \left(\frac{\partial V}{\partial S}\right)_{P,n} \quad \text{(a Maxwell relation)}} \tag{4.2-14}$$

EXAMPLE 4.2

Find an expression for $(\partial V/\partial S)_{P,n}$ for an ideal gas with constant heat capacity.

Solution

For a reversible adiabatic process,

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{nR/(C_V+nR)}$$

Drop the subscript 2:

$$T = T_1\left(\frac{P}{P_1}\right)^{nR/(C_V+nR)}$$

$$\begin{aligned}\left(\frac{\partial V}{\partial S}\right)_{P,n} &= \left(\frac{\partial T}{\partial P}\right)_{S,n}\\ &= \frac{nR}{C_V+nR}\,\frac{T_1}{P_1^{nR/(C_V+nR)}}\,P^{nR/(C_V+nR)-1}\\ &= \frac{nR}{C_V+nR}\,\frac{T_1}{P_1^{nR/(C_V+nR)}}\,P^{nR/(C_V+nR)}\,\frac{1}{P}\\ &= \frac{nR}{C_V+nR}\,\frac{T}{P} = \frac{R}{C_{V,m}+R}\,\frac{T}{P}\end{aligned}$$

Exercise 4.2

a. Evaluate $(\partial V/\partial S)_{P,n}$ for 1.000 mol of helium (assumed ideal) at 1.000 atm and 298.15 K. Take $C_{V,m} = 3R/2$.

b. Evaluate $(\partial V/\partial S)_{P,n}$ for 2.000 mol of helium at 1.000 atm and 298.15 K. Explain the dependence on the amount of substance.

We now obtain some additional useful equations. Equations (4.1-8) and (4.2-3) give

$$dA = -SdT - PdV \quad \text{(closed system)} \tag{4.2-15}$$

so that

$$\boxed{\left(\frac{\partial A}{\partial T}\right)_{V,n} = -S} \tag{4.2-16}$$

$$\boxed{\left(\frac{\partial A}{\partial V}\right)_{T,n} = -P} \tag{4.2-17}$$

A third Maxwell relation is

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_{T,n} = \left(\frac{\partial P}{\partial T}\right)_{V,n} \quad \text{(a Maxwell relation)}} \tag{4.2-18}$$

Equations (4.1-13) and (4.2-3) give

$$dG = -SdT + VdP \quad \text{(closed system)} \tag{4.2-19}$$

so that

$$\boxed{\left(\frac{\partial G}{\partial T}\right)_{P,n} = -S} \tag{4.2-20}$$

$$\boxed{\left(\frac{\partial G}{\partial P}\right)_{T,n} = V} \tag{4.2-21}$$

Our fourth Maxwell relation is

$$\boxed{\left(\frac{\partial S}{\partial P}\right)_{T,n} = -\left(\frac{\partial V}{\partial T}\right)_{P,n} \quad \text{(a Maxwell relation)}} \tag{4.2-22}$$

A mnemonic device for writing the Maxwell relations is to write a blank relation

$$\left(\frac{\partial \cdots}{\partial \cdots}\right)_{\cdots,n} = \left(\frac{\partial \cdots}{\partial \cdots}\right)_{\cdots,n}$$

and then to put P and V in opposite corners and T and S in the other opposite corners. There are four ways to do this, giving the four Maxwell relations. In each relation the independent variable in one derivative is held constant in the other derivative and n is fixed in both of the derivatives. If T and V occur in the same derivative, attach a negative sign to one side. Otherwise, the signs are positive.

We can now derive the formula for ΔS for an isothermal volume change in an ideal gas in a different way from that used in Chapter 4:

$$\Delta S = \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V}\right)_{T,n} dV = \int_{V_1}^{V_2} \left(\frac{\partial P}{\partial T}\right)_{V,n} dV$$

$$= \int_{V_1}^{V_2} \left(\frac{nR}{V}\right) dV = nR\ln\left(\frac{V_2}{V_1}\right) \tag{4.2-23}$$

We can also obtain an expression for ΔS for nonideal gases, liquids, and solids.

EXAMPLE 4.3

a. Find an expression for $(\partial S/\partial V)_{T,n}$ for n moles of a gas obeying the truncated virial equation of state

$$\frac{PV_{\mathrm{m}}}{RT} = 1 + \frac{B_2}{V_{\mathrm{m}}}$$

where B_2 is a function of T and where V_{m} is the molar volume.

b. Evaluate the expression for $(\partial S/\partial V)_{T,n}$ for 1.000 mol of argon in 25.00 L at 298.15 K. At this temperature, $B_2 = -15.8\ \mathrm{cm^3\ mol^{-1}}$ and $dB_2/dT = 0.25 \times 10^{-6}\ \mathrm{m^3\ mol^{-1}\ K^{-1}}$.

c. Find an expression for ΔS for an isothermal volume change for n moles of a gas obeying the truncated virial equation of state in part a. Compare your result with the corresponding equation for an ideal gas.

d. Find the value of ΔS for expanding 1.000 mol of argon isothermally at 298.15 K from 25.00 L to 50.00 L. Compare the result with the result assuming argon to be an ideal gas.

Solution

a. Keeping V and n constant is the same as keeping V_{m} constant.

$$\left(\frac{\partial S}{\partial V}\right)_{T,n} = \left(\frac{\partial P}{\partial T}\right)_{V,n} = \left(\frac{\partial\left(RT/V_{\mathrm{m}} + RT\,B_2/V_{\mathrm{m}}^2\right)}{\partial T}\right)_{V_{\mathrm{m}}}$$

$$= \frac{R}{V_{\mathrm{m}}} + \frac{R}{V_{\mathrm{m}}^2}\left[B_2 + T\frac{dB_2}{dT}\right]$$

b.

$$\left(\frac{\partial S}{\partial V}\right)_{T,n} = \frac{8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}}{0.025\ \mathrm{m^3\ mol^{-1}}} + \frac{8.3145\ \mathrm{J^{-1}\ mol^{-1}}}{(0.025\ \mathrm{m^3\ mol^{-1}})^2}$$

$$\times\Big[(-15.8 \times 10^{-6}\ \mathrm{m^3\ mol^{-1}})$$

$$+ (298.15\ \mathrm{K})\big(0.25 \times 10^{-6}\ \mathrm{m^3\ mol^{-1}\ K^{-1}}\big)\Big]$$

$$= 332.6\ \mathrm{N\ m^{-2}\ K^{-1}} + 0.58\ \mathrm{N\ m^{-2}\ K^{-1}}$$

$$= 333.2\ \mathrm{N\ m^{-2}\ K^{-1}}$$

$$= 333.2\ \mathrm{J\ K^{-1}\ m^{-3}}$$

The correction for gas nonideality, $0.58\ \mathrm{J\ K^{-1}\ m^{-3}}$, is numerically almost insignificant in this case, but for smaller molar volumes it would be more important.

c. For an isothermal process in a closed system,

$$\Delta S = \int_c dS = \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V}\right)_{r_n} dV = \int_{V_1}^{V_2} \left[\frac{R}{V_\mathrm{m}} + \frac{R}{V_\mathrm{m}^2}\left(B_2 + T\frac{dB_2}{dT}\right)\right] dV$$

$$= n\int_{V_1}^{V_2} \frac{R}{V_\mathrm{m}} dV_\mathrm{m} + n\left(B_2 + T\frac{dB_2}{dT}\right)\int_{V_1}^{V_2} \frac{R}{V_\mathrm{m}^2} dV_\mathrm{m}$$

$$= nR\ln\left(\frac{V_\mathrm{m2}}{V_\mathrm{m1}}\right) - n\left(B_2 + T\frac{dB_2}{dT}\right)\left(\frac{1}{V_\mathrm{m2}} - \frac{1}{V_\mathrm{m1}}\right)$$

d.

$$\Delta S = (1.000\,\mathrm{mol})(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\ln\left(\frac{0.05000}{0.02500}\right)$$

$$- (1.000\,\mathrm{mol})(8.3145\,\mathrm{J^{-1}\,mol^{-1}})$$

$$\times \left(-15.8 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}}\right)$$

$$+ (298.15\,\mathrm{K})(0.20 \times 10^{-6}\,\mathrm{m^3\,mol^{-1}\,K^{-1}})$$

$$\times \left(\frac{1}{0.05000\,\mathrm{m^3\,mol^{-1}}} - \frac{1}{0.02500\,\mathrm{m^3\,mol^{-1}}}\right)$$

$$= 5.763\,\mathrm{J\,K^{-1}} + 0.00729\,\mathrm{J\,K^{-1}} = 5.770\,\mathrm{J\,K^{-1}}$$

The correction for nonideality, $0.007\,\mathrm{J\,K^{-1}}$, is numerically almost insignificant in this case.

We can also derive an expression for ΔS for an isothermal pressure change, using another Maxwell relation:

$$\Delta S = \int_{P_1}^{P_2} \left(\frac{\partial S}{\partial P}\right)_{T,n} dP = -\int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T}\right)_{P,n} dP \tag{4.2-24}$$

EXAMPLE 4.4

a. Find an expression for ΔS for an isothermal pressure change on a pure liquid assuming that the volume of the liquid is constant.

b. Find an expression for ΔS for an isothermal pressure change on a pure liquid, assuming that the volume of the liquid is given by

$$V(T,P) = V(T_1,P_1)[1 + \alpha(T - T_1) - \kappa_\mathrm{T}(P - P_1)]$$

where α and κ_T are equal to constants and where P_1 and T_1 are a reference pressure and a reference temperature.

c. Find ΔS for pressurizing 1.000 mol of liquid water isothermally at 298.15 K from a pressure of 1.00 atm to a pressure of 100.00 atm.

Solution

a.

$$\Delta S = \int_{P_1}^{P_2} \left(\frac{\partial S}{\partial P}\right)_{T,n} dP = -\int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T}\right)_{P,n} dP = -\int_{P_1}^{P_2} V\alpha dP = 0$$

$\Delta S = 0$ since $\alpha = 0$ if V is constant.

b.

$$\Delta S = \int_{P_1}^{P_2} \left(\frac{\partial S}{\partial P}\right)_{T,n} dP = -\int_{P_1}^{P_2} \left(\frac{\partial V}{\partial T}\right)_{P,n} dP = -\int_{P_1}^{P_2} V\alpha dP$$

$$= -\int_{P_1}^{P_2} V(T_1, P_1)[1 + \kappa_\mathrm{T}(P - P_1)]\,\alpha dP$$

$$= -V(T_1, P_1)\int_{P_1}^{P_2} [1 - \kappa_\mathrm{T}(P - P_1)]\,\alpha dP$$

$$= -V(T_1, P_1)\alpha(P_2 - P_1) - V(T_1, P_1)\kappa_\mathrm{T}\alpha\frac{1}{2}(P - P_1)^2$$

c.

$$\Delta S = -(18.0 \times 10^{-6}\,\mathrm{m}^3)(2.07 \times 10^{-4}\,\mathrm{K}^{-1})(99.00\,\mathrm{atm})(101325\,\mathrm{Pa\,atm}^{-1})$$

$$+ (18.0 \times 10^{-6}\,\mathrm{m}^3)(4.57 \times 10^{-10}\,\mathrm{Pa}^{-1})(2.07 \times 10^{-4}\,\mathrm{K}^{-1})$$

$$\times \frac{1}{2}(99.00\,\mathrm{atm})(101325\,\mathrm{Pa\,atm}^{-1})^2$$

$$= -0.0374\,\mathrm{J\,K}^{-1} + 0.000086\,\mathrm{J\,K}^{-1} = -0.0373\ \mathrm{J\,K}^{-1}$$

The smallness of this result indicates that assuming a constant volume for a liquid is numerically a good approximation.

EXAMPLE 4.5

The pressure virial equation of state was shown in Eq. (1.3-4), and it was shown in an example that A_2, the second pressure virial coefficient, is equal to B_2, the second virial coefficient. Find an expression for $(\partial S/\partial P)_{T,n}$ for a gas obeying the pressure virial equation of state truncated at the A_2 term.

Solution

$$\left(\frac{\partial S}{\partial P}\right)_{T,n} = -\left(\frac{\partial V}{\partial T}\right)_{P,n} = -\left(\frac{\partial}{\partial T}\left(\frac{nRT}{p} + nA_2\right)\right)_{P,n} = -\frac{nR}{p} - n\frac{dA_2}{dT}$$

Exercise 4.3

Evaluate $(\partial S/\partial P)_{T,n}$ for 1.000 mol of argon at 1.000 atm and 298.15 K. For argon at this temperature, B_2 is equal to $-15.8\,\mathrm{cm}^3\,\mathrm{mol}^{-1}$ and dB_2/dT is approximately equal to $0.25\,\mathrm{cm}^3\,\mathrm{mol}^{-1}\,\mathrm{K}^{-1}$.

EXAMPLE 4.6

Derive the expression for the entropy change for an isothermal pressure change of a gas described by this truncated pressure virial equation of state.

Solution

$$\Delta S = \int_{P_1}^{P_2} \left(\frac{\partial S}{\partial P}\right)_{T,n} dP = -\int_{P_1}^{P_2} \left(\frac{nR}{P} + n\frac{dA_2}{dT}\right) dP$$

$$= -nR\ln\left(\frac{P_2}{P_1}\right) - n\frac{dA_2}{dT}(P_2 - P_1)$$

Exercise 4.4

Calculate ΔS for the expansion of 1.000 mol of argon from 10.00 atm to 1.000 atm at 298.15 K, assuming the truncated pressure virial equation of state. Compare your result with that obtained by assuming argon to be ideal.

PROBLEMS

Section 4.2: Fundamental Relations for Closed Simple Systems

4.4 The *fundamental equation* or *fundamental relation of thermodynamics* for a particular system is a formula giving S and a function of U, V, and n, or giving U as a function of S, V, and n for that system. If this relation is known, all thermodynamic information about the system can be obtained from it. For an ideal monatomic gas with constant heat capacity,[1]

$$S = nS_0/n_0 + nR\ln{(U/U_0)^{3/2}(V/V_0)(n/n_0)^{-5/2}}$$

where S_0, n_0, and V_0 are constants.

a. Solve this equation for $U = U(S, V, n)$.

b. Use Eq. (4.2-5) to obtain an expression for T. Use this expression to obtain an expression for U as a function of T and n.

c. Use Eq. (4.2-6) to obtain an expression for P. Use this expression to obtain an expression for P as a function of T, V, and n.

4.5 A system obeys the fundamental thermodynamic relation

$$U = U(S, V, n) = Kn^{5/3}(V - nb)^{-2/3}e^{2S/3nR} - \frac{n^2a}{V}$$

where K is a constant. Find expressions for P, T, and μ. Show that the system obeys the van der Waals equation of state.

4.6 Consider a gas obeying the truncated pressure virial equation of state

$$PV_{\mathrm{m}} = RT + A_2P + A_3P^2$$

where the pressure virial coefficients A_2 and A_3 depend on T.

a. Find an expression for $(\partial S/\partial P)_{T,n}$ for this gas.

b. Write an expression for $G(T, P_2, n) - G(T, P_1, n)$ for this gas.

c. Find the value of ΔG for pressurizing 2.500 mol of argon from 1.000 atm to 25.00 atm at 298.15 K. Assume that $A_3 \approx 0$.

4.7 A gas is represented by the truncated virial equation of state

$$PV_{\mathrm{m}}/RT = 1 + B_2/V_{\mathrm{m}} + B_3/V_{\mathrm{m}}^2$$

where the virial coefficients depend on T.

a. Find an expression for the molar entropy change for an isothermal volume change of the gas.

b. Find the value of ΔS for the expansion of 2.000 mol of argon from 5.00 L to 30.00 L at a constant temperature of 298.15 K. Assume that $B_3 \approx 0$. Compare your answer with the value assuming that argon is ideal.

4.8 Consider a gas that obeys the van der Waals equation of state.

a. Find an expression for $(\partial S/\partial V)_{T,n}$ for this gas.

b. Find the value of ΔS for the isothermal expansion of 2.000 mol of argon from a volume of 5.00 L to a volume of 30.00 L at 298.15 K, assuming the van der Waals equation of state. Compare with the value for the same change in state assuming argon to be ideal.

4.9 Consider a gas obeying the Redlich–Kwong equation of state.

a. Find an expression for $(\partial S/\partial V)_{T,n}$ for this gas.

b. Find the value for ΔS for the isothermal expansion of 2.000 mol of argon from a volume of 10.00 L to a volume of 40.00 L at 298.15 K, assuming the Redlich–Kwong equation of state. Compare with the value for the same change in state assuming argon to be ideal.

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[1] H. B. Callen, *Thermodynamics*, Wiley, New York, 1960, pp. 26ff, 53ff.

4.3 Additional Useful Thermodynamic Identities

We have asserted without proof that $(\partial U/\partial V)_{T,n}$ vanishes for an ideal gas. We can now prove this assertion and can obtain a formula that allows evaluation of this derivative for nonideal gases and liquids. We convert Eq. (4.2-3) to a derivative equation by nonrigorously "dividing" by dV, converting the quotients to partial derivatives, and specifying that T and n are held fixed. The process is mathematically indefensible, but gives the correct derivative relation:

$$\left(\frac{\partial U}{\partial P}\right)_{T,n} = T\left(\frac{\partial S}{\partial V}\right)_{T,n} - P\left(\frac{\partial V}{\partial V}\right)_{T,n} = T\left(\frac{\partial S}{\partial V}\right)_{T,n} - P \qquad (4.3\text{-}1)$$

We apply the Maxwell relation of Eq. (4.2-18) to the first term to obtain

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_{T,n} = T\left(\frac{\partial P}{\partial T}\right)_{V,n} - P \quad \text{(the thermodynamic equation of state)}} \qquad (4.3\text{-}2)$$

The relation shown in Eq. (4.3-2) is called the *thermodynamic equation of state*. For an ideal gas,

$$T\left(\frac{\partial P}{\partial T}\right)_{V,n} = T\frac{nR}{V} = P \qquad (4.3\text{-}3)$$

so that

$$\boxed{\left(\frac{\partial U}{\partial V}\right)_{T,n} = P - P = 0} \qquad (4.3\text{-}4)$$

It is now necessary only to specify that $PV = nRT$ to define an ideal gas.

EXAMPLE 4.7

Show that P is proportional to T in an ideal gas if V and n are constant, using Eqs. (4.3-1) and (4.3-4).

Solution

For an ideal gas

$$T\left(\frac{\partial P}{\partial T}\right)_{V,n} = P$$

$$\left(\frac{\partial P}{\partial T}\right)_{V,n} = \frac{P}{T}$$

At constant V and n,

$$\frac{1}{P}dP = \frac{1}{T}dT$$

$$\ln(P) = \ln(T) + \ln(\mathit{constant})$$

$$\frac{P}{T} = \mathit{constant} \text{ at constant } V \text{ and } n$$

EXAMPLE 4.8

For a gas obeying the truncated virial equation of state,

$$\frac{PV_{\mathrm{m}}}{RT} = 1 + \frac{B_2}{V_{\mathrm{m}}}$$

show that

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = RT^2 \frac{(dB_2/dT)}{V_{\mathrm{m}}^2}$$

Solution

$$P = \frac{RT}{V_{\mathrm{m}}} + \frac{RT\,B_2}{V_{\mathrm{m}}^2}$$

From Eq. (4.3-2)

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = T\left(\frac{\partial P}{\partial T}\right)_{V,n} - P$$

If both V and n are held fixed, then V_{m} is held fixed;

$$T\left(\frac{\partial P}{\partial T}\right)_{V,n} = \frac{RT}{V_{\mathrm{m}}} + \frac{RT}{V_{\mathrm{m}}^2}\left(B_2 + T\frac{dB_2}{dT}\right)$$

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = \frac{RT}{V_{\mathrm{m}}} + \frac{RT}{V_{\mathrm{m}}^2}\left(B_2 + T\frac{dB_2}{dT}\right) - \frac{RT}{V_{\mathrm{m}}} - \frac{RT\,B_2}{V_{\mathrm{m}}^2}$$

$$= \frac{RT^2}{V_{\mathrm{m}}^2}\frac{dB_2}{dT}$$

Exercise 4.5

Find the value of $(\partial U/\partial V)_{T,n}$ for 1.000 mol of argon at 1.000 atm and 298.15 K, using the truncated virial equation of state.

The partial derivative $(\partial U/\partial V)_{T,n}$ is an important measure of the deviation of a system from ideal gas behavior. It has the same units as pressure and is known as the *internal pressure*. If the internal pressure is positive, the energy increases as the volume increases and work is done against the attractive intermolecular forces. The internal pressure is a measure of the net cohesive forces of the system and can have a large positive value for liquids.

To derive a useful equation for the internal pressure, we begin with Eq. (4.3-2) and apply the cycle rule to the partial derivative on the right-hand side of the equation:

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = -T\left(\frac{\partial P}{\partial V}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{P,n} - P$$

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = T\frac{\alpha}{\kappa_{\mathrm{T}}} - P \tag{4.3-5}$$

where α is the coefficient of thermal expansion and κ_{T} is the isothermal compressibility.

EXAMPLE 4.9

Evaluate the internal pressure of liquid benzene at 298.15 K and 1.000 atm.

Solution

$$\begin{aligned}\left(\frac{\partial U}{\partial V}\right)_{T,n} &= (298.15\,\mathrm{K})\frac{\left(1.237 \times 10^{-3}\,\mathrm{K}^{-1}\right)}{9.67 \times 10^{-10}\,\mathrm{Pa}^{-1}} - 101325\,\mathrm{Pa}\\ &= 3.81 \times 10^{8}\,\mathrm{Pa}\end{aligned}$$

This internal pressure is equal to 3760 atm.

Exercise 4.6

a. Evaluate the internal pressure of liquid water at 25°C and 1.000 atm.

b. Calculate the gravitational force per unit area on a column of water 100 m in height. Explain how the internal pressure relates to the fact that in a giant sequoia tree, sap can be brought to a height of nearly 100 m in the tree whereas barometric pressure can raise it only to about 10 m against a vacuum. What can you say about the attractive forces between the sap and the walls of the vessel containing it? If a gas bubble appeared in the sap, what would happen?

An equation for $(\partial H/\partial P)_{T,n}$ that is analogous to Eq. (4.3-2) can be derived in a similar way. We convert Eq. (4.2-11) to a derivative equation:

$$\left(\frac{\partial H}{\partial P}\right)_{T,n} = -T\left(\frac{\partial S}{\partial P}\right)_{T,n} + V\left(\frac{\partial P}{\partial P}\right)_{T,n} = T\left(\frac{\partial S}{\partial P}\right)_{T,n} + V$$

Using the Maxwell relation of Eq. (4.2-22), we obtain

$$\left(\frac{\partial H}{\partial P}\right)_{T,n} = -T\left(\frac{\partial V}{\partial T}\right)_{P,n} + V \tag{4.3-6}$$

EXAMPLE 4.10

Show that for an ideal gas $(\partial H/\partial P)_{T,n} = 0$, using only the equation of state, $PV = nRT$, and Eq. (4.3-6).

Solution

$$\begin{aligned}\left(\frac{\partial H}{\partial P}\right)_{T,n} &= -T\left(\frac{\partial V}{\partial T}\right)_{V,n} V = -T\left(\frac{\partial}{\partial T}\left(\frac{nRT}{P}\right)\right)_{P,n} + V\\ &= -\frac{nRT}{P} + V = 0\end{aligned}$$

Exercise 4.7

a. Find an expression for $(\partial H/\partial P)_{T,n}$ for a gas obeying the truncated pressure virial equation of state:

$$PV_{\mathrm{m}} = RT + A_2P$$

where A_2 is a function of T. It has been shown that the second pressure virial coefficient A_2 is equal to B_2, the second virial coefficient.

b. Evaluate $(\partial H/\partial P)_{T,n}$ for 1.000 mol of argon at 1.000 atm and 298.15 K. Data on B_2 and dB_2/dT are found in Example 4.3.

We can now obtain a useful relation between C_{P} and C_{V} for systems other than ideal gases. Equation (2.5-11) is

$$C_{\mathrm{P}} = C_{\mathrm{V}} + \left[\left(\frac{\partial U}{\partial V}\right)_{T,n} + P\right]\left(\frac{\partial V}{\partial T}\right)_{P,n} \tag{4.3-7}$$

The C_{V} term represents the energy change due to an increase in temperature that would occur if the volume were constant. The $(\partial U/\partial V)$ (internal pressure) term represents the energy absorbed in raising the potential energy of intermolecular attraction, and the $P(\partial V/\partial T)$ term represents work done against the pressure exerted by the surroundings.

We now use the thermodynamic equation of state to write

$$\begin{aligned} C_{\mathrm{P}} &= C_{\mathrm{V}} + \left[T\left(\frac{\partial P}{\partial T}\right)_{V,n} + P - P\right]\left(\frac{\partial V}{\partial T}\right)_{P,n} \\ &= C_{\mathrm{V}} + T\left(\frac{\partial P}{\partial T}\right)_{V,n}\left(\frac{\partial V}{\partial T}\right)_{P,n} \end{aligned} \tag{4.3-8}$$

We apply the cycle rule, Eq. (B-15) of Appendix B, in the form:

$$\left(\frac{\partial P}{\partial T}\right)_{V,n}\left(\frac{\partial T}{\partial V}\right)_{P,n}\left(\frac{\partial V}{\partial P}\right)_{T,n} = -1 \tag{4.3-9}$$

which gives

$$C_{\mathrm{P}} = C_{\mathrm{V}} - T\left(\frac{\partial P}{\partial V}\right)_{T,n}\left[\left(\frac{\partial V}{\partial T}\right)_{P,n}\right]^2 \tag{4.3-10}$$

We obtain

$$C_{\mathrm{P}} = C_{\mathrm{V}} - T\left(\frac{\partial P}{\partial V}\right)_{T,n}\left[\left(\frac{\partial V}{\partial T}\right)_{P,n}\right]^2 = C_{\mathrm{V}} + \frac{TV\alpha^2}{\kappa_{\mathrm{T}}} \tag{4.3-11}$$

where α is the coefficient of thermal expansion and κ_{T} is the isothermal compressibility. Since α (which is occasionally negative) is squared and since κ_{T} is always positive, C_{P} is never smaller than C_{V}.

EXAMPLE 4.11

Calculate $C_{V,m}$ for liquid water at 0.00°C and 1.000 atm. The constant-pressure heat capacity is equal to $75.983\ \mathrm{J\,K^{-1}\,mol^{-1}}$. The coefficient of thermal expansion is equal to $-68.14 \times 10^{-6}\ \mathrm{K^{-1}}$ at this temperature (this is one of the few cases in which this quantity is negative). The compressibility is equal to $5.098 \times 10^{-10}\ \mathrm{Pa^{-1}}$. The molar volume is equal to $18.012\ \mathrm{cm^3 mol^{-1}}$.

Solution

$$C_{P,m} - C_{V,m} = \frac{(273.15\ \mathrm{K})\left(18.012 \times 10^{-6}\ \mathrm{m^3}\right)\left(-68.14 \times 10^{-6}\ \mathrm{K^{-1}}\right)^2}{\left(5.098 \times 10^{-10}\ \mathrm{Pa^{-1}}\right)}$$

$$= 0.04481\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

$$C_{V,m} = 75.983\ \mathrm{J\,K^{-1}\,mol^{-1}} - 0.04481\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

$$= 75.938\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

Exercise 4.8

a. Find the value of $C_{V,m}$ for liquid water at 25.00°C and 1.000 atm. The coefficient of thermal expansion is equal to $2.07 \times 10^{-4}\ \mathrm{K^{-1}}$, the molar volume is equal to $18.0687\ \mathrm{cm^3\,mol^{-1}}$, and the compressibility is equal to $45.24 \times 10^{-6}\ \mathrm{bar^{-1}}$. $C_{P,m}$ is equal to $75.351\ \mathrm{J\,K^{-1}\,mol^{-1}}$.

b. At 3.98°C liquid water has a maximum density and the coefficient of thermal expansion vanishes. What is the value of $C_{P,m} - C_{V,m}$ at this temperature?

c. Show that Eq. (4.3-11) leads to the expression for an ideal gas obtained in Chapter 2:

$$C_{P,m} - C_{V,m} = R \quad \text{(ideal gas)}$$

d. Calculate the value of the ratio $\gamma = C_{P,m}/C_{V,m}$ for liquid water at 25.00°C and 1.000 atm and compare it to the value of the same ratio for argon gas at the same temperature and pressure.

There are a number of organic liquids that have fairly large coefficients of thermal expansion. In these cases the difference between $C_{V,m}$ and $C_{P,m}$ is somewhat larger than is the case with water in the preceding example. For almost all solids the difference between $C_{P,m}$ and $C_{V,m}$ is quite small.

EXAMPLE 4.12

Calculate the value of $C_{V,m}$ for liquid benzene at 20°C and 1.00 atm. The density of benzene at 20°C is $0.8765\ \mathrm{g\,cm^{-3}}$. The value of the isothermal compressibility in the appendix applies at 25°C. Assume that you can use this value at 20°C.

Solution

From Eq. (4.3-11)

$$C_P = C_V + \frac{TV\alpha^2}{\kappa_T}$$

From the appendix, the value of $C_{\mathrm{P,m}}$ for liquid benzene is 135.31 J K^{-1} mol^{-1}. The molar volume is

$$V_{\mathrm{m}} = \left(\frac{78.11\ \mathrm{g\,mol^{-1}}}{0.8765\ \mathrm{g\,cm^{-3}}}\right)\left(\frac{1\ \mathrm{m^3}}{10^6\ \mathrm{cm^3}}\right) = 8.912\times 10^{-5}\ \mathrm{m^3\,mol^{-1}}$$

$$\begin{aligned} C_{\mathrm{V,m}} &= 135.31\ \mathrm{J\,K^{-1}\,mol^{-1}} \\ &\quad - \frac{(293.15\ \mathrm{K})(8.912\times 10^{-5}\ \mathrm{m^3\,mol^{-1}})(1.237\times 10^{-3}\ \mathrm{K^{-1}})^2}{9.67\times 10^{-10}\ \mathrm{Pa^{-1}}} \\ &= 93.96\ \mathrm{J\,K^{-1}\,mol^{-1}} \end{aligned}$$

Exercise 4.9

The constant-pressure specific heat capacity of metallic iron at 298.15 K and 1.000 atm is equal to 0.4498 J K^{-1} g^{-1}. The coefficient of thermal expansion is 3.55×10^{-5} K^{-1}, the density is 7.86 g cm^{-3}, and the isothermal compressibility is 6.06×10^{-7} atm^{-1}. Find the constant-volume specific heat capacity at 298.15 K.

We can now obtain two additional relations for the heat capacities. From Eqs. (2.5-8) and (2.4-4),

$$C_{\mathrm{P}} = \left(\frac{\partial H}{\partial T}\right)_{P,n} \tag{4.3-12}$$

$$C_{\mathrm{V}} = \left(\frac{\partial U}{\partial T}\right)_{V,n} \tag{4.3-13}$$

We take Eq. (4.2-11) for a closed system and convert it to a derivative relation, specifying that P is fixed:

$$\left(\frac{\partial H}{\partial T}\right)_{P,n} = T\left(\frac{\partial S}{\partial T}\right)_{P,n} + V\left(\frac{\partial P}{\partial T}\right)_{P,n} \tag{4.3-14}$$

The derivative of P with respect to anything at constant P is equal to zero, so that

$$C_{\mathrm{P}} = \left(\frac{\partial H}{\partial T}\right)_{P,n} = T\left(\frac{\partial S}{\partial T}\right)_{P,n} \tag{4.3-15}$$

Similarly,

$$C_{\mathrm{V}} = \left(\frac{\partial U}{\partial T}\right)_{V,n} = T\left(\frac{\partial S}{\partial T}\right)_{V,n} \tag{4.3-16}$$

Exercise 4.10

Use Eq. (4.3-15), Eq. (4.3-16), and the cycle rule to show that

$$\frac{C_{\mathrm{P}}}{C_{\mathrm{V}}} = \frac{\kappa_{\mathrm{T}}}{\kappa_{\mathrm{S}}} \tag{4.3-17}$$

where κ_{S} is the **adiabatic compressibility**,

$$\kappa_{\mathrm{S}} = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,n} \tag{4.3-18}$$

PROBLEMS

Section 4.3: Additional Useful Thermodynamic Identities

4.10 Consider a gas obeying the van der Waals equation of state.

a. Find an expression for $(\partial U/\partial V)_{T,n}$ (the internal pressure). Explain why this is an intensive quantity.

b. Find the value of $(\partial U/\partial V)_{T,n}$ for argon at 298.15 K and a molar volume of 0.0244 $\mathrm{m^3\ mol^{-1}}$, using the result of part a. Explain why this is independent of temperature. Compare the internal pressure with the pressure of the gas at this temperature and molar volume.

c. Find the value of the internal pressure $(\partial U/\partial V)_{T,n}$ for argon at 298.15 K and a molar volume of $5.0 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}$ (a liquid-like value). Compare the internal pressure with the pressure of the gas at this temperature and molar volume.

d. Find the value of $(\partial U/\partial V)_{T,n}$ for argon at 298.15 K and a molar volume of 0.0244 $\mathrm{m^3\ mol^{-1}}$, using the truncated virial equation of state as in Exercise 4.5. Compare your answer with that of part b.

4.11 **a.** Show that

$$C_P = VT\alpha(\partial P/\partial T)_{S,n}$$

where α is the coefficient of thermal expansion.

b. Show that

$$C_P - C_V = (P + P_{\mathrm{int}})\alpha V$$

where P_{int} is the internal pressure, $(\partial U/\partial V)_{T,n}$.

4.12 It is shown in the theory of hydrodynamics[2] that the speed of sound, v_s, is given by

$$v_s^2 = \frac{V_m}{M\kappa_S}$$

where κ_S is the adiabatic compressibility, V_m is the molar volume, and M is the molar mass.

a. Show that

$$v_s^2 = \frac{V_m C_P}{M\kappa_T C_V}$$

where κ_T is the isothermal compressibility.

b. Find the speed of sound in air at 298.15 K and 1.000 atm, assuming a mean molar mass of 0.29 $\mathrm{kg\ mol^{-1}}$ and assuming that $C_{V,m} = 5R/2$.

c. Find the speed of sound in helium at 298.15 K and 1.000 atm.

d. For both parts b and c, find the ratio of the speed of sound to the mean speed of the gas molecules, given by Eq. (9.4-6).

4.13 Using the formula in the previous problem, find the speed of sound in liquid benzene at 20°C. Assume that the value of $C_{P,m}$ at 25°C can be used.

4.14 Derive the following equation:

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = -P + \left[\left(\frac{\partial H}{\partial P}\right)_{T,n} - V\right]\left(\frac{\partial P}{\partial V}\right)_{T,n}$$

4.15 Consider a gas that obeys the truncated pressure virial equation of state

$$PV_m = RT + A_2 P + A_3 P^2$$

where the pressure virial coefficients depend on temperature.

a. Find an expression for μ_{JT}, the Joule–Thomson coefficient, for this gas.

b. Show that the Joule–Thomson coefficient in part a does not vanish in the limit of zero pressure, even though the Joule–Thomson coefficient of an ideal gas vanishes.

c. Evaluate the Joule–Thomson coefficient for argon at 298.15 K in the limit of zero pressure, assuming that $C_{P,m} = 5R/2$. Use values in Example 2.15 and the fact that $A_2 = B_2$.

4.16 **a.** Evaluate the Joule–Thomson coefficient for carbon dioxide at $T = 298.15$ K and $P = 1.000$ bar, assuming that $C_{P,m} = 5R/2$. Use the fact that $A_2 = B_2$ and that $A_3 = \frac{1}{RT}(B_3 - B_2^2)$. Obtain a value of B_3 as in Problem 1.46 from the van der Waals parameters.

b. Repeat the calculation for 15.00 bar and the same temperature.

4.17 **a.** Find the change in enthalpy if 1.000 mol of liquid water is pressurized at 0.00°C from 1.000 atm to 50.000 atm.

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[2] H. Lamb, *Hydrodynamics*, 6th ed., Cambridge University Press, New York, 1932, p. 477ff.

b. Find the change in enthalpy if 1.000 mol of solid water (ice) is pressurized at 0.00°C from 1.000 atm to 50.000 atm.

c. From the results of parts a and b, find the value of the molar enthalpy change of fusion of water at 0.00°C and 50.00 atm.

4.18 Find the values of the isothermal compressibility and the adiabatic compressibility of helium gas at 1.000 bar and 298.15 K. Assume the gas to be ideal. Explain in words why the values are different, and explain why the larger value is larger.

4.19 Derive the identify

$$\kappa_S = \kappa_T - \frac{\alpha^2 VT}{C_P}$$

4.20 Find an expression for $\left(\frac{\partial C_V}{\partial V}\right)_{T,n}$ for a gas obeying the van der Waals equation of state.

4.21 Up to a pressure of 100 bar, N_2 gas is adequately described by the truncated virial equation of state

$$\frac{PV_m}{RT} = 1 + \frac{B_2}{V_m}$$

where at 298.15 K

$$B_2 = -5.4 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}$$
$$\frac{dB_2}{dT} = 0.020 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}\ K^{-1}}$$

a. Find w for a reversible isothermal expansion of 1.000 mol of nitrogen gas from a volume of 0.25 L to a volume of 50.0 L at 298.15 K.

b. Find ΔS for the same process.

c. Find q and ΔU for the same process.

d. If the gas expands irreversibly into a vacuum, but still isothermally and still with the same initial and final volumes at 298.15 K, find w, q, ΔS, and ΔU.

4.22 Give a numerical value (in SI units) for each of the following:

a. $\left(\frac{\partial H}{\partial S}\right)_{P,n}$ for 1.000 mol of an ideal gas at 400.0 K and 1.000 atm.

b. $\left(\frac{\partial S}{\partial V}\right)_{T,n}$ for 2.000 mol of an ideal gas at 298.15 K and 1.000 bar.

c. $\left(\frac{\partial U}{\partial V}\right)_{S,n}$ for 3.000 mol of a monatomic ideal gas at 298.15 K and 2.000 atm.

4.23 **a.** Find an expression for $S_m - S_m^\circ$ as a function of V_m for a van der Waals gas.

b. Evaluate the expression for carbon dioxide at $T = 298.15$ K and $V_m = 10.00\ \mathrm{L\ mol^{-1}}$.

4.24 Xenon gas is adequately described by

$$\frac{PV_m}{RT} = 1 + \frac{B_2}{V_m}$$

or

$$PV_m = RT + A_2 P$$

where it can be shown that $A_2 = B_2$. At 298.15 K, $B_2 = -1.302 \times 10^{-4}\ \mathrm{m^3\ mol^{-1}}$, and $d\,B_2/dT = 7.2 \times 10^{-7}\ \mathrm{m^3\ mol^{-1}\ K^{-1}}$.

a. Find the pressure of a sample of xenon at 298.15 K and a molar volume of 24.465 L mol^{-1}.

b. Derive a formula giving $\left(\frac{\partial U}{\partial V}\right)_{T,n}$ for xenon gas.

c. Find the value of $\left(\frac{\partial U}{\partial V}\right)_{T,n}$ for xenon gas at 298.15 K and a molar volume of 24.465 L mol^{-1}.

4.25 The Berthelot equation of state is

$$P = \frac{RT}{V_m - b} - \frac{a}{TV_m^2}$$

a. Find an expression for $\left(\frac{\partial U}{\partial V}\right)_{T,n}$ for a gas obeying this equation of state.

b. Find the value of ΔU if 1.000 mol of argon gas expands from a volume of 1.000 L to a volume of 10.00 L at a constant temperature of 298.15 K.

4.26 Calculate $C_{V,m}$ for benzene at 298.15 K. Assume that the value of α in the appendix for 20°C can be used for 25°C. The density of benzene is 0.8765 g cm^{-3} at 20°C. Assume that this value can be used at 25°C.

4.27 **a.** Derive a formula for ΔS for a pressure change of a liquid. Assume that the coefficient of thermal expansion is independent of pressure.

b. Evaluate ΔS for 1.000 mol of liquid water at 20°C if the pressure is changed from 1.00 atm to 100.00 atm. $\alpha = 2.07 \times 10^{-4}\ \mathrm{K^{-1}}$.

4.4 Gibbs Energy Calculations

For a closed simple system at constant temperature, Eq. (4.2-19) is

$$dG = VdP \quad \text{(simple system, } T \text{ and } n \text{ constant)} \tag{4.4-1}$$

Integration of this formula at constant T and n gives

$$G(T, P_2, n) - G(T, P_1, n) = \int_{P_1}^{P_2} VdP \tag{4.4-2}$$

The Gibbs Energy of an Ideal Gas

For an ideal gas of one substance Eq. (4.4-2) becomes

$$G(T, P_2, n) = G(T, P_1, n) + nRT \int_{P_1}^{P_2} \frac{1}{P} dP$$

$$G(T, P_2, n) = G(T, P_1, n) + nRT \ln\left(\frac{P_2}{P_1}\right) \quad \text{(ideal gas)} \tag{4.4-3}$$

The molar Gibbs energy, G_m, is equal to G/n,

$$\boxed{G_m(T, P_2) = G_m(T, P_1) + RT \ln\left(\frac{P_2}{P_1}\right) \quad \text{(ideal gas)}} \tag{4.4-4}$$

The *standard state* for the Gibbs energy of an ideal gas is the same as for the entropy: a fixed pressure of $P°$, the *standard pressure*, defined to be exactly equal to 1 bar = 100000 Pa. Specifying the standard state does not specify a particular temperature. There is a different standard state for each temperature. At one time a value of 1 atm was used for $P°$. Use of this choice for $P°$ makes no difference to the formulas that we write and makes only a small difference in numerical values. For highly accurate work, one must determine whether the 1-atm standard state or the 1-bar standard state has been used in a given table of numerical values. If state 1 is chosen to be the standard state and if the subscript is dropped on P_2, Eq. (4.4-4) becomes

$$G_m(T, P) = G_m^\circ(T) + RT \ln\left(\frac{P}{P^\circ}\right) \quad \text{(ideal gas)} \tag{4.4-5}$$

where $G_m^\circ(T)$ is the molar Gibbs energy of the gas in the standard state at temperature T.

EXAMPLE 4.13

Obtain a formula to change from the 1-atm standard state to the 1-bar standard state for an ideal gas.

Solution

Let 1 atm be denoted by $P^{\circ\text{atm}}$ with a similar symbol for the 1-atm standard-state molar Gibbs energies. We write

$$\begin{aligned} G_{\text{m}}(T,P) &= G_{\text{m}}^{\circ}(T) + RT\ln(P/P^{\circ}) \\ &= G_{\text{m}}^{\circ}(T) + RT\ln(P^{\circ\text{atm}}/P^{\circ}) + RT\ln(P/P^{\circ\text{atm}}) \end{aligned}$$

This equation has the correct form if

$$\begin{aligned} G_{\text{m}}^{\circ\text{atm}} &= G_{\text{m}}^{\circ}(T) + RT\ln(P^{\circ\text{atm}}/P^{\circ}) \\ &= G_{\text{m}}^{\circ}(T) + RT\ln(1.01325) \\ &= G_{\text{m}}^{\circ}(T) + (0.013\,16)RT \end{aligned}$$

At 298.15 K,

$$G_{\text{m}}^{\circ\text{atm}} - G_{\text{m}}^{\circ}(T) = 32.16\ \text{J mol}^{-1} = 0.03216\ \text{kJ mol}^{-1}$$

The Gibbs Energy of a Real Gas. Fugacity

When a gas requires corrections for nonideality we write a new equation in the same form as Eq. (4.4-5), replacing the pressure by the *fugacity*, f, which has the dimensions of pressure:

$$G_{\text{m}}(T,P) = G_{\text{m}}^{\circ}(T) + RT\ln\left(\frac{f}{P^{\circ}}\right) \quad \text{(definition of the fugacity } f\text{)} \tag{4.4-6}$$

The fugacity plays the same role in determining the molar Gibbs energy of a real gas as does the pressure in determining the molar Gibbs energy of an ideal gas. The quantity $G_{\text{m}}^{\circ}(T)$ is the molar Gibbs energy of the gas in its standard state. The standard state of a real gas is defined to be the corresponding ideal gas at pressure P°. We can obtain an expression for the molar Gibbs energy of a real gas as follows:

$$\begin{aligned} G_{\text{m,real}}(T,P') - G_{\text{m}}^{\circ}(T) &= G_{\text{m,real}}(T,P') \\ &\quad - \lim_{P''\to 0}\left[G_{\text{m,real}}(T,P'') - G_{\text{m,ideal}}(T,P'')\right] - G_{\text{m}}^{\circ}(T) \end{aligned} \tag{4.4-7}$$

where we have added two terms that cancel because the real gas and the corresponding ideal gas become identical in the limit of zero pressure. From Eq. (4.4-1), the first two terms on the right-hand side of Eq. (4.4-7) represent ΔG for changing the pressure of the real gas from 0 to P' at constant temperature:

$$\text{(first two terms)} = \int_0^{P'} V_{\text{m,real}}\,dP \tag{4.4-8}$$

From Eq. (4.4-3), the last two terms in the right-hand side of Eq. (4.4-7) are equal to

$$\text{(last two terms)} = \int_{P^{\circ}}^{0} V_{\text{m,ideal}}\,dP = \int_{P^{\circ}}^{0} \frac{RT}{P}\,dP \tag{4.4-9}$$

The formula in Eq. (4.4-7) is equivalent to integrating from the standard-state pressure P° down to zero pressure with the ideal gas, and then integrating back up to pressure P' with the real gas. This procedure gives the difference between the real gas at pressure P' and the ideal gas at pressure P°.

The integral in Eq. (4.4-9) can be broken into two parts, as follows (we have also exchanged the limits, which changes the sign):

$$\begin{aligned}(\text{last two terms}) &= -\int_0^{P'} \frac{RT}{P}dP - \int_{P'}^{P^\circ} \frac{RT}{P}dP \\ &= -\int_0^{P'} \frac{RT}{P}dP - RT\ln\left(P^\circ/P'\right) \qquad (4.4\text{-}10)\end{aligned}$$

The left-hand side of Eq. (4.4-7) is equal to $RT\ln(f/P^\circ)$, so that if f' denotes the fugacity at pressure P', we can combine the two integrals to write

$$\begin{aligned}G_\mathrm{m}(T,P') - G_\mathrm{m}^\circ(T) &= RT\ln\left(\frac{f'}{P^\circ}\right) \\ &= RT\ln\left(\frac{P'}{P^\circ}\right) + \int_0^{P'}\left(V_\mathrm{m,real} - \frac{RT}{P}\right)dP \qquad (4.4\text{-}11)\end{aligned}$$

which is the same as

$$\boxed{RT\ln\left(\frac{f'}{P'}\right) = \int_0^{P'}\left(V_\mathrm{m,real} - \frac{RT}{P}\right)dP} \qquad (4.4\text{-}12)$$

The integrand of this integral is small if the deviation from ideality is small and vanishes if the gas is ideal.

EXAMPLE 4.14

Find an expression for the fugacity of a gas that obeys the truncated pressure virial equation of state

$$PV_\mathrm{m} = RT + A_2P$$

where the second pressure virial coefficient A_2 is a function of temperature. It was shown in Example 1.9 that the second pressure virial coefficient, A_2, is equal to B_2, the second virial coefficient.

Solution

$$RT\ln\left(f'/P'\right) = \int_0^{P'}\left(\frac{RT}{P} + A_2 - \frac{RT}{P}\right)dP = A_2P'$$

or

$$f' = P'e^{A_2P'/RT}$$

Exercise 4.11

a. For argon at 273.15 K, $B_2 = -21.5\ \mathrm{cm^3\ mol^{-1}}$. Find the value of the fugacity of argon gas at 5.000 atm and 273.15 K.

b. For carbon dioxide at 323.15 K, $B_2 = -103\ \mathrm{cm^3\ mol^{-1}}$. Find the value of the fugacity of carbon dioxide gas at 5.000 atm and 323.15 K.
c. Find the value of the fugacity of carbon dioxide gas at 15.000 atm and 323.15 K.

The Gibbs Energy of Solids and Liquids

The value of the isothermal compressibility of a typical solid or liquid is roughly equal to $10^{-9}\ \mathrm{Pa^{-1}}$ so that a change in pressure of 10 atm (roughly 10^6 Pa) changes the volume by only a tenth of a percent. We assume the volume to be approximately constant in the integrand of Eq. (4.4-2), giving

$$G(T, P_2, n) - G(T, P_1, n) \approx V(P_2 - P_1) \tag{4.4-13}$$

The *standard state* of a substance in a condensed phase (liquid or solid) is the actual pure substance at the standard pressure $P°$ and whatever temperature is of interest. Equation (4.4-13) implies that

$$G_\mathrm{m}(T, P) = G_\mathrm{m}^\circ(T) + V_\mathrm{m}(P - P^\circ) \tag{4.4-14}$$

EXAMPLE 4.15

Calculate $G_\mathrm{m} - G_\mathrm{m}^\circ$ for liquid water at 298.15 K and 10.00 bar.

Solution

$$\begin{aligned} G_\mathrm{m} - G_\mathrm{m}^\circ &= (18.0 \times 10^{-6}\ \mathrm{m^3\ mol^{-1}})(9.00\ \mathrm{bar})\left(\frac{10^5\ \mathrm{N\ m^{-2}}}{1\ \mathrm{bar}}\right) \\ &= 16.2\ \mathrm{J\ mol^{-1}} = 0.0162\ \mathrm{kJ\ mol^{-1}} \end{aligned}$$

This difference can be neglected for many purposes.

Exercise 4.12

a. Find $G_\mathrm{m} - G_\mathrm{m}^\circ$ for solid copper at 293.15 K and 1.100 bar.
b. Find $G_\mathrm{m} - G_\mathrm{m}^\circ$ for solid copper at 293.15 K and 10.00 bar.

The Temperature Dependence of the Gibbs Energy

From Eq. (4.2-19), if the pressure is constant and the system is closed,

$$dG = -SdT \quad \text{(closed system, } P \text{ constant)} \tag{4.4-15}$$

Integration of this equation at constant pressure would give a relation for ΔG for a constant-pressure temperature change.

$$G(T_2, P) - G(T_1, P) = -\int_{T_1}^{T_2} S(T, P)dT \quad \text{(equation } \textit{not} \text{ usable)} \tag{4.4-16}$$

We cannot use this relation, because a constant can be added to the value of the entropy without any physical effect. The assignment of "absolute" entropies is based on a conventional assignment of zero entropy for elements at 0 K and does not provide unique values of entropies. Adding a constant to S would change the value of the integrand in Eq. (4.4-16), changing the value of the integral.

The most we can do is to consider an isothermal process that can be carried out once at temperature T_1 and a fixed pressure P and again at temperature T_2 and pressure P. We write Eq. (4.4-16) once for the initial state and once for the final state. The difference of these equations gives

$$\Delta G(T_2, P) - \Delta G(T_1, P) = -\int_{T_1}^{T_2} \Delta S(T, P)dT \quad \text{(closed system)} \tag{4.4-17}$$

where $\Delta G(T, P)$ and $\Delta S(T, P)$ pertain to a process at a constant temperature T and a constant pressure P. Equation (4.4-17) does not mean that we are considering a nonisothermal process. It gives the difference between ΔG for an isothermal process carried out at T_2 and ΔG for the same isothermal process carried out at T_1.

If ΔS is nearly independent of temperature between T_1 and T_2, Eq. (4.4-17) becomes

$$\Delta G(T_2, P) - \Delta G(T_1, P) \approx -\Delta S(T_2 - T_1) \quad (\Delta S \text{ independent of temperature}) \tag{4.4-18}$$

This equation should be a usable approximation if the difference between T_2 and T_1 is not very large. An alternate to Eq. (4.4-17) is known as the *Gibbs–Helmholtz equation*:

$$\frac{\Delta G(T_2, P)}{T_2} - \frac{\Delta G(T_1, P)}{T_1} = -\int_{T_1}^{T_2} \frac{\Delta H(T, P)}{T^2} dT \tag{4.4-19}$$

If ΔH is nearly independent of temperature,

$$\frac{\Delta G(T_2, P)}{T_2} - \frac{\Delta G(T_1, P)}{T_1} = \Delta H\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{4.4-20}$$

Thermodynamics applies equally to chemical reactions and to physical processes such as fusion or vaporization. We can apply Eqs. (4.4-17) and (4.4-19) to physical processes as well as to chemical reactions.

EXAMPLE 4.16

Derive Eq. (4.4-19).

Solution

$$\left(\frac{\partial \Delta G/T}{\partial T}\right)_P = \frac{1}{T}\left(\frac{\partial \Delta G}{\partial T}\right)_P - \frac{\Delta G}{T^2} = -\frac{\Delta S}{T} - \frac{\Delta G}{T^2} = -\frac{\Delta H}{T^2}$$

$$\begin{aligned} \frac{\Delta G(T_2, P)}{T_2} - \frac{\Delta G(T_1, P)}{T_1} &= \int_{T_1}^{T_2} \left(\frac{\partial(\Delta G/T)}{\partial T}\right)_P dT \\ &= -\int_{T_1}^{T_2} \frac{\Delta H}{T^2} dT \end{aligned} \tag{4.4-21}$$

Exercise 4.13

a. At 373.15 K and 1.000 atm, the Gibbs energy change of vaporization of water is equal to zero, and the entropy change is equal to 109 J K^{-1} mol^{-1}. Find the Gibbs energy change of vaporization of superheated water at 378.15 K and 1.000 atm, using Eq. (4.4-18). What does the sign of your answer mean?

b. Repeat the calculation of part a using Eq. (4.4-19). Assume that ΔH is constant and equal to 40.67 kJ mol^{-1}. Comment on the comparison between your values for parts a and b.

PROBLEMS

Section 4.4: Gibbs Energy Calculations

4.28 **a.** Find the value of ΔG for 1.000 mol of an ideal gas if it is isothermally pressurized from 1.000 atm to 3.000 atm at 298.15 K.

b. Find the value of ΔG for 1.000 mol of an ideal gas if it is isothermally pressurized from 2.000 atm to 4.000 atm at 298.15 K.

c. Explain in words why your answers for parts a and b are not equal although the changes in pressure are equal.

4.29 2.000 mol of helium gas (assume ideal) expands isothermally and irreversibly at a constant external pressure of 1.000 atm and a temperature of 298.15 K from a volume of 10.00 L to a volume of 40.00 L.

a. Find q, w, ΔU, ΔS, ΔS_{surr}, ΔH, ΔA, and ΔG.

b. Find q, w, ΔU, ΔS, ΔS_{surr}, ΔH, ΔA, and ΔG if the process is carried out reversibly at the same temperature.

4.30 **a.** Find the value of ΔG if 1.000 mol of liquid water is pressurized at 0.00°C from 1.000 atm to 50.000 atm. Assume that the liquid water has a fixed volume.

b. Find the value of ΔG if 1.000 mol of solid water is pressurized at 0.00°C from 1.000 atm to 50.000 atm. Assume that the solid water has a fixed volume.

c. Find the value of ΔG if 1.000 mol of solid water (ice) melts at 0.00°C and 1.000 atm.

d. Find the value of ΔG if 1.000 mol of solid water melts at 0.00°C and 50.000 atm. What does the sign of your answer indicate?

4.31 **a.** Write an expression for ΔA for the isothermal expansion of an ideal gas from volume V_1 to volume V_2.

b. Find the value of ΔA for each of the processes in parts a and b of Problem 4.28. Explain the relationship of these values to the values of ΔG for the same processes.

4.32 **a.** At 273.15 K and 1.000 atm, the Gibbs energy change of fusion of water is equal to zero, and the enthalpy change is equal to 6008 J mol^{-1}. Find the Gibbs energy change of fusion of water at 263.15 K and 1.000 atm, using Eq. (4.4-18). What does the sign of your answer mean?

b. Repeat the calculation of part a using Eq. (4.4-20). Comment on the comparison between your values for parts a and b.

4.33 Consider a gas obeying the truncated virial equation of state

$$\frac{PV_{\text{m}}}{RT} = 1 + \frac{B_2}{V_{\text{m}}} + \frac{B_3}{V_{\text{m}}^2}$$

a. Write an expression for ΔA for the isothermal expansion from volume V_1 to volume V_2 for n moles of this gas.

b. Find the value of ΔA for the isothermal expansion of 1.000 mol of argon at 298.15 K from a volume of 10.000 L to a volume of 25.000 L, assuming that $B_3 \approx 0$. Compare with the result assuming argon to be an ideal gas.

c. Manipulate the van der Waals equation of state into the form of the virial equation of state and show that

$B_3 = b^2$. Find the value of ΔA for the isothermal expansion of 1.000 mol of argon at 298.15 K from a volume of 10.000 L to a volume of 25.000 L. Compare with the result assuming argon to be an ideal gas.

4.34 Assume that argon obeys the truncated pressure virial equation of state

$$PV_{\mathrm{m}} = RT + A_2 P$$

with $A_2 = -15.8\ \mathrm{cm^3\ mol^{-1}}$.

a. Find the value of $G_{\mathrm{m}} - G_{\mathrm{m}}^{\circ}$ for argon gas at 298.15 K and 1.000 atm.

b. Repeat the calculation for 298.15 K and 20.00 atm.

4.35 **a.** Find an expression for ΔA for the isothermal expansion of a gas obeying the van der Waals equation of state from volume V_1 to volume V_2.

b. Find the value of ΔA for the isothermal expansion of 1.000 mol of argon gas at 298.15 K from a volume of 10.000 L to a volume of 25.000 L. Compare with the result assuming argon to be an ideal gas, and with the result of Problem 4.33.

4.36 Calculate ΔG for each of the following processes. If ΔG cannot be calculated, write "no numerical calculation possible."

a. 1.000 mol of ice is melted at 0.00°C and 1.000 atm.

b. 1.000 mol of water is heated at a constant pressure of 1.000 atm from 20.00°C to 80.00°C.

c. 2.500 mol of an ideal gas is compressed isothermally at a temperature of 400.0 K from 1.000 bar to 5.35 bar.

d. 1.000 mol of solid water (ice) is pressurized isothermally from 1.000 atm to 50.00 atm.

4.37 **a.** Calculate ΔH°, ΔS°, $\Delta H^{\circ} - T\Delta S^{\circ}$, and ΔG° for the reaction at 298.15 K:
$\mathrm{CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(g)}$.

b. Calculate ΔH°, ΔS°, and ΔG° for the same reaction at 498.15 K. Assume that the heat capacities are constant.

c. If 2.000 mol of methane is burned at constant pressure and a temperature of 498.15 K and 80.0% of the heat produced is put into a steam engine with an efficiency that is 75.0% as great as that of a Carnot engine operating between 200.0°C and 100.0°C, find the amount of work in joules that can be done on the surroundings.

4.38 If ΔG can be defined for the process, calculate ΔG for each of the following processes:

a. 1.000 mol of water is vaporized at 100.0°C and 1.000 atm.

b. 1.000 mol of an ideal gas is heated at a constant pressure of 1.000 atm from 20.00°C to 80.00°C.

c. 1.000 mol of diamond is converted isothermally into graphite at 298.15 K and 1.000 bar.

4.39 Assume that a gas can be described adequately by either of the following equations of state:

$$\frac{PV_{\mathrm{m}}}{RT} = 1 + \frac{B_2}{V_{\mathrm{m}}}$$

or

$$PV_{\mathrm{m}} = RT + A_2 P$$

where it can be shown that $A_2 = B_2$.

a. Find a formula for ΔG for an isothermal pressure change of such a gas.

b. Find a formula for ΔA for an isothermal volume change of a such a gas.

c. Find ΔG for the isothermal expansion at 50.0°C of 2.000 mol of $\mathrm{CO_2}$ from a pressure of 5.000 atm to a pressure of 1.000 atm. For $\mathrm{CO_2}$ at 50.0°C, $B_2 = -1.03 \times 10^{-4}\ \mathrm{m^3\ mol^{-1}}$.

4.40 Assume that a gas can equally well be described by the two equations of state:

$$\frac{PV_{\mathrm{m}}}{RT} = 1 + \frac{B_2}{V_{\mathrm{m}}}$$

and

$$PV_{\mathrm{m}} = RT + A_2 P$$

where it can be shown that $A_2 = B_2$.

a. Find an expression for ΔG and ΔA for isothermally changing the volume of 1.000 mol of the gas from a molar volume V_{m1} to a molar volume V_{m2}.

b. Find the value of ΔG and ΔA for compressing 1.000 mol of argon from 25.00 L to 5.00 L at a constant temperature of 298.15 K. The value of $\mathrm{B_2}$ for argon at this temperature is $-15.8\ \mathrm{cm^3\ mol^{-1}}$.

4.5 Multicomponent Systems

In an equilibrium open multicomponent system with one gas or liquid phase the number of variables required to specify the equilibrium macroscopic state is $c + 2$, where c stands for the number of independent substances, called *components*. The number of components is equal to the number of substances whose amounts can separately be varied under the given conditions. It is also equal to the minimum number of substances from which the system can be prepared under the given conditions. For example, if a gaseous system at equilibrium contains NO_2 it will also contain N_2O_4. The system can be prepared by adding only NO_2 or by adding only N_2O_4 and allowing the system to equilibrate. Two substances are present, but there is only one component.

The Chemical Potential and Partial Molar Quantities

In an equilibrium one-phase simple system containing c components, the Gibbs energy depends on $c + 2$ variables, which can be chosen as T, P, and the mole fractions of all components:

$$G = G(T, P, n_1, n_2, \ldots, n_c) \tag{4.5-1}$$

where n_i is the amount of substance number i (measured in moles). The differential of G is

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \sum_{i=1}^{c} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n'} dn_i \tag{4.5-2}$$

where the subscript n stands for keeping the amounts of all of the components fixed and the subscript n' stands for keeping the amount of every component fixed except for component number i.

The first two partial derivatives in Eq. (4.5-2) are no different from the partial derivatives in Eqs. (4.2-20) and (4.2-21) for a closed system. In those equations, the amounts of all substances present were held fixed because the system was closed. In Eq. (4.5-2), the amounts of all substances are held fixed because that is how partial derivatives are defined. Therefore, we can write

$$\boxed{dG = -SdT + VdP + \sum_{i=1}^{c} \mu_i dn_i} \tag{4.5-3}$$

where μ_i is called the *chemical potential* and is defined by

$$\boxed{\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n'} \qquad \text{(definition of the chemical potential)}} \tag{4.5-4}$$

Equation (4.5-3) is called the *Gibbs equation* or the *fundamental relation of chemical thermodynamics*. We could also choose to write

$$dG = \left(\frac{\partial G}{\partial T}\right)_{V,n} dT + \left(\frac{\partial G}{\partial V}\right)_{T,n} dV + \sum_{i=1}^{c} \left(\frac{\partial G}{\partial n_i}\right)_{T,V,n'} dn_i \tag{4.5-5}$$

However, the partial derivatives in this equation are not equal to any simple thermodynamic variables as are the partial derivatives in Eq. (4.5-2). We therefore say that the *natural independent variables* for the Gibbs energy are $T, P, n_1, n_2, \ldots, n_c$.

EXAMPLE 4.17

Use an analogue of Eq. (B-7) of Appendix B to write a relation between $(\partial G/\partial n_i)_{T,V,n'}$ and μ_i.

Solution

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,V,n'} = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n'} + \left(\frac{\partial G}{\partial P}\right)_{T,n}\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n'}$$

$$= \mu_i + V\left(\frac{\partial P}{\partial n_i}\right)_{T,V,n'}$$

The internal energy, the enthalpy, and the Helmholtz energy have their own sets of natural independent variables. From Eq. (4.5-3), Eq. (4.5-8), and the relation $G = H - TS$,

$$dH = dG + TdS + SdT$$

$$dH = -SdT + VdP + \sum_{i=1}^{c} \mu_i dn_i + TdS + SdT$$

$$dH = TdS + VdP + \sum_{i=1}^{c} \mu_i dn_i \tag{4.5-6}$$

The natural independent variables for H are S, P, n_1, n_2, …, n_c. We can see from Eq. (4.5-6) that

$$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n'} \tag{4.5-7}$$

Similarly, since $U = H - PV$,

$$dU = TdS - PdV + \sum_{i=1}^{c} \mu_i dn_i \tag{4.5-8}$$

so that the natural independent variables for U are S, V, n_1, n_2, …, n_c. Also

$$dA = -SdT - VdP + \sum_{i=1}^{c} \mu_i dn_i \tag{4.5-9}$$

so that the natural independent variables for A are T, V, $n_1, n_2, \ldots, n_c$. By inspection

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n'} \tag{4.5-10}$$

and

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n'} \tag{4.5-11}$$

Exercise 4.14

Derive Eqs. (4.5-8) and (4.5-9).

The chemical potential is equal to four different partial derivatives with different variables held fixed. The partial derivative in Eq. (4.5-4) identifies the chemical potential as the *partial molar Gibbs energy*. A general *partial molar quantity* is a partial derivative of an extensive quantity with respect to the amount of one component, keeping T, P, and the amounts of all other components fixed. If the letter Y stands for any extensive quantity (U, H, A, G, S, V, and so on), *the partial molar quantity for substance number* i is denoted by $\overline{Y}_i$ and defined by

$$\overline{Y}_i = \left(\frac{\partial Y}{\partial n_i}\right)_{T,P,n'} \tag{4.5-12}$$

The chemical potential μ_i is equal to $\overline{G}_i$. The partial derivatives in Eqs. (4.5-7), (4.5-10), and (4.5-11) to which μ_i is equal are not partial molar quantities, because P and T are not both held fixed in the differentiations.

EXAMPLE 4.18

Find a relationship between the chemical potential and the partial molar enthalpy.

Solution

We begin with the relationship between G and H:

$$G = H - TS$$

Differentiation of both sides at constant T, P, and n' gives

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n'} = \left(\frac{\partial H}{\partial n_i}\right)_{T,P,n'} - T\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n'}$$

or

$$\mu_i = \overline{H}_i - T\overline{S}_i$$

Exercise 4.15

a. Show that $\mu_i = \overline{A}_i + P\overline{V}_i$
b. Show that $\mu_i = \overline{U}_i + P\overline{V}_i - T\overline{S}_i$

There are some equations similar to the Maxwell relations that apply to multicomponent open systems. We begin with the Gibbs equation, Eq. (4.5-3):

$$dG = -SdT + VdP + \sum_{i=1}^{c} \mu_i dn_i \tag{4.5-13}$$

Using the Euler reciprocity relation, Eq. (B-13) of Appendix B,

$$\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n'} = \overline{S}_i = -\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n} \tag{4.5-14}$$

A second use of the Euler reciprocity relation gives

$$\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n'} = \overline{V}_i = \left(\frac{\partial \mu_i}{\partial P}\right)_{T,n} \tag{4.5-15}$$

Various similar equations can be derived.

Exercise 4.16

Verify Eq. (4.5-14) and Eq. (4.5-15).

The Partial Molar Quantities in a One-Component System

The equilibrium thermodynamic state of a simple one-component open system can be specified by T, P, and n, the amount of the single component. This gives the differential relation for a general extensive quantity, Y, in a one-component system:

$$dY = \left(\frac{\partial Y}{\partial T}\right)_{P,n} dT + \left(\frac{\partial Y}{\partial P}\right)_{T,n} dP + \left(\frac{\partial Y}{\partial n}\right)_{T,P} dn \tag{4.5-16}$$

In a one-component system the molar quantity Y_{m} is given by

$$Y_{\mathrm{m}} = \frac{Y}{n} \tag{4.5-17}$$

The molar quantity Y_{m} is an intensive quantity. Because an intensive quantity cannot depend on an extensive quantity, Y_{m} depends only on T and P. Therefore

$$\overline{Y} = \left(\frac{\partial Y}{\partial n}\right)_{T,P} = \left(\frac{\partial (nY_{\mathrm{m}})}{\partial n}\right)_{T,P} = Y_{\mathrm{m}} \tag{4.5-18}$$

In a one-component system any partial molar quantity is equal to the corresponding molar quantity. The most important examples are

$$\mu = \overline{G} = G_{\mathrm{m}} = \frac{G}{n} \quad \text{(one-component system)} \tag{4.5-19}$$

and

$$\overline{V} = V_{\mathrm{m}} = \frac{V}{N} \quad \text{(one-component system)} \tag{4.5-20}$$

Partial Molar Quantities of a One-Component Ideal Gas

As with any pure substance the partial molar volume of a one-component ideal gas is equal to the molar volume:

$$\overline{V} = V_{\mathrm{m}} = \frac{V}{n} = \frac{RT}{P} \quad \text{(ideal gas)} \tag{4.5-21}$$

The chemical potential of a one-component ideal gas is equal to the molar Gibbs energy. From Eq. (4.4-5),

$$\mu = \overline{G} = G_{\mathrm{m}} = G_{\mathrm{m}}^{\circ}(T) + RT\ln\left(\frac{P}{P^{\circ}}\right) \quad \text{(ideal gas)} \tag{4.5-22}$$

where G_{m}° is the molar Gibbs energy in the standard state. It is equal to μ°, the chemical potential in the standard state. The standard state for the Gibbs energy of an ideal gas is the ideal gas at pressure P° (exactly 1 bar). The relation of Eq. (4.5-22) is the same as

$$\mu = \mu^{\circ} + RT\ln\left(\frac{P}{P^{\circ}}\right) \quad \text{(ideal gas)} \tag{4.5-23}$$

The partial molar entropy of an ideal gas is obtained by use of Eq. (4.2-20):

$$S_{\mathrm{m}} = -\left(\frac{\partial G_{\mathrm{m}}}{\partial T}\right)_{P} = -\left(\frac{\partial G_{\mathrm{m}}^{\circ}}{\partial T}\right)_{P} + R\ln\left(\frac{P}{P^{\circ}}\right)$$

$$S_{\mathrm{m}} = S_{\mathrm{m}}^{\circ} - R\ln\left(\frac{P}{p^{\circ}}\right) \quad \text{(ideal gas)} \tag{4.5-24}$$

where S_{m}° is equal to $-(\partial\mu^{\circ}/\partial T)_{P}$. The partial molar enthalpy of a one-component ideal gas is obtained from Eq. (4.1-14):

$$\overline{H} = H_{\mathrm{m}} = G_{\mathrm{m}} + TS_{\mathrm{m}}$$

$$= G_{\mathrm{m}}^{\circ} + RT\ln\left(\frac{P}{P^{\circ}}\right) + T\left[S_{\mathrm{m}}^{\circ} - R\ln\left(\frac{P}{P^{\circ}}\right)\right]$$

$$\overline{H} = G_{\mathrm{m}}^{\circ} + TS_{\mathrm{m}}^{\circ} = H_{\mathrm{m}}^{\circ} \quad \text{(ideal gas)} \tag{4.5-25}$$

The partial molar enthalpy of an ideal gas does not depend on pressure.

EXAMPLE 4.19

Find the expression for the partial molar Helmholtz energy of a one-component ideal gas as a function of temperature and pressure.

Solution

$$\begin{aligned}\overline{A} = A_\mathrm{m} = \mu - PV_\mathrm{m} &= \mu^\circ + RT\ln\left(\frac{P}{P^\circ}\right) - P\frac{RT}{P}\\ &= \mu^\circ + RT\ln\left(\frac{P}{P^\circ}\right) - RT\end{aligned}$$

According to Dalton's law of partial pressures, each gas in a mixture of ideal gases behaves as though it were alone in the container. Equation (4.5-23) applies to any substance in an ideal gas mixture:

$$\mu_i = \mu_i^\circ + RT\ln\left(\frac{P_i}{P^\circ}\right) \quad \text{(substance } i \text{ in an ideal gas mixture)} \tag{4.5-26}$$

where μ_i° is the chemical potential of substance i in the standard state at pressure P° and P_i is its partial pressure. All of the other equations for one-component ideal gases apply as well.

EXAMPLE 4.20

Calculate $\mu_i - \mu_i^\circ$ for argon gas in dry air at 298.15 K and 1.000 atm, assuming that the gases are ideal. The mole fraction of argon is 0.00934.

Solution

$$\begin{aligned}\mu_i - \mu_i^\circ &= RT\ln\left(\frac{P_i}{P^\circ}\right)\\ &= (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15)\ln\left(\frac{(0.00934\,\mathrm{atm})(101325\,\mathrm{Pa\,atm^{-1}})}{100000\,\mathrm{Pa}}\right)\\ &= -11550\,\mathrm{J\,mol^{-1}}\end{aligned}$$

Exercise 4.17

a. Calculate $\mu_i - \mu_i^\circ$ for argon gas at 298.15 K and a partial pressure of 1.000 atm.
b. Calculate $\mu_i - \mu_i^\circ$ for argon gas at 298.15 K and a partial pressure of 10.00 atm.

In a mixture of gases that cannot be assumed to be ideal, we define f_i, the fugacity of component i, by the relation

$$\mu_i = \mu_i^\circ + RT\ln\left(\frac{f_i}{P^\circ}\right) \quad \text{(definition of } f_i\text{)} \tag{4.5-27}$$

where μ_i° is the same standard-state chemical potential as for the pure gas: the hypothetical ideal-gas state at pressure P° and whatever temperature is being considered. We will not discuss the evaluation of the fugacity in a mixture of nonideal gases.

PROBLEMS

Section 4.5: Multicomponent Systems

4.41 Following are data on the density of ethanol-water solutions at 20°C. Calculate the volume of a solution containing 0.700 mol of water and the appropriate amount of ethanol for each of the data points except for the 0% and 100% data points. Determine the partial molar volume of ethanol at an ethanol mole fraction of 0.300, by either graphical or numerical means.

% ethanol by mass	density/g mL^{-1}
0	0.99823
46.00	0.9224
48.00	0.9177
50.00	0.9131
52.00	0.9084
54.00	0.9039
56.00	0.8995
58.00	0.8956
100.00	0.7893

4.42 The partial specific volume of a system is defined as $(\partial V/\partial w_i)_{P,T,w'}$, where w_i is the mass of component number i and where the subscript w' stands for keeping the mass of every substance fixed except for substance number i. All of the relations involving partial molar quantities can be converted to relations for partial specific quantities by consistently replacing n_i by w_i for every substance and by replacing x_i by the mass fraction y_i:

$$y_i = w_i/w_{\text{total}}$$

for every substance. Using the data of Problem 4.41, find the partial specific volume of ethanol in the mixture with mass fraction 0.500.

4.43 **a.** The pressure on a sample of liquid water is changed from 1.000 bar to 100.000 bar at a constant temperature of 298.15 K. Find the change in the chemical potential of the water. State any assumptions.

b. The same change in pressure is carried out at the same temperature on an ideal gas. Find the change in its chemical potential.

4.44 Assume that the volume of a two-component solution at constant temperature and pressure is given by

$$V = n_1 V_{m1}^* + n_2 V_{m2}^* + na_{20}x_1^2 + na_{11}x_1x_2 + na_{02}x_2^2$$

where V_{m1}^* and V_{m2}^* are the molar volumes of the pure substances, n_1 is the amount of substance 1, n_2 is the amount of substance 2, $n = n_1 + n_2$, x_1 and x_1 are the mole fractions, and the a coefficients are constants. Obtain an expression for the partial molar volume of each substance and write an expression for $n_1\overline{V}_1 + n_2\overline{V}_2$.

4.6 Euler's Theorem and the Gibbs–Duhem Relation

Euler's theorem is a mathematical theorem that applies to homogeneous functions. A function of several independent variables, $f(n_1, n_2, n_3, \ldots, n_c)$, is said to be *homogeneous of degree* k if

$$f(an_1, an_2, an_3, \ldots, an_c) = a^k f(n_1, n_2, n_3, \ldots, n_c) \tag{4.6-1}$$

where a is a positive constant. For example, if every independent variable is doubled, the new value of the function is equal to the old value times 2^k. If T and P are held fixed, any extensive quantity is homogeneous of degree 1 in the amounts of the components, $n_1, n_2, \ldots, n_c$, and any intensive quantity is homogeneous of degree 0 in the amounts of the components. For example, if the amount of every component is doubled at constant T and P, the value of every extensive quantity doubles while the value of every intensive quantity remains unchanged. If f is a homogeneous function of degree

k with independent variables $n_1, n_2, \ldots, n_c$, *Euler's theorem* states that

$$kf = \sum_{i=1}^{c} n_i \left(\frac{\partial f}{\partial n_i}\right)_{n'} \quad \text{(Euler's theorem)} \tag{4.6-2}$$

where the subscript n' stands for holding all of the n's constant except for n_i. A proof of this theorem is found in Appendix D.

Let Y stand for any extensive quantity. Since Y is homogeneous of degree 1 in the n's if T and P are constant, Euler's theorem becomes

$$Y = \sum_{i=1}^{c} n_i \left(\frac{\partial Y}{\partial n_i}\right)_{T,P,n'} = \sum_{i=1}^{c} n_i \overline{Y}_i \tag{4.6-3}$$

where $\overline{Y}_i$ is the partial molar quantity for substance i and where c is the number of components. Remember that T and P are held constant in the differentiations of the partial molar quantities. Two important examples of Eq. (4.6-3) are

$$G = \sum_{i=1}^{c} n_i \mu_i \tag{4.6-4}$$

and

$$V = \sum_{i=1}^{c} n_i \overline{V}_i \tag{4.6-5}$$

Equation (4.6-3) is a remarkable relation that gives the value of an extensive quantity as a weighted sum of partial derivatives. An unbiased newcomer to thermodynamics would likely not believe this equation without its mathematical proof.

Euler's theorem can also be written in terms of the *mean molar quantity* Y_m, defined by $Y_\mathrm{m} = Y/n$, where n is the total amount of all components:

$$Y_\mathrm{m} = \frac{1}{n} \sum_{i=1}^{c} n_i \overline{Y}_i = \sum_{i=1}^{c} x_i \overline{Y}_i \tag{4.6-6}$$

where x_i is the *mole fraction* of substance number i, equal to n_i/n.

EXAMPLE 4.21

In a solution of acetone (component 1) and chloroform (component 2) $x_1 = 0.531$ and $\overline{V}_1 = 74.2\ \mathrm{cm^3\ mol^{-1}}$. If $V_\mathrm{m} = 77.0\ \mathrm{cm^3\ mol^{-1}}$ at this composition, find $\overline{V}_2$.

Solution

From Euler's theorem

$$\begin{aligned}\overline{V}_2 &= \frac{V_\mathrm{m} - x_1 \overline{V}_1}{x_2} \\ &= \frac{77.0\,\mathrm{cm^3\,mol^{-1}} - (0.531)\left(74.2\,\mathrm{cm^3\,mol^{-1}}\right)}{0.469} \\ &= 80.2\,\mathrm{cm^3\,mol^{-1}}\end{aligned}$$

The Gibbs–Duhem Relation

From Euler's theorem, Eq. (4.6-3), we can write an expression for dY, the differential of an extensive quantity denoted by Y:

$$dY = \sum_{i=1}^{c} n_i d\overline{Y}_i + \sum_{i=1}^{c} \overline{Y}_i dn_i \tag{4.6-7}$$

This equation represents the effect on Y of any infinitesimal change in the state of the system such as changing its temperature or pressure or adding one of the substances. Considering Y to be a function of T, P, and the n's, we write another expression for dY:

$$dY = \left(\frac{\partial Y}{\partial T}\right)_{P,n} dT + \left(\frac{\partial Y}{\partial P}\right)_{T,n} dP + \sum_{i=1}^{c} \overline{Y}_i dn_i \tag{4.6-8}$$

We equate the right-hand sides of the two equations for dY and cancel equal sums:

$$\boxed{\sum\nolimits_{i=1}^{c} n_i d\overline{Y}_i = \left(\frac{\partial Y}{\partial T}\right)_{P,n} dT + \left(\frac{\partial Y}{\partial P}\right)_{T,n} dP} \tag{4.6-9}$$

Equation (4.6-9) is called the *generalized Gibbs–Duhem relation.*

The *original Gibbs–Duhem relation* is a special case that applies to the Gibbs energy at constant T and P:

$$\boxed{\sum\nolimits_{i=1}^{c} n_i d\mu_i = 0 \quad \text{(the original Gibbs–Duhem equation, valid at constant } T \text{ and } P\text{)}} \tag{4.6-10}$$

In a two-component mixture, this equation specifies how much the chemical potential of one component must decrease if the chemical potential of the other component increases at constant temperature and pressure:

$$d\mu_1 = -\frac{x_2}{x_1} d\mu_2 \quad \text{(two components at constant } T \text{ and } P\text{)} \tag{4.6-11}$$

EXAMPLE 4.22

A two-component ideal gas mixture at constant temperature and pressure has the partial pressure of gas number 1 changed by dP_1. Show that the expression for the chemical potential of a component of an ideal gas mixture, Eq. (4.5-26), is compatible with Eq. (4.6-11).

Solution

We need to manipulate $-\frac{x_2}{x_1} d\mu_2$ into an expression for $d\mu_1$. From Eq. (4.5-23)

$$\mu_i = \mu_i^\circ + RT \ln\left(\frac{P_i}{P^\circ}\right) \quad (i = 1, 2)$$

At constant T and P,

$$d\mu_2 = \left(\frac{\partial \mu_2}{\partial P_2}\right) dP_2 = \frac{RT}{P_2} dP_2 = -\frac{RT}{P_2} dP_1$$

where we have used the relation $dP_2 = -dP_1$, which follows from our condition that $P_1 + P_2 = P = \text{constant}$.

$$-\frac{x_2}{x_1}d\mu_2 = \frac{x_2 RT}{x_1 P_2}dP_1$$

From Dalton's law of partial pressures, $x_2/P_2 = x_1/P_1$, so that

$$-\frac{x_2}{x_1}d\mu_2 = \frac{RT}{P_1}dP_1 = d\mu_1$$

The Gibbs–Duhem relation is often written as a derivative relation instead of a differential relation. It is necessary that the partial derivatives be taken with T and P constant since the Gibbs–Duhem relation is valid only for constant T and P. For a two-component system,

$$x_1\left(\frac{\partial\mu_1}{\partial x_1}\right)_{T,P} + x_2\left(\frac{\partial\mu_2}{\partial x_1}\right)_{T,P} = 0 \quad (\text{constant } T \text{ and } P) \tag{4.6-12}$$

Both derivatives must be taken with respect to the same mole fraction. For a system with more than two components, the equation is

$$\sum_{i=1}^{c} x_i\left(\frac{\partial\mu_i}{\partial x_k}\right)_{T,P} = 0 \quad (\text{constant } T \text{ and } P) \tag{4.6-13}$$

where every partial derivative must be with respect to the same variable x_k. Equation (4.6-13) is valid for any kind of changes in the mole fractions if T and P are constant.

The Experimental Determination of Partial Molar Quantities

The partial molar volume is the most easily measured partial molar quantity, so we discuss it as an example. Other partial molar quantities can be evaluated in the same way if data are available. Assume that we measure the volume of the system as a function of the amount of the component of interest, keeping the pressure, temperature, and amounts of other substances fixed. If this volume can be represented by a polynomial or some other formula, the partial molar volume can be obtained by differentiation. If only the data points are available, the partial molar volume can be obtained by numerical differentiation.[3]

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[3] D. P. Shoemaker, C. W. Garland, and J. W. Nibler, *Experiments in Physical Chemistry*, 6th ed., McGraw-Hill, New York, 1996, pp. 757ff. See also Robert G. Mortimer, *Mathematics for Physical Chemistry*, 3rd ed., Academic Press, San Diego, CA, 2005, pp. 335–336.

EXAMPLE 4.23

At constant temperature and pressure, the volume of a solution made from component 1 and component 2 is represented by

$$V = b_1 n_1 + b_2 n_2 + b_{12} n_1 n_2 + b_{11} n_1^2 + b_{22} n_2^2$$

where n_1 and n_2 are the amounts of the two components in moles and the b's are constants at constant temperature and pressure. Find an expression for $\overline{V}_2$.

Solution

$$\overline{V}_2 = \left(\frac{\partial V}{\partial n_2}\right)_{T,P,n_1} = b_2 + b_{12} n_1 + 2b_{22} n_2$$

The Method of Intercepts

This method is a graphical method for the determination of partial molar quantities in a two-component solution. From Euler's theorem, the mean molar volume is given by

$$V_{\mathrm{m}} = x_1 \overline{V}_1 + x_2 \overline{V}_2 \tag{4.6-14}$$

where the x's are the mole fractions. Since $x_2 = 1 - x_1$ in a two-component system,

$$V_{\mathrm{m}} = x_1 \overline{V}_1 + (1 - x_1)\overline{V}_2 = (\overline{V}_1 - \overline{V}_2)x_1 + \overline{V}_2 \tag{4.6-15}$$

Figure 4.2 shows V_{m}, the mean molar volume of a solution of ethanol (component 1) and water (component 2), as a function of x_1. Let x_1' be a particular value of x_1 for which we desire the values of the partial molar quantities $\overline{V}_1$ and $\overline{V}_2$. To apply the method, we draw a tangent line to the curve at $x_1 = x_1'$, as shown in the figure. The intercepts of this line at the edges of the figure give the values of the two partial molar quantities for the composition $x_1 = x_1'$. A proof of the validity of this method is contained in Appendix D.

A modified version of the method generally gives better accuracy. In this method we make a graph of the change in the mean molar quantity on mixing (forming the solution from the pure substances):

$$\Delta V_{\mathrm{m,mix}} = V_{\mathrm{m}} - (x_1 V_{\mathrm{m},1}^* + x_2 V_{\mathrm{m},2}^*) \quad \text{(definition)} \tag{4.6-16}$$

where $V_{\mathrm{m},1}^*$ is the molar quantity of pure substance 1 and similarly for substance 2. Since $x_2 = 1 - x_1$, we can write

$$\Delta V_{\mathrm{m,mix}} = V_{\mathrm{m}} - V_{\mathrm{m},2}^* + x_1(V_{\mathrm{m},1}^* - V_{\mathrm{m},2}^*) \tag{4.6-17}$$

One plots experimental values of $\Delta V_{\mathrm{m,mix}}$ and constructs the tangent line at $x_1 = x_1'$. The intercepts of the tangent line are given by

$$\text{left intercept} = \overline{V}_1(x_1') - V_{\mathrm{m},1}^* \tag{4.6-18}$$

$$\text{right intercept} = \overline{V}_2(x_1') - V_{\mathrm{m},2}^* \tag{4.6-19}$$

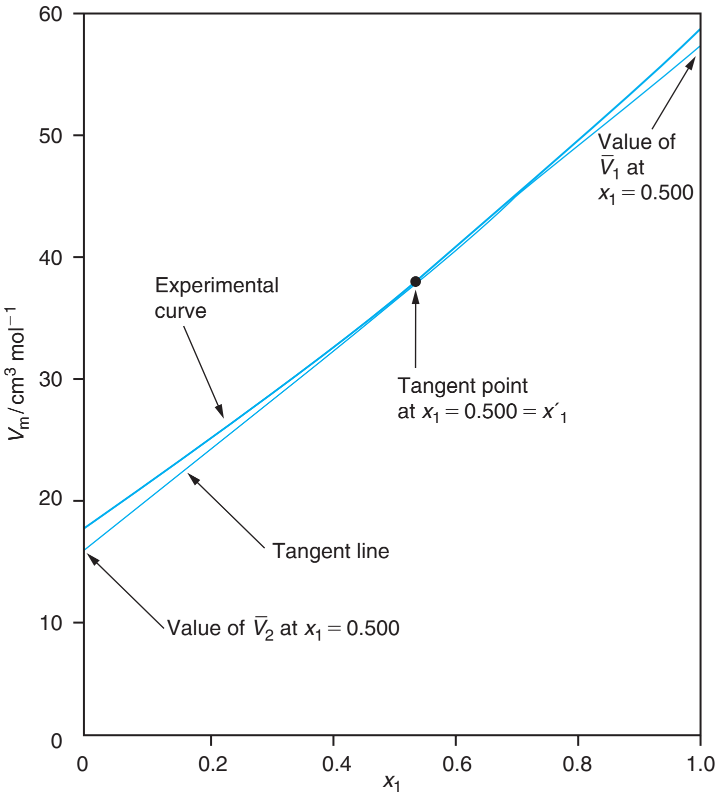

Figure 4.2 The Mean Molar Volume of an Ethanol-Water Solution as a Function of Mole Fraction of Ethanol.

EXAMPLE 4.24

From the intercepts in Figure 4.3, determine the partial molar volumes of ethanol (substance 1) and water (substance 2) if the mole fraction of ethanol is equal to 0.500. The molar volumes of the pure substances are $V^*_{m,1} = 58.4\,\text{cm}^3\,\text{mol}^{-1}$, $V^*_{m,2} = 18.02\,\text{cm}^3\,\text{mol}^{-1}$.

Solution

The tangent line is drawn in the figure.

$$\text{right intercept} = \overline{V}_1 - V^*_{m,1} = -0.83\,\text{cm}^3\,\text{mol}^{-1}$$

$$\text{left intercept} = \overline{V}_2 - V^*_{m,2} = -1.31\,\text{cm}^3\,\text{mol}^{-1}$$

$$\overline{V}_1 = 58.4\,\text{cm}^3\,\text{mol}^{-1} - 0.83\,\text{cm}^3\,\text{mol}^{-1} = 57.6\,\text{cm}^3\,\text{mol}^{-1}$$

$$\overline{V}_2 = 18.02\,\text{cm}^3\,\text{mol}^{-1} - 1.31\,\text{cm}^3\,\text{mol}^{-1} = 16.7\,\text{cm}^3\,\text{mol}^{-1}$$

If the method is to be applied to the partial molar Gibbs energy, the partial molar energy, the partial molar enthalpy, or the partial molar entropy, the second version of the method must be used since the actual values of G, U, H, and S are not defined (they can have any constants added to their values without physical effect).

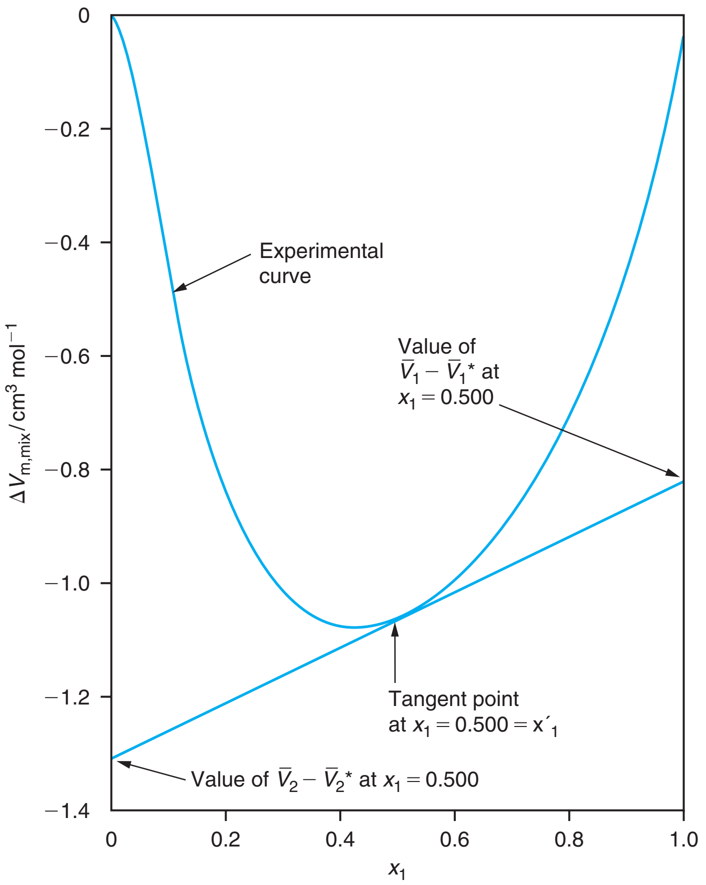

Figure 4.3 The Change in the Mean Molar Volume on Mixing for an Ethanol-Water Solution as a Function of Mole Fraction of Ethanol.

PROBLEMS

Section 4.6: Euler's Theorem and the Gibbs–Duhem Relation

4.45 Determine which (if any) of the following functions are homogeneous with respect to all three independent variables x, y, and z. Find the degree of each homogeneous function. All letters except f, x, y, and z denote constants. For the expressions that are homogeneous, verify that they conform to Euler's theorem.

a. $f(x, y, z) = ax^2 + bx^3y^{-1} + cy^2 + dyz$

b. $f(x, y, z) = ax^2y^{-2} + b\ln(y/z) + c\tan(x^3y^{-3})$

c. $f(x, y, z) = ax^2 + b\cos(x^2y^{-2}) + cz^2$

4.46 Determine which (if any) of the following functions are homogeneous with respect to all three independent variables x, y, and z. Find the degree of each homogeneous function. All letters except f, x, y, and z denote constants. For the expressions that are homogeneous, verify that they conform to Euler's theorem.

a. $f(x, y, z) = az^3 + bx^3\cos(x^4y^{-4}) + c\exp(yz^{-1})$

b. $f(x, y, z) = ax^4 + bx^2yz\sin(x/z)$

c. $f(x, y, z) = a\cos(x/y) + b\sin(x/z)$

4.47 A mixture of 0.500 mol of ideal gas 1 and 1.500 mol of ideal gas 2 is produced at a constant temperature of 350.0 K and a constant pressure of 1.000 bar.

a. Find ΔS_{mix}.

b. Find ΔG_{mix}.

c. Find the value of $\mu - \mu^\circ$ for each gas.

d. A small change in composition is made at constant temperature and pressure such that μ_1 changes by $0.100\ \mathrm{J\ mol^{-1}}$. Find the corresponding change in μ_2. Approximate your answer as though the changes were infinitesimal.

4.48 **a.** From the data of Problem 4.41, make a graph of $\Delta V_{\mathrm{m,mix}}$ as a function of ethanol mole fraction and determine the partial molar volume of each substance for the solution with ethanol mole fraction equal to 0.300, using the method of intercepts.

b. From the values of the partial molar volumes of water and ethanol in the solution of part a, find the volume of a solution containing 0.600 mol of ethanol and 1.400 mol of water. Compare this value with the value obtained by interpolating in the list of density values given in Problem 4.41.

Summary of the Chapter

In this chapter we have obtained two types of mathematical tools for the application of thermodynamics to real systems: (1) criteria for spontaneous processes in terms of properties of a system; (2) useful formulas.

The second law of thermodynamics provides the general criterion for spontaneous processes: No process can decrease the entropy of the universe. For a closed simple system at constant pressure and temperature the Gibbs energy G cannot increase, and for a closed simple system at constant temperature and volume the Helmholtz energy A cannot increase.

Several fundamental relations were obtained for closed simple systems. The first relations were for the differentials of the different energy-related state variables for closed simple systems. For example,

$$dG = -SdT + VdP$$

The Maxwell relations were derived from these differentials. For example

$$\left(\frac{\partial S}{\partial P}\right)_{T,n} = -\left(\frac{\partial V}{\partial T}\right)_{P,n}$$

The Maxwell relations were used to obtain a number of useful formulas, including the thermodynamic equation of state:

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = T\left(\frac{\partial P}{\partial T}\right)_{V,n} - P$$

The molar Gibbs energy of a pure substance was expressed as the molar Gibbs energy in the standard state, G_{m}°, plus another term. For an ideal gas

$$G_{\mathrm{m}} = G_{\mathrm{m}}^\circ + RT\ln(P/P^\circ)$$

and for an incompressible solid or liquid

$$G_{\mathrm{m}} = G_{\mathrm{m}}^\circ + V_{\mathrm{m}}(P - P^\circ)$$

The description of open multicomponent systems was based on the Gibbs equation,

$$dG = -TdS + VdP + \sum_{i=1}^{c} \mu_i dn_i$$

where μ_i is the chemical potential of component i, and additional useful formulas were obtained from this.

For any extensive quantity, represented by Y, Euler's theorem is

$$Y = \sum_{i=1}^{c} n_i \overline{Y}_i$$

where $\overline{Y}_i$ is the partial molar quantity. The generalized Gibbs–Duhem relation is

$$\sum_{i=1}^{c} n_i d\overline{Y}_i = \left(\frac{\partial Y}{\partial T}\right)_{P,n} dT + \left(\frac{\partial Y}{\partial P}\right)_{T,n} dP$$

and the original Gibbs–Duhem relation is

$$\sum_{i=1}^{c} n_i d\mu_i = 0 \quad \text{(constant } T \text{ and } P\text{)}$$

ADDITIONAL PROBLEMS

4.49 Label the following statements as true or false. If a statement is true only under certain conditions, label it as false.

a. The minimum of the Gibbs energy of the system always corresponds to the maximum of the entropy of the system plus surroundings.

b. The minimum of the Helmholtz energy of a system always corresponds to the maximum of the entropy of the system plus surroundings.

c. The minimum of the Gibbs energy always corresponds to the minimum of the energy of the system plus surroundings.

d. If a system is at constant temperature and pressure, the minimum in the Gibbs energy of the system corresponds to the maximum of the entropy of the system plus surroundings.

e. If a system is at constant temperature and volume, the minimum in the Helmholtz energy corresponds to the maximum of the entropy of the system plus surroundings.

f. In a reversible adiabatic process, the state of the surroundings is unaffected.

g. In a reversible adiabatic process, the entropy of the surroundings is unaffected.

h. In an irreversible adiabatic process, the entropy of the surroundings is unaffected.

4.50 For each of the following processes, tell whether each of the quantities ΔS, ΔG, q, and w is positive, zero, or negative. Present your answers in the form of a table with entries +, 0, or −:

a. Liquid water is vaporized at 100°C and a partial pressure of water vapor equal to 1.000 atm.

b. Liquid water is vaporized at 100°C and a partial pressure of water vapor equal to 0.900 atm.

c. Liquid water is frozen at −10°C and a pressure of 1.000 atm.

d. Liquid water is frozen at 0°C and a pressure of 1.000 atm.

4.51 **a.** Find the value of the heat capacity at constant volume for 1.000 mol of liquid water at 20.00°C.

b. Find the value of the adiabatic compressibility of liquid water at 25.00°C.

c. Find the speed of sound in liquid water at 20.00°C, using the formula from Problem 4.12:

$$v_s^2 = \frac{V_m C_P}{M\kappa_T C_V} = \frac{V_m \gamma}{M\kappa_T}$$

d. Find the final volume of 1.000 mol of liquid water if it is compressed adiabatically from 1.000 bar and 25.00°C to a pressure of 100.00 bar. Assume that the adiabatic compressibility is constant.

e. Find the final temperature for the process of part d.

f. Find ΔU for the process of part d.

4.52 For each of the following proposed processes, say: (1) whether the process is spontaneous, nonspontaneous, or reversible; (2) whether ΔG is positive, negative, or equal to zero; (3) whether ΔH is positive, negative, or equal to zero; (4) whether ΔS is positive, negative, or equal to zero; and (5) whether ΔH is smaller or larger in magnitude than $T\Delta S$. Assume that each initial state is a metastable state.

a. Liquid water is vaporized at 1.000 atm and 100°C.

b. Liquid water is vaporized at 1.000 atm and 105°C.

c. Liquid water is vaporized at 1.000 atm and 95°C.

d. Solid water melts at 1.000 atm and 5°C.

e. Solid water melts at 1.000 atm and 0°C.

f. Water vapor at 25°C and a partial pressure of 23.756 torr condenses to a liquid.

g. Solid water melts at 10.000 atm and 0°C.

4.53 A nonideal gas is described equally well by either of two truncated virial equations of state:

$$\frac{PV_{\mathrm{m}}}{RT} = 1 + \frac{B_2}{RT} \quad \text{and} \quad PV_{\mathrm{m}} = RT + A_2 P$$

where A_2 and B_2, the second virial coefficients, are functions of T, and can be shown to equal each other.

a. Find expressions for the following:

- **i.** $G_{\mathrm{m}}(T, P') - G^{\circ}_{\mathrm{m}}(T)$
- **ii.** $S_{\mathrm{m}}(T, P') - S^{\circ}_{\mathrm{m}}(T)$
- **iii.** $H_{\mathrm{m}}(T, P') - H^{\circ}_{\mathrm{m}}(T)$
- **iv.** $A_{\mathrm{m}}(T, P') - A^{\circ}_{\mathrm{m}}(T)$
- **v.** $U_{\mathrm{m}}(T, P') - U^{\circ}_{\mathrm{m}}(T)$

b. Evaluate each of the quantities in part a for carbon dioxide at 0°C, using data in Table A.4.

4.54 Show that $(\partial T/\partial V)_{S,n} < 0$ unless $(\partial V/\partial T)_{P,n} < 0$. What is the sign of $(\partial T/\partial V)_{S,n}$ for water in the temperature range between 0.00°C and 3.98°C?

4.55 **a.** Use the fundamental equation of Problem 4.4 to obtain an expression for $S - S_0$ as a function of T and P for a monatomic ideal gas. Use the facts that $U = 3nRT/2$ and that $PV = nRT$.

b. Carry out a line integration of dS from (T_0, P_0) to (T', P') for a closed ideal gas system with $n = n_0$ to obtain the same expression.

c. Use the fundamental equation of Problem 4.4 to obtain an expression for $S - S_0$ as a function of T and V for an ideal gas. Use the facts that $U = 3nRT/2$ and that $PV = nRT$.

d. Carry out a line integration of dS from (T_0, V_0) to (T', V') for a closed ideal gas system with $n = n_0$ to obtain the same expression.

4.56 Consider the reaction

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l)$$

a. Calculate the value of ΔH°, ΔU°, ΔG°, and ΔA° for this reaction at 298.15 K. Calculate the value of ΔA° from the value of ΔG° in the same way that you calculate the value of ΔU° from the value of ΔH° (see Chapter 2).

b. If the heat from this reaction is used to power a steam turbine with an efficiency that is 60.0% as great as that of a Carnot engine operating between 200.0°C and 400.0°C, find the maximum amount of work that can be done by the combustion of 2.000 mol of hydrogen gas.

c. This reaction is carried out in fuel cells in spacecraft. Calculate the maximum amount of net work (work other than P–V work) that can be done by the reaction of 2.000 mol of hydrogen gas. Calculate the total amount of work that can be done. Comment on the comparison between your results from parts b and c.

4.57 Calculate ΔV and ΔS for pressurizing 2.000 mol of liquid benzene from 1.000 atm to 1000.0 atm at 25.00°C. The density of benzene at this temperature and 1.000 atm is 0.8765 g cm^{-3}. Use an average value for the isothermal compressibility over this range of pressures.

5

Phase Equilibrium

PRINCIPAL FACTS AND IDEAS

1. The laws of thermodynamics determine equilibrium between phases.
2. The fundamental fact of phase equilibrium is that at equilibrium the chemical potential of any substance must have the same value in all phases in which that substance appears.
3. The Gibbs phase rule gives the number of independent intensive variables in a multicomponent multiphase system at equilibrium:

$$f = c - p + 2$$

   where f is the number of independent intensive variables, c is the number of components, and p is the number of phases.
4. The Gibbs phase rule allows phase diagrams to be understood.
5. The Clausius and Clausius–Clapeyron equations govern the curves in phase diagrams.
6. Thermodynamics allows analysis of the stability of phases in systems.
7. Surface effects must be included in a complete thermodynamic treatment, but are usually negligible.

5.1

The Fundamental Fact of Phase Equilibrium

The principal business of this chapter is to establish the thermodynamic relations obeyed by two or more phases that are at equilibrium with each other. A *phase* is a portion of a system (or an entire system) inside which intensive properties do not change abruptly as a function of position. The principal kinds of phases are solids, liquids, and gases, although plasmas (ionized gases), liquid crystals, and glasses are sometimes considered to be separate types of phases. Solid and liquid phases are called *condensed phases* and a gas phase is often called a *vapor phase.* Several elements such as carbon exhibit solid-phase *allotropy*. That is, there is more than one kind of solid phase of the element. For example, diamond and graphite are both solid carbon, but have different crystal structures and different physical properties. With compounds, this phenomenon is called *polymorphism* instead of allotropy. Most pure substances have only one liquid phase, but helium exhibits allotropy in the liquid phase.

In a multicomponent system there can often be several solid phases or several liquid phases at equilibrium. For example, if one equilibrates mercury, a mineral oil, a methyl silicone oil, water, benzyl alcohol, and a perfluoro compound such as perfluoro (*N*-ethyl piperidine) at room temperature, one can obtain six coexisting liquid phases.[1] Each of these phases consists of a large amount of one substance with small amounts of the other substances dissolved in it. Under ordinary conditions, a system can exhibit only a single gas phase. However, if certain gaseous mixtures are brought to supercritical temperatures and pressures, where the distinction between gas and liquid disappears, two fluid phases can form without first making a gas–liquid phase transition.

Equilibrium between Phases

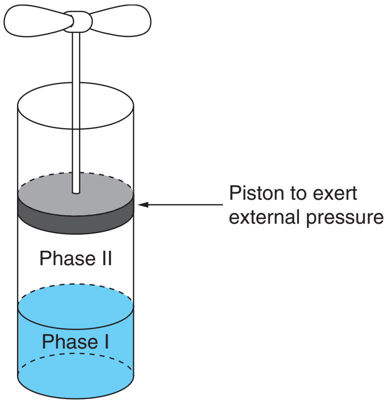

Figure 5.1 A Two-Phase Simple System.

An equilibrium two-phase simple system containing several substances is depicted schematically in Figure 5.1. This system is closed to the surroundings, but each phase is open to the other and both phases are at the same temperature and pressure. If the contribution of the surface area between the phases is negligible (a good approximation in most cases), the Gibbs energy of the system is the sum of the Gibbs energies of the two phases:

$$G = G^{(\mathrm{I})} + G^{(\mathrm{II})} \tag{5.1-1}$$

where we denote the two phases by the superscripts (I) and (II).

The substances in the system whose amounts can be varied independently are called *components*. We denote the number of components by c. Since the system is closed, if component number i moves out of one phase it must move into the other phase:

$$dn_i^{(\mathrm{I})} = -dn_i^{(\mathrm{II})} \tag{5.1-2}$$

For an infinitesimal change of state involving changes in T and P and a transfer of matter from one phase to the other,

$$\begin{aligned} dG &= dG^{(\mathrm{I})} + dG^{(\mathrm{II})} \\ &= -S^{(\mathrm{I})}dT + V^{(\mathrm{I})}dP + \sum_{i=1}^{c} \mu_i^{(\mathrm{I})} dn_i^{(\mathrm{I})} - S^{(\mathrm{II})}dT + V^{(\mathrm{II})}dP + \sum_{i=1}^{c} \mu_i^{(\mathrm{II})} dn_i^{(\mathrm{II})} \end{aligned} \tag{5.1-3}$$

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[1] J. Kochansky, *J. Chem. Educ.*, **68**, 653 (1991).

If T and P are constant, the fundamental criterion of equilibrium implies that dG must vanish for an infinitesimal change that maintains equilibrium:

$$\begin{aligned} dG &= \sum_{i=1}^{c} \mu_i^{(\mathrm{I})} dn_i^{(\mathrm{I})} + \sum_{i=1}^{c} \mu_i^{(\mathrm{II})} dn_i^{(\mathrm{II})} \\ &= \sum_{i=1}^{c} \left[\mu_i^{(\mathrm{I})} - \mu_i^{(\mathrm{II})}\right] dn_i^{(\mathrm{I})} = 0 \quad \text{(at equilibrium)} \end{aligned} \tag{5.1-4}$$

where we used the fact that $dn_i^{(\mathrm{I})} = -dn_i^{(\mathrm{II})}$. We want to show not only that the last sum in Eq. (5.1-4) vanishes, but that each term vanishes. Assume that we can find a semipermeable membrane that will selectively allow component i to pass, but not the others. The term of the sum for component i must vanish since all of the other dn's vanish. Since dn_i is not necessarily equal to zero, the other factor in the term must vanish, and we can write

$$\mu_i^{(\mathrm{I})} = \mu_i^{(\mathrm{II})} \quad \text{(at equilibrium)} \tag{5.1-5a}$$

If more than two phases are present at equilibrium, we conclude that the chemical potential of any substance has the same value in every phase in which it occurs. We write a second version of Eq. (5.1-5a):

$$\mu_i^{(\alpha)} = \mu_i^{(\beta)} \quad \text{(system at equilibrium)} \tag{5.1-5b}$$

where the superscripts (α) and (β) designate any two phases of a multiphase system.

The properties of a system at equilibrium do not depend on how the system arrived at equilibrium. Therefore, Eq. (5.1-5) is valid for any system at equilibrium, not only for a system that arrived at equilibrium under conditions of constant T and P. We call it the *fundamental fact of phase equilibrium: In a multiphase system at equilibrium the chemical potential of any substance has the same value in all phases in which it occurs.*

Nonequilibrium Phases

Consider a two-phase simple system that is maintained at constant temperature and pressure but is not yet at equilibrium. Assuming that the nonequilibrium state of the system can be treated as a metastable state, the criterion for spontaneous processes is given by Eq. (4.1-17):

$$dG \le 0 \quad (T \text{ and } P \text{ constant}) \tag{5.1-6}$$

Since dT and dP vanish and since the system as a whole is closed,

$$dG = \sum_{i=1}^{c} \mu_i^{(\mathrm{I})} dn_i^{(\mathrm{I})} + \sum_{i=1}^{c} \mu_i^{(\mathrm{II})} dn_i^{(\mathrm{II})} = \sum_{i=1}^{c} \left[\mu_i^{(\mathrm{I})} - \mu_i^{(\mathrm{II})}\right] dn_i^{(\mathrm{I})} \le 0 \tag{5.1-7}$$

Each term separately must be negative since the introduction of semipermeable membranes would show each term to obey the inequality separately. The two factors in each term of the sum in Eq. (5.1-7) must be of opposite signs:

$$\mu_i^{(\mathrm{I})} > \mu_i^{(\mathrm{II})} \quad \text{implies that } dn_i^{(\mathrm{I})} \le 0 \tag{5.1-8}$$

$$\mu_i^{(\mathrm{I})} < \mu_i^{(\mathrm{II})} \quad \text{implies that } dn_i^{(\mathrm{I})} \ge 0 \tag{5.1-9}$$

This result can be summarized: *At constant temperature and pressure, any substance tends to move spontaneously from a phase of higher chemical potential to a phase of lower chemical potential.* The name "chemical potential" was chosen by analogy with the fact that a mechanical particle experiences a force pushing it in the direction of lower potential energy.

Exercise 5.1

Argue that a substance will move spontaneously from any phase in which its chemical potential has a higher value to a phase in which it has a lower value if each phase is at constant volume and if both phases are at the same constant temperature.

Transport of Matter in a Nonuniform Phase

Consider a one-phase system that has a uniform temperature and pressure but a nonuniform composition. Imagine dividing the system into small regions (subsystems), each one of which is small enough so that the concentration of each substance is nearly uniform inside it. Any substance will move spontaneously from a subsystem of higher value of its chemical potential to an adjacent subsystem with a lower value of its chemical potential. The fundamental fact of phase equilibrium for nonuniform systems can be stated: *In a system with uniform temperature and pressure, any substance tends to move from a region of higher chemical potential to a region of lower chemical potential.* A nonuniformity of the chemical potential is the driving force for diffusion, which we will discuss in Chapter 10.

PROBLEMS

Section 5.1: The Fundamental Fact of Phase Equilibrium

5.1 For water at equilibrium at 1.000 atm and 273.15 K, find the values of $G_\mathrm{m}^{(\mathrm{liq})} - G_\mathrm{m}^{(\mathrm{solid})}$, $A_\mathrm{m}^{(\mathrm{liq})} - A_\mathrm{m}^{(\mathrm{solid})}$, $H_\mathrm{m}^{(\mathrm{liq})} - H_\mathrm{m}^{(\mathrm{solid})}$, $U_\mathrm{m}^{(\mathrm{liq})} - U_\mathrm{m}^{(\mathrm{solid})}$, and $S_\mathrm{m}^{(\mathrm{liq})} - S_\mathrm{m}^{(\mathrm{solid})}$.

5.2 For water at equilibrium at 1.000 atm and 373.15 K, find the values of $G_\mathrm{m}^{(\mathrm{gas})} - G_\mathrm{m}^{(\mathrm{liq})}$, $A_\mathrm{m}^{(\mathrm{gas})} - A_\mathrm{m}^{(\mathrm{liq})}$, $H_\mathrm{m}^{(\mathrm{gas})} - H_\mathrm{m}^{(\mathrm{liq})}$, $U_\mathrm{m}^{(\mathrm{gas})} - U_\mathrm{m}^{(\mathrm{liq})}$, and $S_\mathrm{m}^{(\mathrm{gas})} - S_\mathrm{m}^{(\mathrm{liq})}$. State any assumptions.

5.3 For water at equilibrium at 23.756 torr and 298.15 K, find the values of $G_\mathrm{m}^{(\mathrm{gas})} - G_\mathrm{m}^{(\mathrm{liq})}$, $A_\mathrm{m}^{(\mathrm{gas})} - A_\mathrm{m}^{(\mathrm{liq})}$, $H_\mathrm{m}^{(\mathrm{gas})} - H_\mathrm{m}^{(\mathrm{liq})}$, $U_\mathrm{m}^{(\mathrm{gas})} - U_\mathrm{m}^{(\mathrm{liq})}$, and $S_\mathrm{m}^{(\mathrm{gas})} - S_\mathrm{m}^{(\mathrm{liq})}$. State any assumptions.

5.4 Repeat the calculation of Exercise 5.12 assuming that $C_{P,\mathrm{m}}$ for the liquid is constant but that $C_{P,\mathrm{m}}$ for the vapor is given by the polynomial formula in Table A.6 in the appendix.

5.2

The Gibbs Phase Rule

The Gibbs phase rule gives the number of independent intensive variables in a simple system that can have several phases and several components. The equilibrium thermodynamic state of a one-phase simple system with c components is specified by the values of $c + 2$ thermodynamic variables, at least one of which must be an extensive variable. All other equilibrium variables are dependent variables. The *intensive state* is the state of the system so far as only intensive variables are concerned. Changing the size of the system without changing any intensive variables does not affect the intensive state. Intensive variables cannot depend on extensive variables, so specification of the equilibrium intensive state of a one-phase simple system requires $c + 1$ independent variables, all of which must be intensive. A convenient set of independent variables to specify the equilibrium intensive state of a one-phase simple system consists of T, P, and $c - 1$ mole fractions. Only $c - 1$ mole fractions can be independent variables, since the mole fractions automatically obey the relation

$$\sum_{i=1}^{c} x_i = 1 \tag{5.2-1}$$

If all of the mole fractions but one are specified, the last one is determined.

Counting the Number of Phases and Components in a System

We denote the number of phases in a system by p. In counting phases, we count only regions that are different in their intensive properties from other regions. For example, liquid water and crushed ice make up a two-phase system, just like a system of liquid water and a single ice cube. The *components* of a system are substances whose amounts can be varied independently. The number of components is equal to the number of chemical species present minus the number of relations that constrain the amounts of the species. There are three principal types of constraints: (1) relations due to chemical equilibrium; (2) a relation due to a requirement of electrical neutrality (which we always assume to exist); and (3) relations due to the way the system was prepared (such as a specification that two substances are in their stoichiometric ratio).

The number of components is also equal to the number of substances from which the system could be prepared, given the conditions imposed on the system. A mixture of gaseous hydrogen, oxygen, and water vapor can remain unreacted for a very long time at room temperature if no catalyst is present. We can treat this metastable mixture as if no reaction were possible and say that there are three components. If a platinum catalyst is introduced into the system, a chemical equilibrium is rapidly established, reducing the number of components to two (not counting the catalyst). In the presence of the catalyst the amount of water vapor is determined by the amounts of hydrogen and oxygen and the nature of the chemical equilibrium. If the additional constraint is added that the hydrogen and oxygen are in the stoichiometric ratio of 2 moles to 1, then the system has only one component. In this case the system could be produced from water vapor in the presence of the catalyst.

EXAMPLE 5.1

Determine the number of components in:

a. An aqueous solution containing Na^+, Cl^-, and Br^-.
b. An aqueous solution containing Na^+, K^+, Li^+, Cl^-, and Br^-.
c. A gaseous system containing NO_2 and N_2O_4 at chemical equilibrium with each other.
d. An aqueous solution containing Ca^{2+} ions and Cl^- ions.

Solution

a. There are three components. The system can be produced from three pure substances: water, NaCl, and NaBr. The number can also be determined by counting up water and the three ions and subtracting unity for the condition of electrical neutrality.

b. There are five components. Although six species are present, there is a requirement of electrical neutrality. It would be possible to make the system with five substances: water, NaCl, KBr, KCl, and LiCl. No NaBr or LiBr is needed.

c. There is one component, since the amount of N_2O_4 is determined by the amount of NO_2 and the conditions of the equilibrium.

d. There are two components, since electrical neutrality imposes a relation on the amounts of Ca^{2+} and Cl^- ions.

Exercise 5.2

Determine the number of components in:

a. A solution made from water, NaCl, and KBr.

b. An aqueous solution containing Na^+, Cl^-, K^+, and Br^-. Explain any difference from part a.

c. A gaseous system containing PCl_5, PCl_3, and Cl_2 at chemical equilibrium.

d. A solid mixture containing powdered graphite and powdered diamond without a catalyst or other means of converting one phase to the other.

e. A gaseous mixture containing carbon dioxide and water vapor.

f. A gaseous mixture containing carbon dioxide and water vapor that was produced by the combustion of a stoichiometric mixture of methane and oxygen. Assume that the residual amounts of methane and oxygen are negligible.

g. A system containing solid Na_2SO_4 and an aqueous phase containing Na^+ and SO_4^{2-} ions, which was produced by dissolving some of the sodium sulfate decahydrate.

The Gibbs Phase Rule

If the phases in a multiphase simple system of p phases and c components are separated from each other so that they cannot equilibrate, there are $c + 1$ independent intensive variables for each phase, a total of $p(c + 1)$ variables. Now place the phases in contact with each other, open them to each other, and allow them to equilibrate. There are three aspects of equilibrium. *Thermal equilibrium* implies that all phases have the same temperature, *mechanical equilibrium* implies that all phases have the same pressure, and *phase equilibrium* implies that the chemical potential of every substance has the same value in every phase.

Each new equality turns one variable into a dependent variable. Specifying that one variable has the same value in two phases means one equality, specifying that one variable has the same value in three phases means two equalities, and so on. There are $p - 1$ equalities for one variable and p phases. The number of variables that have equal values in all phases is $c + 2$ (T, P and the chemical potentials of c components), for a total of $(p - 1)(c + 2)$ equalities. This means that f, the number of independent intensive variables after equilibration of all phases, is equal to

$$f = p(c + 1) - (p - 1)(c + 2) = pc + p - pc + c - 2p + 2$$

$$f = c - p + 2 \quad \text{(Gibbs phase rule)} \tag{5.2-2}$$

This equation is the *phase rule* of Gibbs. The number of independent intensive variables denoted by f is called the number of *degrees of freedom* or the *variance*. Try not to be confused by the fact that the term "variance" is also used for the square of a standard deviation of a distribution.

PROBLEMS

Section 5.2: The Gibbs Phase Rule

5.5 Give the number of independent intensive variables for each of the following systems at equilibrium:

a. SO_2, SO_3, and O_2 in a one-phase gaseous system, with the chemical reaction among these substances at equilibrium and with each substance added separately.

b. The same substances as in part a, but with the system produced by placing only SO_3 in the container.

c. N_2, H_2, and NH_3 in a one-phase gaseous system, with each substance added separately and allowed to come to chemical equilibrium by the equation

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

d. $NH_3(g)$ placed in a container and allowed to come to chemical equilibrium according to the equation of the previous part.

e. Ice VI, ice VII, and ice VIII.

5.6 Give the number of independent intensive variables for each of the following systems at equilibrium:

a. Ice and liquid water.

b. Ice and water vapor.

c. CO, O_2, and CO_2 in a single gas phase, with no catalyst present so that the chemical reaction cannot equilibrate, and with each substance added separately.

d. The system as in part c, but with a catalyst so that the chemical reaction can equilibrate.

e. The system as in part c, but with the system prepared by adding only CO_2.

5.7 Give the number of components and the number of independent intensive variables for each of the following systems at equilibrium:

a. H_2, I_2, and HI in a single gas phase at a temperature such that the following equilibrium can be established:

$$H_2 + I_2 \rightleftharpoons 2HI$$

b. $CaCO_3(s)$, CaO(s), and $CO_2(g)$ at a temperature such that the following equilibrium can be established:

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

c. An aqueous solution of acetic acid. Make a list of the major species present in the solution.

5.8 A researcher exhibits a photo showing four phases, which he claims are ice I, ice II, liquid water, and water vapor. What is your comment?

5.3 Phase Equilibria in One-Component Systems

In a phase diagram such as that of Figure 1.4, the temperature is plotted on the horizontal axis and the pressure is plotted on the vertical axis. An open area represents a single phase. For a one-component one-phase system the number of independent intensive variables at equilibrium is

$$f = 1 - 1 + 2 = 2 \quad \text{(one component, one phase)}$$

The temperature and pressure can both be independent, and any point in the area can represent a possible intensive state of the system. For one component and two phases, the number of independent intensive variables at equilibrium is

$$f = 1 - 2 + 2 = 1 \quad \text{(one component, two phases)}$$

The pressure must be a function of the temperature:

$$P = P(T) \quad (c = 1,\ p = 2) \tag{5.3-1}$$

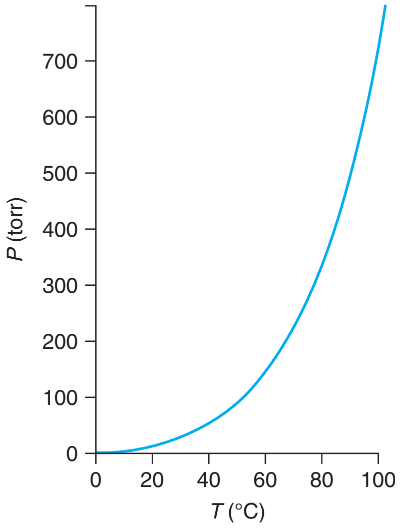

Figure 5.2 The Equilibrium Vapor Pressure of Water as a Function of Temperature. Data from R. C. Weast, *Handbook of Chemistry and Physics*, 64th ed., CRC Press, Boca Raton, FL, p. D192.

This function is represented by a *coexistence curve* in the phase diagram. Figure 1.4 shows a solid–vapor curve, a solid–liquid curve, and a liquid–vapor curve. The equilibrium pressure when a liquid phase or a solid phase is equilibrated with a vapor (gas) phase is called the *vapor pressure* of that phase. Figure 5.2 shows the equilibrium vapor pressure of liquid water as a function of temperature.

If one component and three phases are present, $f = 0$ and there is no choice about the temperature, the pressure, or any other intensive variable. This three-phase state is represented by a *triple point* at which three coexistence curves intersect. The solid–liquid–vapor triple point of water occurs at a temperature of 273.16 K (this value defines the size of the kelvin) and a pressure of 4.562 torr.

Figure 5.3 shows the phase diagram of water. Water exhibits polymorphism, so there are several coexistence curves. The pressure scale in this diagram is so compressed that the liquid–vapor curve of Figure 5.2 is too close to the horizontal axis to be visible. Eight different equilibrium crystal forms of water are shown, denoted by Roman numerals. Ice IV is a metastable phase that was mistaken for an equilibrium phase when it was given this number.[2] We do not count it as one of the equilibrium crystal forms of water.

In the novel *Cat's Cradle*[3] a fictional form of ice is discovered that melts at 114°F. Since it is more stable than liquid water at room temperature, ultimately all of the

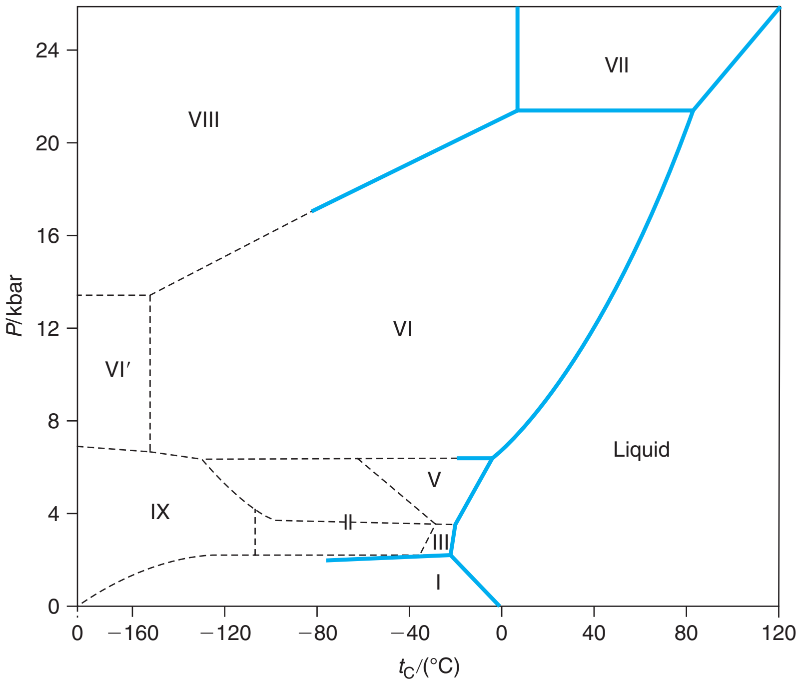

Figure 5.3 The Phase Diagram of Water. From B. Kamb, in E. Whalley, S. Jones, and L. Gold, eds., *Physics and Chemistry of Ice*, University of Toronto Press, Toronto, 1973.

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[2] Professor Martin Chaplin of London South Beach University maintains a website on the properties of water, incuding metastable ice IV. Since the web address of the site can change, the site is best accessed by searching for Professor Chaplin's name.

[3] Kurt Vonnegut, *Cat's Cradle*, Delacorte Press, New York, 1963.

water on the earth except in very hot regions freezes to this form of ice, destroying life as we know it. In the late 1960s, it was thought for a time that liquid water might exhibit polymorphism. It was claimed there was a second liquid phase of water, which was named *polywater* since it seemed to consist of polymers of water molecules.[4] This phase appeared to have a lower chemical potential than ordinary liquid water at the same temperature and pressure. Numerous experimental and theoretical studies of polywater were published before it was discovered that the small capillaries in which the polywater was supposedly prepared were leaching substances into the water, forming solutions. If it had been a real phase, polywater would have threatened life just as did the fictional form of ice in Vonnegut's novel.

Helium has different phase diagrams for the two principal isotopes, and both isotopes exhibit liquid-phase allotropy. Figure 5.4 shows the low-temperature phase diagrams of ^{4}He and ^{3}He. The diagram for ^{4}He (the more abundant isotope) shows two different liquid forms, called helium I and helium II. There are two triple points, one for the two liquid forms and the vapor phase, and one for the two liquid forms and the solid phase. The diagram for ^{3}He shows three different liquid phases and three triple points. Neither isotope exhibits coexistence between the solid and the vapor, and the solid phases of both isotopes can exist only at pressures larger than 1 atm. Helium is apparently the only substance that cannot be frozen at 1 atm pressure.

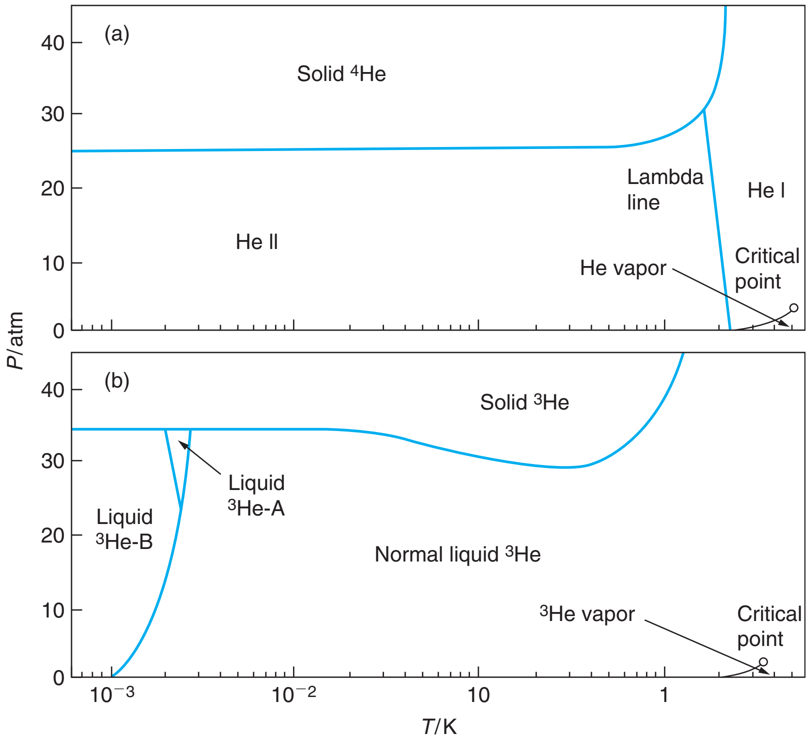

Figure 5.4 The Low-Temperature Phase Diagrams of ^{3}He and ^{4}He. From P. V. E. McClintock, D. J. Meridith, and J. K. Wigmore, *Matter at Low Temperatures*, Wiley, New York, 1984, p. 18.

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[4] E. R. Lippincott *et al.*, *Science*, **164**, 1482 (1969); A. Cherkin, *Nature*, **224**, 1293 (1969).

The Clapeyron Equation

In a one-component system the chemical potential is equal to the molar Gibbs energy, so that if phases I and II of a single substance are at equilibrium

$$G_{\mathrm{m}}^{(\mathrm{I})} = G_{\mathrm{m}}^{(\mathrm{II})} \tag{5.3-2}$$

We impose an infinitesimal change dT in the temperature of the system, maintaining equilibrium during the change. Since P is a function of T, the pressure will change by an amount dP that is determined by dT, and the molar Gibbs energies of the two phases, $G_{\mathrm{m}}^{(\mathrm{I})}$ and $G_{\mathrm{m}}^{(\mathrm{II})}$, will undergo changes that are given in terms of dP and dT by Eq. (4.2-19):

$$dG_{\mathrm{m}}^{(\mathrm{I})} = -S_{\mathrm{m}}^{(\mathrm{I})}dT + V_{\mathrm{m}}^{(\mathrm{I})}dP \tag{5.3-3}$$

$$dG_{\mathrm{m}}^{(\mathrm{II})} = -S_{\mathrm{m}}^{(\mathrm{II})}dT + V_{\mathrm{m}}^{(\mathrm{II})}dP \tag{5.3-4}$$

The molar Gibbs energies remain equal to each other after the change, so that $dG_{m}^{(\mathrm{I})} = dG_{\mathrm{m}}^{(\mathrm{II})}$, and

$$-S_{\mathrm{m}}^{(\mathrm{I})}dT + V_{\mathrm{m}}^{(\mathrm{I})}dP = -S_{\mathrm{m}}^{(\mathrm{II})}dT + V_{\mathrm{m}}^{(\mathrm{II})}dP \tag{5.3-5}$$

The Clapeyron equation is named after Benoit-Pierre-Emile Clapeyron, 1799–1864, a French engineer who translated Carnot's cycle into the language of calculus.

Nonrigorously "dividing" this equation by dT, we obtain the *Clapeyron equation*:

$$\boxed{\frac{dP}{dT} = \frac{S_{\mathrm{m}}^{(\mathrm{II})} - S_{\mathrm{m}}^{(\mathrm{I})}}{V_{\mathrm{m}}^{(\mathrm{II})} - V_{\mathrm{m}}^{(\mathrm{I})}} = \frac{\Delta S_{\mathrm{m}}}{\Delta V_{\mathrm{m}}} \quad \text{(Clapeyron equation)}} \tag{5.3-6}$$

For a reversible phase change at constant pressure $\Delta G = 0$, so that

$$\Delta S_{\mathrm{m}} = \frac{\Delta H_{\mathrm{m}}}{T} \tag{5.3-7}$$

The Clapeyron equation can be written

$$\boxed{\frac{dP}{dT} = \frac{\Delta H_{\mathrm{m}}}{T\Delta V_{\mathrm{m}}} \quad \begin{array}{l}\text{(another version of the}\\ \text{Clapeyron equation)}\end{array}} \tag{5.3-8}$$

We can use the Clapeyron equation to interpret the slopes of the curves in a phase diagram.

EXAMPLE 5.2

Interpret the curves in the phase diagram of water, Figure 5.3, that appear to be vertical and horizontal line segments.

Solution

A horizontal line segment corresponds to zero value of dP/dT, implying that $\Delta H_{\mathrm{m}} = 0$ and $\Delta S_{\mathrm{m}} = 0$ for the phase transition. For example, between ice VI and ice VII it appears that $\Delta S_{\mathrm{m}} = 0$ and $\Delta V_{\mathrm{m}} \neq 0$. A vertical line segment corresponds to an undefined (infinite) value for dP/dT, implying that $\Delta V_{\mathrm{m}} = 0$ and $\Delta S_{\mathrm{m}} \neq 0$. For example, ice VII and ice VIII appear to have the same molar volume.

Exercise 5.3

For most substances a solid–liquid coexistence curve has a positive slope, but in the water phase diagram the ice I–liquid curve has a negative slope. Explain this phenomenon. In the ^{3}He phase diagram a horizontal region occurs in the solid–normal liquid curve and a region with a negative slope also occurs. Interpret these two phenomena given that the explanation of the negative slope is not the same as with the liquid water–ice I curve.

In order to have a representation of the function $P = P(T)$ corresponding to the equilibrium of two phases, we integrate the Clapeyron equation written in the form

$$dP = \frac{\Delta S_\mathrm{m}}{\Delta V_\mathrm{m}} dT \qquad (5.3\text{-}9)$$

For a solid–liquid or a solid–solid phase transition, we assume that the phases have nearly constant volume so that ΔV_m is nearly constant. For a sufficiently small range of temperature we can assume that ΔS_m is nearly constant, so that

$$P_2 - P_1 \approx \frac{\Delta S_\mathrm{m}}{\Delta V_\mathrm{m}}(T_2 - T_1) \qquad (5.3\text{-}10a)$$

where P_1 is the pressure corresponding to temperature T_1 and P_2 is the pressure corresponding to temperature T_2. We can also write this equation in the form

$$P = P(T) = P_1 + \frac{\Delta S_\mathrm{m}}{\Delta V_\mathrm{m}}(T - T_1) = P_1 + \frac{\Delta H_\mathrm{m}}{T_1 \Delta V_\mathrm{m}}(T - T_1) \qquad (5.3\text{-}10b)$$

Equation (5.3-10) represents a linear function. In the water phase diagram several of the solid–solid equilibrium curves are nearly linear, and this equation should be an adequate approximation for these curves.

EXAMPLE 5.3

Estimate the pressure on a system of liquid and solid water if the equilibrium melting temperature is equal to −0.100°C. The density of ice is 0.917 g cm^{-3}, the density of liquid water is 1.000 g cm^{-3}, and the molar enthalpy change of fusion is 6008 J mol^{-1}.

Solution

$$\Delta V_\mathrm{m} = (18.01\ \mathrm{g\ mol^{-1}})\left[\frac{1}{1.00\ \mathrm{g\ cm^{-3}}} - \frac{1}{0.917\ \mathrm{g\ cm^{-3}}}\right]\frac{1\ \mathrm{m^3}}{10^6\ \mathrm{cm^3}}$$

$$= -1.63 \times 10^{-6}\mathrm{m^3\ mol^{-1}}$$

$$P_2 - P_1 \approx \frac{6008\ \mathrm{J\ mol^{-1}}}{(273.15\ \mathrm{K})\left(-1.63 \times 10^{-6}\mathrm{m^3\ mol^{-1}}\right)} - 0.100\ \mathrm{K}$$

$$\approx 1.35 \times 10^6\ \mathrm{J\ m^{-3}} = 1.35 \times 10^6\ \mathrm{N\ m^{-2}} = 1.35 \times 10^6\ \mathrm{Pa} = 13.3\ \mathrm{atm}$$

$$P_2 \approx 14.3\ \mathrm{atm}$$

For some solid–liquid or solid–solid phase transitions, it might be a better approximation to assume that the quotient $\Delta H_{\mathrm{m}}/\Delta V_{\mathrm{m}}$ is approximately constant. If so, one can integrate

$$dP = \frac{1}{\Delta V_{\mathrm{m}}}\frac{\Delta H_{\mathrm{m}}}{T}dT$$

to obtain

$$P_2 - P_1 \approx \frac{\Delta H_{\mathrm{m}}}{\Delta V_{\mathrm{m}}}\ln\left(\frac{T_2}{T_1}\right) \quad (\Delta H_{\mathrm{m}}\ \text{constant}) \tag{5.3-11a}$$

or

$$P = P(T) = P_1 + \frac{\Delta H_{\mathrm{m}}}{\Delta V_{\mathrm{m}}}\ln\left(\frac{T}{T_1}\right) \quad (\Delta H_{\mathrm{m}}\ \text{constant}) \tag{5.3-11b}$$

The relation of Eq. (5.3-11) is probably a better approximation than that of Eq. (5.3-10) for large temperature differences. An even better approximation can be obtained by assuming that the heat capacities of the two phases are nearly constant.

Exercise 5.4

Estimate the pressure of the system of Example 5.3, using Eq. (5.3-11) instead of Eq. (5.3-10). Compare the answer with that of Example 5.3 to see whether the assumption of constant ΔH gives different results from the assumption of constant ΔS.

EXAMPLE 5.4

Integrate the Clapeyron equation for a solid–solid or liquid–solid phase transition under the assumption that ΔV_{m} is constant and that $\Delta H_{\mathrm{m}}(T) = \Delta H_{\mathrm{m}}(T_1) + \Delta C_{\mathrm{P,m}}(T - T_1)$ where $\Delta C_{\mathrm{P,m}}$ is constant.

Solution

$$\begin{aligned} P_2 - P_1 &= \frac{1}{\Delta V_{\mathrm{m}}}\int_{T_1}^{T_2}\frac{\Delta H_{\mathrm{m}}(T_1) + \Delta C_{\mathrm{P,m}}(T - T_1)}{T}dT \\ &= \frac{\Delta H_{\mathrm{m}}(T_1)}{\Delta V_{\mathrm{m}}}\ln\left(\frac{T_2}{T_1}\right) + \frac{1}{\Delta V_{\mathrm{m}}}\Delta C_{\mathrm{P}},m(T_2 - T_1) - \frac{1}{\Delta V_{\mathrm{m}}}\Delta C_{\mathrm{P}},mT_1\ln\left(\frac{T_2}{T_1}\right) \end{aligned}$$

Exercise 5.5

Estimate the pressure of the system of Example 5.3, assuming that $\Delta C_{\mathrm{P,m}}$ is constant.

The Clausius–Clapeyron Equation

The Clausius–Clapeyron equation is obtained by integrating the Clapeyron equation in the case that one of the two phases is a vapor (gas) and the other is a *condensed phase* (liquid or solid). We make two approximations: (1) that the vapor is an ideal gas, and (2) that the molar volume of the condensed phase is negligible compared with that of the vapor (gas) phase. These are both good approximations.

Exercise 5.6

Compare the molar volumes of liquid water at 100°C and water vapor at 100°C and 1.00 atm. Assume that the water vapor is an ideal gas.

For a liquid–vapor transition with our approximations

$$\Delta V_{\mathrm{m}} = V_{\mathrm{m}}^{(\mathrm{gas})} - V_{\mathrm{m}}^{(\mathrm{liq})} \approx V_{\mathrm{m}}^{(\mathrm{gas})} \approx \frac{RT}{P} \tag{5.3-12}$$

The same approximation holds for a solid–vapor transition. From Eqs. (5.3-8) and (5.3-12) we obtain the derivative form of the *Clausius–Clapeyron equation*. For a liquid–vapor transition

$$\frac{dP}{dT} = \frac{P\Delta_{\mathrm{vap}}H_{\mathrm{m}}}{RT^2} \tag{5.3-13}$$

where $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ is the molar enthalpy change of vaporization. For sublimation (a solid–vapor transition), $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ is replaced by $\Delta_{\mathrm{sub}}H_{\mathrm{m}}$, the molar enthalpy change of sublimation. We omit the subscript and apply the equation to either case. To obtain a representation of P as a function of T, we need to integrate Eq. (5.3-13). We multiply by dT and divide by P:

$$\frac{1}{P}\frac{dP}{dT}dT = \frac{1}{P}dP = \frac{\Delta H_{\mathrm{m}}}{RT^2}dT \tag{5.3-14}$$

Carrying out a definite integration with the assumption that ΔH_{m} is constant gives the integral form of the Clausius–Clapeyron equation:

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H_{\mathrm{m}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad \text{(Clausius–Clapeyron equation)} \tag{5.3-15}$$

Exercise 5.7

Carry out the steps to obtain Eq. (5.3-15).

EXAMPLE 5.5

Using the vapor pressure values for water at 25°C and 100°C, find the enthalpy change of vaporization of water.

Solution

$$\begin{aligned}\Delta_{\mathrm{vap}}H_{\mathrm{m}} &= \frac{-RT_2T_1}{T_1 - T_2}\ln\left(\frac{P_2}{P_1}\right)\\ &= \frac{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})(373.15\,\mathrm{K})}{75.00\,\mathrm{K}}\ln\left(\frac{760.0\,\mathrm{torr}}{23.756\,\mathrm{torr}}\right)\\ &= 4.274 \times 10^4\,\mathrm{J\,mol^{-1}} = 42.74\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

This value is an average value for the temperature range. As we expect, it is intermediate between the experimental values: 44.0 kJ mol^{-1} at 25°C and 40.7 kJ mol^{-1} at 100°C.

Exercise 5.8

The normal boiling temperature of ethanol is equal to 78.5°C and the molar enthalpy change of vaporization is equal to 40.5 kJ mol^{-1}. Estimate the vapor pressure of ethanol at 100.0°C.

If the enthalpy change of a particular substance is not known, and one wishes to estimate the vapor pressure of a liquid at one temperature from knowledge of the vapor pressure at another temperature, Trouton's rule (see Section 3.4) can be used as an approximation.

EXAMPLE 5.6

The normal boiling temperature of chloroform is 61.7°C. Estimate the vapor pressure of chloroform at 50.0°C, using Trouton's rule to estimate $\Delta_{\text{vap}}H_{\text{m}}$.

Solution

$$\Delta_{\text{vap}}H_{\text{m}} = T\Delta_{\text{vap}}S_{\text{m}} \approx (334.8\ \text{K})(88\ \text{J K}^{-1}\ \text{mol}^{-1}) = 2.95 \times 10^4\ \text{J mol}^{-1}$$

$$\ln\left(\frac{P_2}{P_1}\right) \approx \frac{\Delta_{\text{vap}}H_{\text{m}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{P_2}{1.00\ \text{atm}}\right) \approx -\frac{29500\ \text{J mol}^{-1}}{8.3145\ \text{J K}^{-1}\text{mol}^{-1}}\left(\frac{1}{323.15\ \text{K}} - \frac{1}{334.8\ \text{K}}\right) \approx -0.382$$

$$P_2 = (1.000\ \text{atm})e^{-0.382} = 0.68\ \text{atm} = 520\ \text{torr} = 69\ \text{kPa}$$

Exercise 5.9

Estimate the vapor pressure of chloroform at 50.0°C, using the experimental value of the enthalpy change of vaporization, 31.38 kJ mol^{-1}.

A modified version of the Clausius–Clapeyron equation can be derived using the assumption that $\Delta C_{\text{P,m}}$ is constant:

$$\Delta H_{\text{m}}(T) = \Delta H_{\text{m}}(T_1) + \Delta C_{\text{P,m}}(T - T_1)$$

The derivation of this equation is assigned in Problem 5.27.

The Effect of Total Pressure on the Vapor Pressure

The vapor pressure that we have discussed thus far is measured with no other substances present. We are often interested in the vapor pressure of a liquid that is open to the atmosphere. The other gases in the atmosphere exert an additional pressure on the liquid that modifies its vapor pressure. Small amounts of the other gases dissolve in the liquid, but we neglect these impurities in the liquid. Denote the vapor pressure corresponding to a total pressure of P' by P. From the fundamental fact of phase equilibrium for a one-component system,

$$G_{\text{m}}^{(\text{liq})} = G_{\text{m}}^{(\text{gas})} \qquad (5.3\text{-}16)$$

Let P_1 be the vapor pressure when $P' = P'_1$ and let P_2 be the vapor pressure when $P' = P'_2$. We assume the vapor phase to be ideal and assume the liquid to have a fixed volume. Using Eqs. (4.4-14) and (4.4-4) we can write

$$\Delta G_{\mathrm{m}}^{(\mathrm{liq})} = V_{\mathrm{m}}^{(\mathrm{liq})}(P'_2 - P'_1) = \Delta G_{\mathrm{m}}^{(\mathrm{gas})} = RT\ln(P_2/P_1) \tag{5.3-17}$$

$$\boxed{P_2 = P_1 \exp\left(\frac{V_{\mathrm{m}}^{(\mathrm{liq})}(P'_2 - P'_1)}{RT}\right)} \tag{5.3-18}$$

EXAMPLE 5.7

At 298.15 K, the vapor pressure of water is equal to 23.756 torr if no other substance is present. Calculate the vapor pressure of water if enough air is present in the vapor phase to give a total pressure of 1.000 atm = 760.0 torr.

Solution

The molar volume of water at this temperature is $18.05\ \mathrm{cm^3\ mol^{-1}} = 18.05 \times 10^{-6}\ \mathrm{m^3\ mol^{-1}}$.

$$\frac{V_{\mathrm{m}}^{(\mathrm{liq})}(P'_2 - P'_1)}{RT} = \frac{(18.05 \times 10^{-6}\ \mathrm{m^3\ mol^{-1}})(760.0\ \mathrm{torr} - 23.756\ \mathrm{torr})}{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})}\left(\frac{101325\ \mathrm{Pa}}{760.0\ \mathrm{torr}}\right)$$

$$= 7.14 \times 10^{-4}$$

$$P = (23.756\ \mathrm{torr})\, e^{7.14\times10^{-4}} = 23.772\ \mathrm{torr}$$

For many purposes, this increase in the vapor pressure due to atmospheric pressure is negligible.

Exercise 5.10

Find the total pressure necessary to change the vapor pressure of water by 1.00 torr at 100.0°C.

PROBLEMS

Section 5.3: Phase Equilibria in One-Component Systems

5.9 Estimate the pressure at which diamond and graphite coexist at equilibrium at 298.15 K. The density of diamond is $3.52\ \mathrm{g\ mL^{-1}}$, and that of graphite is $2.25\ \mathrm{g\ mL^{-1}}$. The molar Gibbs energy of diamond is higher than that of graphite by $2.90\ \mathrm{kJ\ mol^{-1}}$ at 298.15 K. Assume that each phase has constant density. How accurate do you think this assumption is?

5.10 The density of rhombic sulfur at 20°C is $2.07\ \mathrm{g\ cm^{-3}}$, and the density of monoclinic sulfur at 20°C is $1.957\ \mathrm{g\ cm^{-3}}$. Assume that you can use these values at 25°C. The Gibbs energy of formation of monoclinic sulfur is $0.096\ \mathrm{kJ\ mol^{-1}}$, and the Gibbs energy of formation of rhombic sulfur is equal to zero by definition.

a. Estimate ΔG for producing 1.000 mol of monoclinic sulfur from rhombic sulfur at 101.0 bar and 298.15 K. Assume that ΔV_{m} is independent of pressure.

b. Is there a pressure at which the two forms could coexist at equilibrium at 298.15 K?

5.11 For the equilibrium between solid and liquid helium the derivative dP/dT approaches zero as the temperature approaches zero. What does this indicate?

5.12 **a.** The vapor pressure of solid water (ice I) is equal to 2.149 torr at $-10°C$ and to 4.579 torr at 0°C. Find the average enthalpy change of sublimation of ice for this range of temperature.

b. The vapor pressure of water is equal to 23.756 torr at 25°C. Calculate the average enthalpy change of vaporization for the range of temperature from 0°C to 25°C.

c. Find the enthalpy change of fusion of water.

5.13 The triple point of ammonia is at 196.2 K and 49.42 torr. The molar enthalpy change of vaporization is equal to 24.65 kJ mol^{-1} at this temperature.

a. Find the normal boiling temperature of ammonia.

b. The actual boiling temperature is $-33°C$. Find the average value of the molar enthalpy change of vaporization for the range between the triple point and the normal boiling temperature.

5.14 Find the slope of the solid–liquid coexistence curve at the triple point in the water phase diagram.

5.15 **a.** The vapor pressure of solid carbon dioxide is equal to 34.63 torr at $-110.0°C$ and is equal to 672.2 torr at $-80.0°C$. Find the enthalpy change of sublimation for carbon dioxide.

b. Find the temperature at which the vapor pressure of solid carbon dioxide is equal to 760.0 torr (the normal sublimation temperature).

5.16 Mercury(II) sulfide, HgS, occurs in two crystalline forms, called "red" and "black." For the conversion of the red form to the black form at 525°C, $\Delta G° = -0.157$ kJ mol^{-1} and $\Delta H° = 4.184$ kJ mol^{-1}.

a. Assuming that $\Delta H°$ is independent of temperature, find the temperature at which the two forms can coexist at equilibrium at 1.000 bar. Which is more stable above this temperature? Which is more stable below this temperature?

b. The densities are 8.1 g cm^{-1} for the red form and 7.7 g cm^{-1} for the black form. Find the pressure at which the two forms can coexist at equilibrium at 525°C. Which form is more stable above this pressure? Which is more stable below this pressure?

5.17 **a.** Find the pressure needed in an autoclave or pressure cooker to attain a temperature of 120.0°C with liquid water and water vapor both present. Express the pressure in atmospheres and in psi(gauge), which means the pressure in excess of barometric pressure, measured in pounds per square inch. Assume that the barometric pressure is 1.00 atm, which is the same as 14.7 pounds per square inch.

b. Find the freezing temperature of water at a pressure equal to the pressure of part a.

5.18 The enthalpy change of vaporization of ethanol at its normal boiling temperature of 78.5°C is 40.48 kJ mol^{-1}.

a. Find the temperature at which the vapor pressure is equal to 755.0 torr.

b. Find the pressure that must be exerted on the liquid phase to make the vapor pressure equal to 760.0 torr at the temperature of part a.

5.19 Estimate the boiling temperature of water at an altitude of 1.00 mile, the altitude of Denver, Colorado. Assume that the atmosphere is at equilibrium at a temperature of 20°C and use the Boltzmann distribution to estimate the barometric pressure. State any other assumptions.

5.20 The vapor pressure of solid p-dibromobenzene is well represented from $-45°C$ to 74°C by

$$\log_{10}(P/\text{torr}) = -\frac{3850}{T} + 8.80$$

where T is the Kelvin temperature. Find $\Delta_{\text{sub}}H_{\text{m}}$ and $\Delta_{\text{sub}}S_{\text{m}}$ at 15°C. Assume the vapor to be ideal and the molar volume of the solid to be negligible compared to that of the liquid.

5.21 **a.** The vapor pressure of water at 50.00°C is equal to 92.51 torr. Find the average value of the enthalpy change of vaporization between this temperature and the normal boiling temperature.

b. Find the value of the vapor pressure of water at 65°C.

5.22 Estimate the boiling temperature of water at an altitude of 8.5 km, the altitude of Mount Everest. Assume that the atmosphere is at equilibrium at a temperature of 0°C and use the Boltzmann distribution to estimate the barometric pressure. State any other assumptions.

5.23 At $-78.5°\text{C}$, the vapor pressure of solid carbon dioxide is equal to 760 torr. The triple point is at 216.55 K and 5.112 atm. Find the average enthalpy change of sublimation.

5.24 The normal boiling point of oxygen is 90.18 K. The vapor pressure at 100.0 K is equal to 2.509 atm. Find the enthalpy change of vaporization.

5.25 The following data give the vapor pressure of liquid aluminum as a function of temperature:

T/K	1557	1760	1908	2022	2220	2329
P/torr	1	10	40	100	400	760

Using a linear least-squares procedure, find the enthalpy change of vaporization of aluminum.

5.26 Find the pressure necessary to lower the freezing temperature of water to $-10.00°\text{C}$.

5.27 **a.** Derive a modified version of the Clausius–Clapeyron equation using the relation

$$\Delta H_\text{m}(T) = \Delta H_\text{m}(T_1) + \Delta C_{P,\text{m}}[T - T_1]$$

where $\Delta C_{P,\text{m}}$ is assumed to be constant.

b. Using data from Table A.8 and the vapor pressure of water at 25.0°C, equal to 23.756 torr, calculate the vapor pressure of water at 50.0°C using the modified Clausius–Clapeyron equation of part a and using the unmodified form of Eq. (5.3-15). Compare both results with the experimental value, 92.5 torr.

5.28 Find the pressure on the liquid phase that can raise the vapor pressure of water by 1.00% at 25°C.

5.29 Find the vapor pressure of water at 60.00°C, assuming that the heat capacities of liquid and gaseous water are constant between 25°C and 60°C and given that at 25°C the vapor pressure is 23.756 torr. Compare your answer with the experimental value of 149.38 torr.

5.30 The average enthalpy change of vaporization of benzene between room temperature and the normal boiling temperature is $34.085\ \text{kJ mol}^{-1}$. The vapor pressure at 26.1°C is 100.0 torr.

a. Find the normal boiling temperature. Compare with the correct value, 80.1°C. State any assumptions.

b. Find the entropy change of vaporization at the normal boiling temperature. Compare with the prediction of Trouton's rule. State any assumptions.

5.4 The Gibbs Energy and Phase Transitions

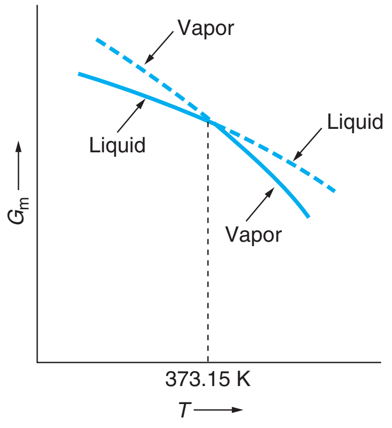


Figure 5.5 The Molar Gibbs Energy of Water as a Function of Temperature Near the Liquid–Vapor Phase Transition (Schematic).

We ask the following question: Why is water a liquid with a molar volume of $18\ \text{mL mol}^{-1}$ at 1.000 atm and 373.14 K, but a vapor with a molar volume of $30\ \text{L mol}^{-1}$ at 1.000 atm and 373.16 K? Why should such a small change in temperature make such a large change in structure when we generally expect a small cause to produce a small effect? The thermodynamic answer to this question comes from the fact that at equilibrium at constant T and P, the Gibbs energy of the system must be at a minimum.

Figure 5.5 shows schematically the molar Gibbs energy (chemical potential) of liquid and gaseous water as a function of temperature at 1.000 atm pressure. In order to construct Figure 5.5, we have used Eq. (4.2-20):

$$\left(\frac{\partial G_\text{m}}{\partial T}\right)_P = -S_\text{m} \tag{5.4-1}$$

The molar entropy of the water vapor is greater than the molar entropy of the liquid water, so that the tangent to the vapor curve in Figure 5.5 has a more negative slope than that of the liquid curve. The temperature at which the curves intersect is the temperature of phase coexistence at this pressure, since this is the temperature at which the values of the molar Gibbs energy in the two phases are equal. We have continued the curves past the coexistence point with broken curves to represent metastable states. If one phase has a more negative value of the molar Gibbs energy than the other phase,

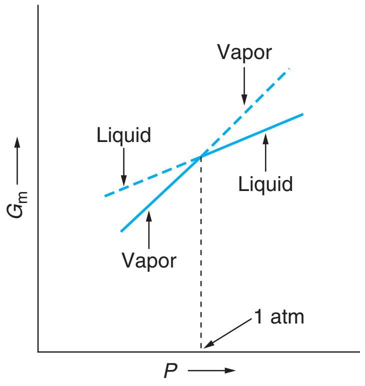


Figure 5.6 The Molar Gibbs Energy of Water as a Function of Pressure Near the Liquid–Vapor Phase Transition (Schematic).

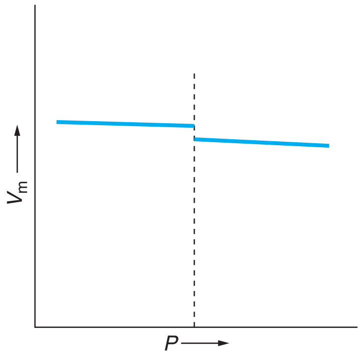


Figure 5.7 The Molar Volume as a Function of Pressure at a First-Order Phase Transition (Schematic).

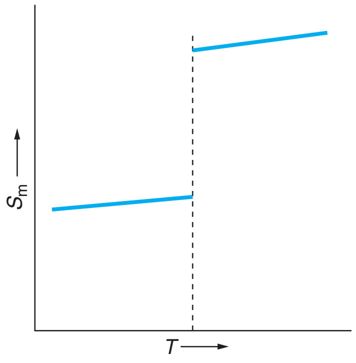


Figure 5.8 The Molar Entropy as a Function of Temperature at a First-Order Phase Transition (Schematic).

it is the equilibrium phase. Above the coexistence temperature, the vapor curve lies lower, so that the vapor is the stable phase, and the *superheated* liquid is metastable. Below the normal boiling temperature, the liquid is stable and the *supercooled vapor* is metastable. Near the coexistence temperature a small change in temperature can change the equilibrium state of the substance from gas to liquid or from liquid to gas as it moves from one curve to the other.

We can also consider the fact that the molar Gibbs energy is given by

$$G_{\mathrm{m}} = H_{\mathrm{m}} - TS_{\mathrm{m}} \tag{5.4-2}$$

At constant temperature, we can minimize G_{m} either by lowering H_{m} or by raising S_{m}. The second term is more important at high temperature than at low temperature since it is proportional to T. The phase of higher molar entropy is the more stable phase at high temperature and the phase of lower molar enthalpy is the more stable phase at low temperature.

Figure 5.6 shows schematically the molar Gibbs energy of liquid and gaseous water as a function of pressure at constant temperature. The two curves intersect at the equilibrium pressure for the phase transition at this temperature. The slope of the tangent to the curve is given by Eq. (4.2-21):

$$\left(\frac{\partial G_{\mathrm{m}}}{\partial P}\right)_T = V_{\mathrm{m}} \tag{5.4-3}$$

The molar volume of the vapor is greater than that of the liquid phase, so that the tangent to the vapor curve has a more positive slope than that of the liquid curve. At any pressure, the lower curve represents the equilibrium phase. If the temperature is 373.15 K, the liquid is the stable phase at a pressure greater than 1.000 atm, but at a pressure less than 1.000 atm the vapor is the stable phase.

It is also possible to construct schematic graphs like those of Figures 5.5 and 5.6 for solid–liquid, solid–solid, and solid–vapor phase transitions.

Exercise 5.11

Sketch rough graphs representing the molar Gibbs energy of water as a function of the temperature and as a function of the pressure in the vicinity of the solid–liquid phase transition. Liquid water has a smaller molar volume than solid water but a larger molar entropy.

Classification of Phase Transitions

Phase transitions are classified according to the partial derivatives of the Gibbs energy. Ordinary phase transitions such as vaporizations, freezings, and so on, are called *first-order phase transitions*, which means that at least one of the first derivatives $(\partial G_{\mathrm{m}}/\partial T)_P$ or $(\partial G_{\mathrm{m}}/\partial P)_T$ is discontinuous at the phase transition. In most first-order transitions, both of these derivatives are discontinuous. From Chapter 4 we know that $(\partial G_{\mathrm{m}}/\partial T)_P$ is equal to $-S_{\mathrm{m}}$ and that $(\partial G_{\mathrm{m}}/\partial P)_T$ is equal to V_{m}. Figure 5.7 shows schematically the molar volume as a function of pressure as it would appear for a solid–liquid or a solid–solid transition. Figure 5.8 shows schematically the molar entropy as a function of temperature as it would appear for a liquid–vapor transition.

Consider the second derivatives of the Gibbs energy in the vicinity of a first-order phase transition. Equations (4.2-20) and (4.3-15) give

$$\left(\frac{\partial^2 G_\text{m}}{\partial T^2}\right)_P = -\left(\frac{\partial S_\text{m}}{\partial T}\right)_P = -\frac{C_\text{P,m}}{T} \tag{5.4-4}$$

Equations (4.2-21) and (1.2-14) give

$$\left(\frac{\partial^2 G_\text{m}}{\partial P^2}\right)_T = \left(\frac{\partial V_\text{m}}{\partial P}\right)_T = -V_\text{m}\kappa_\text{T} \tag{5.4-5}$$

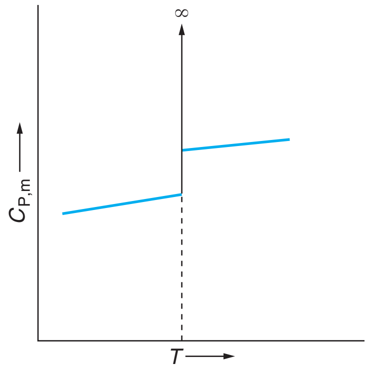


Figure 5.9 The Constant-Pressure Heat Capacity as a Function of Temperature at a First-Order Phase Transition. Because of the discontinuity in the entropy as a function of temperature, there is an infinite spike in the heat capacity at the phase transition.

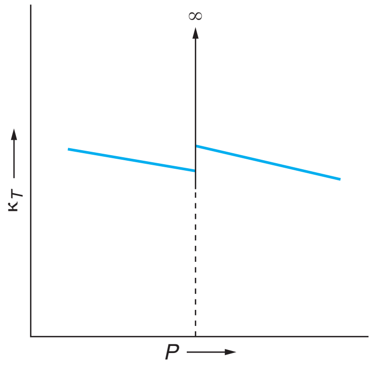


Figure 5.10 The Isothermal Compressibility as a Function of Pressure at a First-Order Phase Transition (Schematic). Because of the discontinuity in the molar volume as a function of pressure, there is an infinite spike in the compressibility at the phase transition.

where $C_\text{P,m}$ is the molar heat capacity at constant pressure and κ_T is the isothermal compressibility. If S_m has a discontinuity, then $C_\text{P,m}$ must have a *singularity* (a point at which it becomes infinite) at the phase transition. If V_m has a discontinuity, then κ_T must have a singularity. Figure 5.9 schematically shows $C_\text{P,m}$ as a function of T in the vicinity of a first-order phase transition, and Figure 5.10 shows κ_T as a function of P in the vicinity of a first-order phase transition. The upward-pointing arrow indicates an infinite value at a single point. The infinite value of the heat capacity at the first-order phase transition corresponds to the fact that a nonzero amount of heat produces no change in the temperature as one phase is converted to the other. The infinite value of the compressibility corresponds to the fact that a finite volume change occurs as one phase is converted to the other with no change in the pressure.

There are phase transitions that are not first-order transitions. A *second-order phase transition* is one in which both of the first derivatives of the Gibbs energy are continuous but at least one of the second derivatives is discontinuous. Figure 5.11 schematically shows $C_\text{P,m}$ as a function of T in the vicinity of a second order phase transition, and Figure 5.12 shows κ_T as a function of P in the vicinity of a second-order phase transition. Neither the compressibility nor the heat capacity becomes infinite, although both quantities have discontinuities in these figures. The molar entropies of the two phases must be equal to each other and the molar volumes of the two phases must be equal to each other.

The order of a phase transition must be determined experimentally. To establish whether a phase transition is second order, careful measurements of the compressibility and the heat capacity must be made in order to determine whether these quantities diverge (become infinite) at the phase transition. Second-order phase transitions are not common. The transition between normal and superconducting states is said to be the only well-established second-order transition.

There are some phase transitions that do not fall either into the first-order or second-order category. These include paramagnetic-to-ferromagnetic transitions in some magnetic materials and a type of transition that occurs in certain solid metal alloys that is called an *order–disorder transition*. Beta brass, which is a nearly equimolar mixture of copper and zinc, has a low-temperature equilibrium state in which every copper atom in the crystal lattice is located at the center of a cubic unit cell, surrounded by eight zinc atoms at the corners of the cell. At 742 K, an order-disorder transition occurs from the ordered low-temperature state to a disordered high-temperature state in which the atoms are randomly mixed in a single crystal lattice. The phase transition between normal liquid helium and liquid helium II was once said to be a second-order transition. Later experiments indicated that the heat capacity of liquid helium appears to approach infinity at the transition, so that the transition is not second

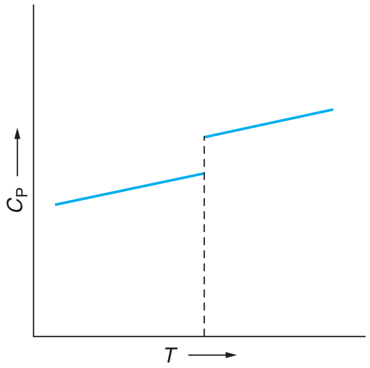


Figure 5.11 The Constant-Pressure Heat Capacity as a Function of Temperature at a Second-Order Phase Transition (Schematic).

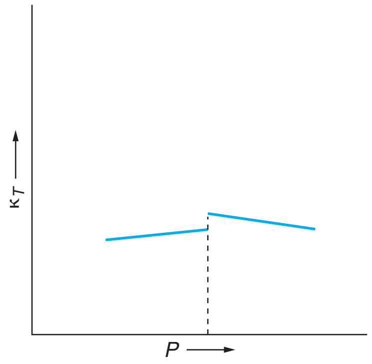


Figure 5.12 The Isothermal Compressibility as a Function of Pressure at a Second-Order Phase Transition (Schematic).

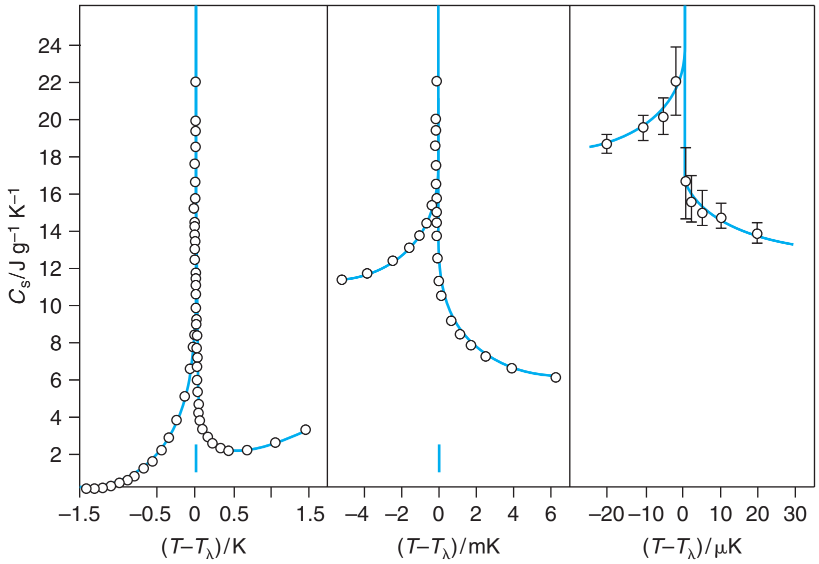


Figure 5.13 The Heat Capacity of Helium Near the Lambda Transition. The heat capacity appears to become infinite, as in a first-order phase transition, but it rises smoothly instead of showing a spike at one point as does a first-order phase transition.

order. The heat capacity rises smoothly toward infinity instead of rising abruptly as in a first-order transition. A plot of the heat capacity versus the temperature resembles the Greek letter lambda as shown in Figure 5.13, and the transition is called a *lambda transition*. The order-disorder transition in beta brass is also a lambda transition.

The Critical Point of a Liquid–Vapor Transition

The tangents to the two curves in Figure 5.6 represent the molar volumes. In the case of a liquid–vapor transition the two molar volumes become more and more nearly equal to each other as the temperature is increased toward the critical temperature. The tangents to the curves approach each other more and more closely until there is only one curve at the critical temperature. The discontinuity in the graph of the molar volume in Figure 5.7 gradually shrinks to zero at the critical temperature. However, there is a vertical tangent at the critical pressure as schematically shown in Figure 5.14. The isothermal compressibility is infinite, but it does not suddenly jump to an infinite value at one point as it does below the critical temperature. It rises smoothly (and steeply) toward an infinite value at the critical point.

At the critical point, the two curves representing S_m in Figure 5.8 also merge into a single curve. The molar entropy of the liquid and the molar entropy of the gas phase approach each other. The discontinuity in the curve of Figure 5.8 shrinks to zero, but there is a vertical tangent at the critical point. The heat capacity rises smoothly and steeply toward an infinite value. Its behavior is similar to that of the heat capacity at a lambda transition.

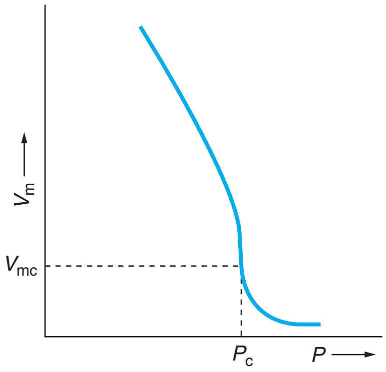


Figure 5.14 The Molar Volume Near a Liquid–Vapor Critical Point.

EXAMPLE 5.8

Estimate the critical temperature of water by finding the temperature at which $\Delta_{\text{vap}}H_{\text{m}}$ vanishes. Assume that $\Delta C_{P,\text{m}}$ is temperature-independent so that

$$\Delta_{\text{vap}}H_{\text{m}}(T) = \Delta_{\text{vap}}H_{\text{m}}(T_1) + \Delta C_{P,\text{m}}(T - T_1)$$

Let $T_1 = 373.15\text{ K}$ and use the value of $\Delta C_{P,\text{m}}$ that applies at 500 K. Compare your answer with the correct value, 647.2 K, and explain any significant difference.

Solution

$$\Delta_{\text{vap}}H_{\text{m}}(T_1) + \Delta C_{P,\text{m}}(T - T_1) = 40669\text{ J mol}^{-1} + (-41.761\text{ J K}^{-1}\text{mol}^{-1}) \times (T - 373.15\text{ K})$$

We set this expression equal to zero: and divide by 1 J mol^{-1}

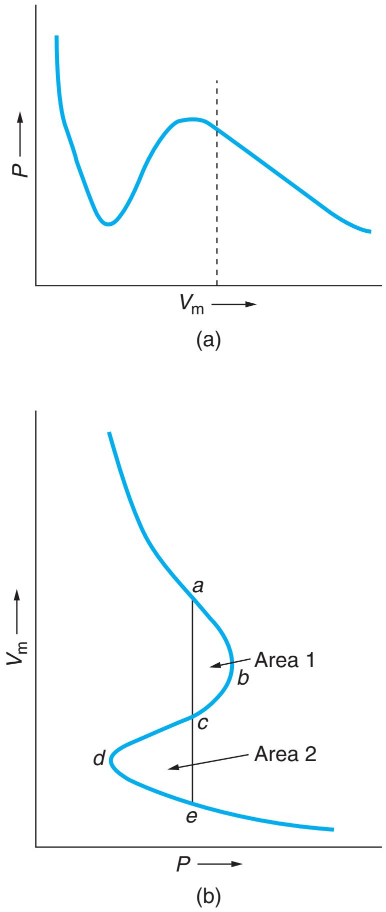
$$0 = 40699 - (41.761\text{ K}^{-1})T + 15583$$

$$T = \frac{56252}{41.761\text{ K}^{-1}} = 1347\text{ K}$$

The agreement is poor, probably because the assumption that $\Delta C_{P,\text{m}}$ is constant is poor.

Exercise 5.12

Estimate the critical temperature of water by finding the temperature at which $\Delta_{\text{vap}}S_{\text{m}}$ vanishes. Assume that $\Delta C_{P,\text{m}}$ is temperature-independent.



(a)

(b)

Figure 5.15 The Pressure and the Molar Volume for a Fluid Obeying an Equation of State Such as the van der Waals Equation (Schematic). (a) The pressure as a function of molar volume. (b) The molar volume as a function of pressure.

The Maxwell Equal-Area Construction

As shown in Figures 1.7 and 1.8, a single surface represents the pressure of both the liquid and the gas as a function of T and V_{m}. A completely successful equation of state would represent both phases, including the area of tie lines below the critical point. Figure 5.15a schematically shows the pressure as a function of molar volume at a fixed subcritical temperature as described by an approximate equation of state such as the van der Waals equation. Instead of the tie line that actually describes the behavior of the fluid as in Figure 1.4, there is an S-shaped portion of the curve (a "loop").

If we assume that the liquid portion of the curve and the gas part of the curve represent the behavior of the system to some approximation, we can replace the "loop" by a tie-line segment that connects the points at which the liquid and the solid have the same value of the molar Gibbs energy. To do this we exchange the roles of the variables in Figure 5.15a to obtain Figure 5.15b. We want to find two points, labeled a and e, that correspond to equal values of the molar Gibbs energy (chemical potential) in the two phases.

Since the curve corresponds to fixed temperature, the $-S_{\text{m}}dT$ term in dG_{m} vanishes, and

$$d\mu = dG_{\text{m}} = V_{\text{m}}dP \quad \text{(constant temperature)} \tag{5.4-6}$$

In order to have the molar Gibbs energy at points a and e equal to each other, the integral of dG_{m} along the curve from point a to point e must vanish. We write this integral in the following way since the curve does not represent a single-valued function:

$$G_{\mathrm{m}}(e) - G_{\mathrm{m}}(a) = 0 = \int_{P_a}^{P_b} V_{\mathrm{m}} dP + \int_{P_b}^{P_c} V_{\mathrm{m}} dP + \int_{P_c}^{P_d} V_{\mathrm{m}} dP + \int_{P_d}^{P_e} V_{\mathrm{m}} dP \quad (5.4\text{-}7)$$

The area to the right of the vertical line segment between points a and c is called area 1 and is equal to

$$\text{area 1} = \int_{P_a}^{P_b} V_{\mathrm{m}} dP - \int_{P_c}^{P_b} V_{\mathrm{m}} dP = \int_{P_a}^{P_b} V_{\mathrm{m}} dP + \int_{P_b}^{P_c} V_{\mathrm{m}} dP \quad (5.4\text{-}8)$$

The area to the left of the line segment between points c and e is called area 2 and is equal to

$$\text{area 2} = \int_{P_d}^{P_c} V_{\mathrm{m}} dP - \int_{P_d}^{P_e} V_{\mathrm{m}} dP = -\int_{P_c}^{P_d} V_{\mathrm{m}} dP - \int_{P_d}^{P_e} V_{\mathrm{m}} dP \quad (5.4\text{-}9)$$

This construction is named for the same James Clerk Maxwell who devised the Maxwell equations of electrodynamics and the Maxwell relations of thermodynamics and contributed to the founding of gas kinetic theory.

Comparison of Eq. (5.4-7) with Eqs. (5.4-8) and (5.4-9) shows that when $G_{\mathrm{m}}(e) - G_{\mathrm{m}}(a) = 0$, area 1 and area 2 are equal to each other. The adjustment of the locations of points a and e to make these areas equal gives a tie line between the coexisting liquid and gas states and is known as the *Maxwell equal-area construction*.

The van der Waals equation of state provides a qualitatively correct description of the liquid–vapor transition when the equal-area construction is applied to it. The other common equations of state provide varying degrees of accuracy in describing the liquid–vapor transition when the equal-area construction is applied to them. Gibbons and Laughton obtained good agreement with experiment using their modification of the Redlich–Kwong equation of state (see Table 1.1).[5]

The Temperature Dependence of the Gibbs Energy Change

The temperature derivative of the Gibbs energy is given by Eq. (4.2-20):

$$\left(\frac{\partial G}{\partial T}\right)_{P,n} = -S \quad (5.4\text{-}10)$$

However, we cannot use this equation to calculate a value of ΔG for a temperature change because the value of the entropy can always have an arbitrary constant added to it without any physical effect. We can write an analogous equation for the temperature dependence of ΔG for an isothermal process:

$$\left(\frac{\partial \Delta G}{\partial T}\right)_{P,n} = -\Delta S \quad (5.4\text{-}11)$$

The interpretation of this equation is that although ΔG pertains to an isothermal process, it gives the comparison of isothermal processes at different temperatures.

A useful version of this equation can be written

$$\left(\frac{\partial(\Delta G/T)}{\partial T}\right)_{P,n} = \frac{1}{T}\left(\frac{\partial \Delta G}{\partial T}\right)_{P,n} - \frac{\Delta G}{T^2} = -\frac{\Delta S}{T} - \frac{\Delta G}{T^2} = -\frac{\Delta H}{T^2} \quad (5.4\text{-}12)$$

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[5] R. M. Gibbons and A. P. Laughton, *J. Chem. Soc., Faraday Trans. 2*, **80**, 1019 (1984).

We can use this equation to calculate ΔG for an isothermal process at temperature T_2 from its value at temperature T_1. We multiply by dT and integrate from T_1 to T_2:

$$\int_{T_1}^{T_2} \left(\frac{\partial(\Delta G/T)}{\partial T}\right)_{P,n} dT = -\int_{T_1}^{T_2} \frac{\Delta H}{T^2} dT \tag{5.4-13}$$

If ΔH is temperature-independent,

$$\frac{\Delta G(T_2)}{T^2} - \frac{\Delta G(T1)}{T_1} = \Delta H\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{5.4-14}$$

EXAMPLE 5.9

The Gibbs energy of formation of monoclinic sulfur at 298.15 K is 0.096 kJ mol^{-1}, and the Gibbs energy of formation of rhombic sulfur is equal to zero by definition. The enthalpy change of formation of monoclinic sulfur at 298.15 K is 0.33 kJ mol^{-1}.

a. Assume that ΔH is temperature-independent and find the Gibbs energy to form monoclinic sulfur from rhombic sulfur at 500.0 K.

b. Can there be a temperature at which the rhombic and monoclinic forms of sulfur can be at equilibrium at 1 bar pressure?

Solution

a. From Eq. (5.4-14)

$$\frac{\Delta G^\circ(500.0\,\mathrm{K})}{500.0\,\mathrm{K}} = \frac{96\,\mathrm{J\,mol^{-1}}}{298.15\,\mathrm{K}} + \frac{330\,\mathrm{J\,mol^{-1}}}{8.3145\,\mathrm{J\,K^{-1}mol^{-1}}}\left(\frac{1}{500.0\,\mathrm{K}} - \frac{1}{298.15\,\mathrm{K}}\right)$$

$$= 0.322\,\mathrm{J\,K^{-1}\,mol^{-1}} - 0.0537\,\mathrm{J\,K^{-1}\,mol^{-1}} = 0.268\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

$$\Delta G^\circ(500.0\,\mathrm{K}) = (0.268\,\mathrm{J\,K^{-1}mol^{-1}})(500.0\,\mathrm{K}) = 134\,\mathrm{J\,mol^{-1}} = 0.134\,\mathrm{kJ\,mol^{-1}}$$

b. Since ΔG° becomes more positive as the temperature increases, no higher temperature can be found such that the two phases will equilibrate. Since T cannot be negative, no lower temperature can be found, because the rate of change of ΔG with temperature is too small to reach equilibration at a positive value of T.

PROBLEMS

Section 5.4: The Gibbs Energy and Phase Transitions

5.31 1.000 mol of ammonia is vaporized at a constant pressure of 1.000 atm and a constant temperature of 240 K, the normal boiling temperature. The enthalpy change of vaporization at this temperature is 25.11 kJ mol^{-1}.

a. Find ΔG, ΔS, w, and q.

b. The gaseous ammonia is expanded from 1.000 atm to 0.100 atm. Find ΔG, ΔS, w, and q.

5.32 Construct an accurate graph of the standard-state molar entropy of water as a function of temperature from 298.15 K to 398.15 K at a constant pressure of 1.000 atm, using data in Tables A.7 and A.8 of the appendix. Assume that the heat capacities are constant.

5.33 Construct an accurate graph of the molar Gibbs energy of water as a function of pressure from 0.100 atm to 1.900 atm at a constant temperature of 273.15 K. Since the zero of the Gibbs energy is arbitrary, let the molar Gibbs energy of the solid and liquid at 1.000 atm equal zero.

5.34 **a.** Write a computer program to carry out the Maxwell equal-area construction, assuming the van der Waals equation of state. It is probably best to choose a trial value of the coexistence pressure and to calculate the two areas, and then to carry out successive approximations until the areas are as nearly equal as you desire.

b. Using the equal-area construction, find the vapor pressure of water at 100.0°C according to the van der Waals equation of state.

c. Find the molar volumes of the coexisting liquid and vapor phases of water at 100.0°C according to the van der Waals equation of state and the equal-area construction.

d. Find the value of the compression factor, Z, for water vapor in coexistence with liquid water at 100.0°C.

5.35 Find the difference in the slopes of the two tangent lines at the cusp in each of the following graphs for pure water:

a. A graph of G_m as a function of T at 1.000 atm in the vicinity of 0.0°C.

b. A graph of G_m as a function of P at 273.15 K in the vicinity of 1.000 atm.

c. A graph of G_m as a function of T at 1.000 atm in the vicinity of 100.0°C.

d. A graph of G_m as a function of P at 373.15 K in the vicinity of 1.000 atm.

5.5 Surfaces in One-Component Systems

Many of the thermodynamic equations that we have presented are valid only in the case that surface contributions to the energy can be neglected. For example, we assumed that the thermodynamic energy of a one-component one-phase fluid system depended on T, V, and n, but not on the surface area. Although this is ordinarily an excellent approximation, there is a significant surface contribution to the energy of a liquid in the case of a small droplet or a liquid in a small capillary tube.

The Energy Attributed to a Surface

The surface contribution to the energy of a liquid is primarily due to intermolecular attractions. Since molecules at the surface of the liquid have fewer nearest neighbors than molecules in the bulk (interior) of the liquid, they have a different average potential energy than molecules in the bulk.

EXAMPLE 5.10

For liquid carbon tetrachloride in contact with its vapor, estimate the surface energy per unit area, using the enthalpy change of vaporization to estimate the net attractive energy of the molecules.

Solution

In a solid lattice, carbon tetrachloride molecules can pack together like spheres and are surrounded by 12 nearest-neighbor molecules. Since the liquid is somewhat disordered and is less dense than the solid, we assume that each molecule in the interior of the liquid has approximately 10 nearest neighbors. Molecules at the surface of the liquid have no nearest neighbors on the vapor side, and we assume that a molecule at the surface has approximately seven nearest neighbors.

The molar enthalpy change of vaporization of CCl_4 at 20°C is equal to 33.77 kJ mol^{-1}, so that the molar energy change of vaporization is

$$\begin{aligned}\Delta_{\text{vap}}U_{\text{m}} &= \Delta_{\text{vap}}H_{\text{m}} - \Delta(PV) \approx \Delta_{\text{vap}}H_{\text{m}} - RT \\ &= 33770\ \text{J mol}^{-1} - (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(293\ \text{K}) = 31330\ \text{J mol}^{-1}\end{aligned}$$

The energy change of vaporization per molecule is

$$\frac{31330\,\text{J mol}^{-1}}{6.022\times 10^{23}\,\text{mol}^{-1}} = 5.203\times 10^{-20}\ \text{J}$$

We assume that this energy is the amount by which the potential energy of the molecule is increased when it breaks free from its neighbors and enters the vapor phase, where attractions to other molecules are negligible. When a molecule is brought to the surface, it gains energy roughly equal to 30% of this value, since it on the average loses approximately 3 of its 10 nearest neighbors. The surface energy per molecule is thus

$$(\text{surface energy per molecule}) \approx (6.203\times 10^{-20}\ \text{J})(0.30) = 1.6\times 10^{-20}\ \text{J}$$

The density of CCl_4 at 20°C is equal to 1.594 g cm^{-3}, and its molar mass is 153.82 g mol^{-1}. This gives a molar volume of 96.5 cm^3 mol^{-1}, and a volume per molecule of

$$(\text{volume per molecule}) = \frac{96.5\times 10^{-6}\ \text{m}^3\ \text{mol}^{-1}}{6.022\times 10^{23}\ \text{mol}^{-1}} = 1.60\times 10^{-28}\ \text{m}^3$$

A sphere with this volume has radius equal to 3.4×10^{-10} m. We assume that on the average each molecule on the surface occupies an area equal to the area of a square 6.8×10^{-10} m on a side:

$$\text{area per molecule} = (6.8\times 10^{-10}\ \text{m})^2 = 4.6\times 10^{-19}\ \text{m}^2$$

The surface energy per square meter is denoted by γ and is approximately equal to

$$\gamma \approx \frac{1.56\times 10^{-20}\,\text{J}}{3.6\times 10^{-19}\,\text{m}^2} = 0.043\,\text{J m}^{-2}$$

This value agrees only roughly with the experimental value at 20°C, 0.02695 J m^{-2}.

Exercise 5.13

a. Estimate the surface energy per square meter for liquid water, assuming that the principal intermolecular force is hydrogen bonding, with a bond energy of 20 kJ mol^{-1} for each hydrogen bond. Assume that a molecule in the interior of a sample of liquid water has four hydrogen-bonded nearest neighbors and that a molecule in the surface has three. Remember that each hydrogen bond involves two atoms. Compare your result with the experimental value at 25°C, 0.072 J m^{-2}.

b. For 1.00 mol of liquid water contained in a beaker with diameter 3.00 cm, find the ratio of the surface energy of the upper surface to the energy required to vaporize 1.00 mol of water.

c. Explain why gases have negligible surface energy.

In a system consisting of water and diethyl ether near room temperature, there is a liquid phase that is mostly water, a liquid phase that is mostly diethyl ether, and a vapor phase. There is one surface between the two liquid phases and one surface between the upper liquid phase and the vapor phase. In addition, each phase has a surface with the container. The energy, Gibbs energy, and other energy-related functions depend separately on the area of each of these surfaces. The most important type of surface in this system is the liquid–vapor surface. In many cases a system will have only one significant surface. A liquid droplet suspended in a gas has only one surface. If a system has only one component and one significant surface the energy is a function of T, P, $\mathscr{A}$ (the surface area), and n, so that

$$dU = TdS - PdV + \gamma d\mathscr{A} + \mu dn \tag{5.5-1}$$

where

$$\gamma = \left(\frac{\partial U}{\partial \mathscr{A}}\right)_{S,V,n} \tag{5.5-2}$$

We can also write

$$\begin{aligned} dG &= dU + PdV + VdP - SdT - TdS \\ &= -SdT + VdP + \gamma d\mathscr{A} + \mu dn \end{aligned} \tag{5.5-3}$$

so that

$$\gamma = \left(\frac{\partial G}{\partial \mathscr{A}}\right)_{T,P,n} \tag{5.5-4}$$

The quantity γ can be interpreted as the energy per unit area at constant S and V or as the Gibbs energy per unit area at constant T and P. Work to create surface area is an example of *net work* as discussed in Section 4.1. From Eq. (4.1-31) we recognize γ as equal to the reversible work per unit area required to produce new surface at constant T and P. In the case of a liquid–vapor surface, we identify it with the surface energy calculated in Example 5.10 or Exercise 5.13.

Surface Tension

We now show that the surface energy corresponds to a force per unit length. The system depicted in Figure 5.16 has a liquid phase in contact with a vapor phase. There is a rectangular wire frame that protrudes from the surface of the liquid with a length equal to L and a height above the liquid surface equal to x. There is a film of liquid within the frame. We reversibly move the frame upward by a distance dx, increasing the area inside the frame by Ldx and the energy by

$$dU = TdS + \gamma d\mathscr{A} \tag{5.5-5}$$

We assume that the volume of the system does not change, so there is no PdV term in this equation. The system is closed so there is no μdn term. Since there are two sides to the liquid layer, the area of the surface increases by $2Ldx$, and

$$dU = TdS + 2L\gamma dx \tag{5.5-6}$$

Since $dq_{\text{rev}} = TdS$

$$dw_{\text{rev}} = dU - dq_{\text{rev}} = dU - TdS = \gamma d\mathscr{A} = 2L\gamma dx = F_{\text{rev}}dx$$

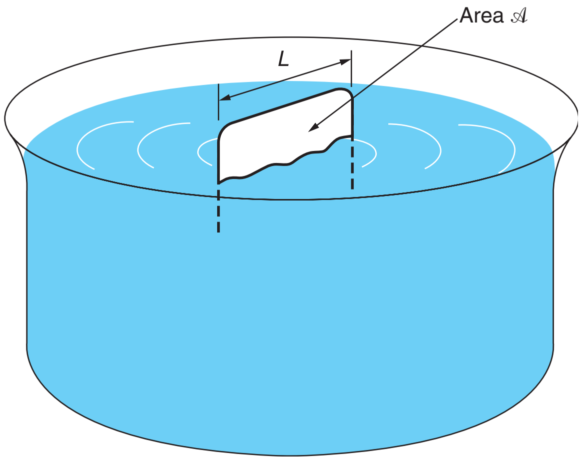

Figure 5.16 A Wire Frame of Adjustable Size to Illustrate Surface Tension. As the wire frame is raised, a thin film of liquid fills the area within the frame.

so that

$$\gamma = \frac{F_{\mathrm{rev}}}{2L} \tag{5.5-7}$$

We recognize γ as the force per unit length exerted by the surface. For this reason it is called the *surface tension*. The SI units of surface tension can be given as N m^{-1} (newtons per meter) or as J m^{-2} (joules per square meter). Table A.10 in Appendix A gives values of the surface tension for several pure substances in contact with a vapor phase of the same substance.

The surface tension for a liquid in contact with its vapor is always positive. The surface of a liquid in contact with a vapor phase can lower its energy by decreasing its surface area. The surface acts somewhat like a stretched elastic film. This is the reason that droplets of a liquid tend to have spherical shapes, since the sphere has the smallest area per unit volume of any three-dimensional object. Another effect is that a liquid such as water is drawn into a vertical glass tube as shown in Figure 5.17a. The surface of liquid water in a glass capillary tube is very nearly tangent to the surface. Figure 5.17b shows another case, in which the liquid surface meets the solid surface at an angle, which is called the *contact angle* and denoted by θ. In the case of water on glass, the contact angle is nearly equal to zero, corresponding to strong attraction between the water and the glass. A nonzero contact angle corresponds to weaker attractions.

The liquid rises into the tube because the surface tension balances the gravitational force on the column of liquid in the tube. If the radius of a vertical tube is r and if the contact angle is zero, the vertical surface tension force is equal to $2\pi r\gamma$. If the density of the liquid is ρ, the gravitational force on the column of liquid is equal to $\pi r^2 h\rho g$, where g is the acceleration due to gravity, and where h is the height of the column. Equating the magnitudes of these quantities,

$$2\pi r\gamma = \pi r^2 h\rho g$$

so that the height of the column is

$$\boxed{h = \frac{2\gamma}{\rho g r} \quad \text{(zero contact angle)}} \tag{5.5-8}$$

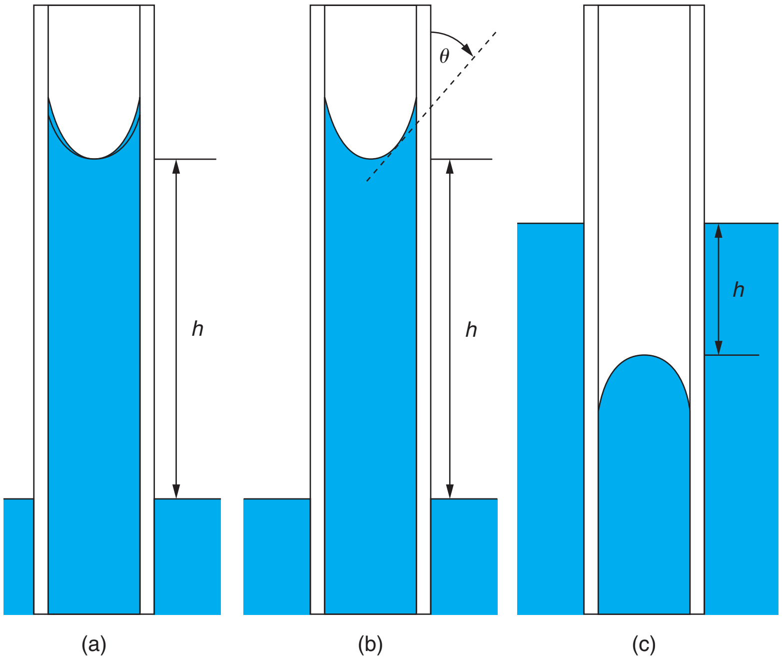

Figure 5.17 Capillary Rise or Depression of a Liquid in a Tube. (a) A liquid that wets the solid surface. (b) A liquid that partially wets the solid surface. (c) Capillary depression of mercury in a glass capillary.

EXAMPLE 5.11

Find the height to which water at 20°C will rise in a glass capillary tube of diameter 0.60 mm.

Solution

From Table A.10, $\gamma = 0.07275\ \mathrm{J\ m^{-2}}$.

$$h = \frac{2\gamma}{\rho g r} = \frac{2\,(0.07275\ \mathrm{J\ m^{-2}})}{(1000\ \mathrm{kg\ m^{-3}})(9.80\ \mathrm{m\ s^{-2}})(0.30\times 10^{-3}\ \mathrm{m})} = 0.049\ \mathrm{m} = 4.9\ \mathrm{cm}$$

Exercise 5.14

Find the height to which the surface of water will rise in a glass tube with a diameter equal to 6.0 cm.

If the contact angle θ is not equal to zero, the surface tension force is exerted at an angle of θ from the vertical. Its upward component is equal to $2\pi r\gamma\ \cos(\theta)$, and the height to which the liquid rises is

$$h = \frac{2\gamma\ \cos(\theta)}{\rho g h} \tag{5.5-9}$$

Mercury atoms are attracted so weakly to glass compared with their attractions for each other that mercury forms a contact angle with glass nearly equal to 180°. The surface tension force is downward, and a mercury meniscus is depressed in a glass capillary tube, as shown in Figure 5.17c.

Exercise 5.15

Assuming a contact angle of 180°, calculate the distance to which a mercury meniscus is depressed in a glass capillary tube of radius 0.500 mm at 20°C.

The Laplace Equation

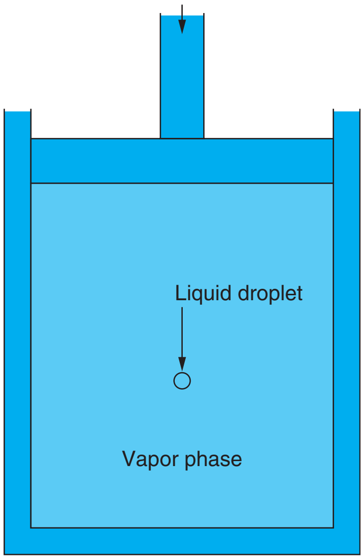

Figure 5.18 System to Illustrate the Pressure Difference in a Spherical Droplet. The droplet is surrounded by the vapor phase, and is assumed to be small enough that it does not immediately settle to the bottom of the vessel.

If a liquid droplet is small enough, it will remain suspended in a vapor phase almost indefinitely. Figure 5.18 depicts a system that consists of a small droplet of liquid suspended in a gaseous phase of the same substance. The system is contained in a cylinder with a movable piston. The piston is displaced reversibly so that an amount of work is done if the volume changes by dV:

$$dw_{\text{rev}} = -P^{(\text{g})}dV = -P^{(\text{g})}(dV^{(\text{g})} + dV^{(\text{l})}) \tag{5.5-10}$$

where $P^{(\text{g})}$ is the pressure of the gas phase, $V^{(\text{g})}$ is the volume of the gas phase, and $V^{(\text{l})}$ is the volume of the liquid phase. The surface tension exerts an additional pressure inside a small liquid droplet, so that $P^{(\text{l})}$, the pressure inside the droplet, differs from $P^{(\text{g})}$. Only $P^{(\text{g})}$ enters in the expression for dw_{rev} because only the gas phase is in contact with the piston.

We can write a different expression for the reversible work by considering the phases separately. The surface work term in Eq. (5.5-7) is added to the usual expression for dw_{rev} for the liquid phase,

$$dw_{\text{rev}} = -P^{(\text{g})}dV^{(\text{g})} - P^{(\text{l})}dV^{(\text{l})} + \gamma d\mathscr{A} \tag{5.5-11}$$

We assume that the vapor phase has negligible surface tension with the cylinder and piston, so no such term is added for the vapor phase. Equating the two expressions for dw_{rev} and canceling the term $P^{(\text{g})}dV^{(\text{g})}$ from both sides, we obtain

$$(P^{(\text{l})} - P^{(\text{g})})\, dV^{(\text{l})} = \gamma d\mathscr{A} \tag{5.5-12}$$

The droplet is assumed to be spherical, so

$$dV^{(\text{l})} = d\left(\frac{4}{3}\pi r^3\right) = 4\pi r^2 dr \tag{5.5-13a}$$

$$d\mathscr{A} = d(4\pi r^2) = 8\pi r dr \tag{5.5-13b}$$

The Laplace equation is named for Pierre Simon, Marquis de Laplace, 1749–1827, a great French mathematician, physicist, and astronomer who also proposed that the solar system condensed from a rotating gas cloud.

Substituting these relations into Eq. (5.5-12) and canceling the common factor dr, we obtain the *Laplace equation*:

$$P^{(\text{l})} - P^{(\text{g})} = \frac{2\gamma}{r} \quad \text{(Laplace equation)} \tag{5.5-14}$$

EXAMPLE 5.12

Find the additional pressure inside a water droplet of radius 1.00 μm at 25°C.

Solution

At this temperature, the surface tension of water is equal to 0.07197 N m^{-1}.

$$P(\mathrm{l}) - P(\mathrm{g}) = \frac{(2)(0.07197\,\mathrm{N\,m^{-1}})}{1.00 \times 10^{-6}\,\mathrm{m}} = 1.44 \times 10^{5}\,\mathrm{N\,m^{-2}} = 1.41\,\mathrm{atm}$$

If the pressure on a sample of liquid is increased, its vapor pressure increases, as seen in Eq. (5.3-18). Using the relation of Eq. (5.5-14) for the additional pressure on the liquid phase in Eq. (5.3-18) we obtain

$$P_{\mathrm{vap}} = P_{\mathrm{vap}}^{(p)} \exp\left[\frac{V_{\mathrm{m}}^{(\mathrm{l})} 2\gamma}{rRT}\right] \tag{5.5-15}$$

or

$$\boxed{\ln\left(\frac{P_{\mathrm{vap}}}{P_{\mathrm{vap}}^{(p)}}\right) = \frac{2V_{\mathrm{m}}^{(\mathrm{l})}\gamma}{rRT}} \tag{5.5-16}$$

where $P_{\mathrm{vap}}^{(p)}$ is the vapor pressure at a planar surface.

EXAMPLE 5.13

The vapor pressure of a planar surface of water at 298.15 K is 23.756 torr. Find the radius of a water droplet that has a vapor pressure that is 1.000 torr higher than this value at 298.15 K. At this temperature, the surface tension of water is equal to 0.07197 N m^{-1}.

Solution

$$r = \frac{2(1.806 \times 10^{-5}\,\mathrm{m^3\,mol^{-1}})(0.07197\,\mathrm{N\,m^{-1}})}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})\ln\left(\frac{24.756\,\mathrm{torr}}{23.756\,\mathrm{torr}}\right)}$$

$$= 2.544 \times 10^{-8}\,\mathrm{m} = 2.544 \times 10^{-5}\,\mathrm{mm} = 25.44\,\mathrm{nm}$$

Since small droplets of a liquid have a larger vapor pressure than large droplets, small droplets tend to evaporate while large droplets grow by condensation. This is the mechanism by which raindrops grow large enough to fall. The initial formation of a small droplet from the vapor is called *homogeneous nucleation* and often requires a very large partial pressure (large degree of supersaturation). Most raindrops apparently nucleate on specks of solid material (this is called *heterogeneous nucleation*). Seeding of supersaturated air with small crystals of silver iodide has been used in efforts to produce rain by providing nucleation sites. Silver iodide is used because it is possible to make 10^{15} particles from a single gram of solid silver iodide by spraying a solution of silver iodide in acetone into the atmosphere through a suitable nozzle. The crystal structure of silver iodide is also favorable for the attachment of water molecules.

The surface of a cavity inside a liquid acts like the surface of a droplet, exerting force that tries to reduce the size of the cavity. It reduces the pressure in the liquid at the surface of the cavity while increasing the pressure inside the cavity. The vapor pressure of the liquid is decreased below that of a planar surface.

EXAMPLE 5.14

Show that the vapor pressure inside a spherical cavity is given by

$$\ln\left(\frac{P_{\mathrm{vap}}}{P_{\mathrm{vap}}^{(p)}}\right) = -\frac{2V_{\mathrm{m}}^{(\mathrm{l})}\gamma}{rRT} \tag{5.5-17}$$

Solution

We can repeat the derivation of Eq. (5.5-14), the Laplace equation, with the role of liquid and gas reversed. The result is that the pressure of the gas (inside the cavity) is greater than that of the liquid (outside the cavity):

$$P(\mathrm{g}) - P(\mathrm{l}) = P(\mathrm{inside}) - P(\mathrm{outside}) = \frac{2\gamma}{r}$$

We have already obtained a relation between the total pressure and the vapor pressure, Eq. (5.3-18):

$$P_2 = P_1 \exp\left(\frac{V_{\mathrm{m}}(P_2' - P_1')}{RT}\right)$$

where P' represents the total pressure and P represents the vapor pressure. Since the pressure in the liquid is smaller, and vapor pressure of the liquid is obtained by substituting $P(\mathrm{g}) - P(\mathrm{l})$ for $P_2' - P_1'$, giving

$$P_{\mathrm{vap}} = P_{\mathrm{vap}}^{(\mathrm{p})} \exp\left(\frac{-V_{\mathrm{m}}(P(\mathrm{g}) - P(\mathrm{l}))}{RT}\right) = P_{\mathrm{vap}}^{(\mathrm{p})} \exp\left(-\frac{2V_{\mathrm{m}}\gamma}{rRT}\right)$$

Exercise 5.16

Find the vapor pressure of water at 298.15 K inside a spherical cavity with diameter 0.0200 mm.

Because the lessening of the vapor pressure at the surface of a cavity is greater for a smaller cavity, the formation of a cavity requires a higher temperature than vaporizing the liquid from a planar surface. For this reason, a liquid can often be superheated well above its normal boiling temperature if its container is smooth and there are no particles in the liquid at which cavities can begin to form. The superheated liquid can suddenly boil ("bump") when the metastable *superheated liquid* finally begins to form cavities. This effect has been observed when heating water in a microwave oven if the water is contained in a vessel with a smooth inner surface. In an organic chemistry laboratory "boiling stones" with rough surfaces are often placed in a liquid to avoid superheating.

PROBLEMS

Section 5.5: Surfaces in One-Component Systems

5.36 Estimate the surface tension of ethanol as was done for carbon tetrachloride in Example 5.10. The enthalpy change of vaporization is roughly equal to 40 kJ mol^{-1}. State any assumptions or approximations. Compare your answer to the correct value, and explain any discrepancy.

5.37 Explain why interfacial tensions between two liquid phases are generally smaller in magnitude than surface tensions between liquid and vapor phases.

5.38 If the surface region is assumed to be two molecular diameters thick, and if the average density in the surface region is assumed to be half of that of the liquid, estimate the fraction of the molecules of a sample of water that are in the surface region if the water exists as (a) spherical droplets with diameter 10.0 μm and (b) a spherical "drop" containing 1.00 mol.

5.39 The surface tension of water at 25°C is equal to 0.07197 N m^{-1}. Find the capillary rise of water in a glass tube of diameter 0.095 mm at this temperature. State any assumptions. Assume that the contact angle equals 0.

5.40 Give an alternate derivation of the capillary rise formula for zero contact angle beginning with the Laplace equation, Eq. (5.5-14), and assuming that the meniscus is a hemisphere.

5.41 Calculate the capillary rise of pure water in a glass capillary of radius 0.350 mm at 298.15 K. Assume zero contact angle.

5.42 Find the height of the column of pure water in a capillary tube of diameter 0.125 mm at 25°C. The surface tension of water at this temperature is 0.0720 J m^{-2}.

5.43 One method of measuring the surface tension of a liquid is to measure the force necessary to pull a fine wire ring out of the surface of the liquid. For ethanol at 20°C, calculate the force for a ring 25.0 mm in diameter. Remember that there is a surface on both the inner and outer diameter of the ring.

5.44 The surface tension of mercury at 20°C is equal to 0.4355 N m^{-1}. The density of mercury is equal to 13.56 g cm^{-3}. The contact angle of mercury against glass is 180°. Find the capillary depression (distance of the meniscus below the liquid surface) for mercury in a glass capillary tube of radius 0.35 mm at 20°C.

5.45 **a.** If the barometric pressure is 760.00 torr, find the pressure at 25°C inside a droplet of water with diameter 1.25 $\mu\mathrm{m} = 1.25 \times 10^{-6}$ m.

b. Find the partial pressure of water vapor that would be at equilibrium with the droplet of part a at 25°C. The normal vapor pressure of water at this temperature (for a planar surface) is 23.756 torr.

5.46 Calculate the vapor pressure of a droplet of ethanol with a radius of 0.00400 mm at 19°C. The vapor pressure at a planar surface is equal to 40.0 torr at this temperature.

5.47 Give an alternate derivation of the expression for the vapor pressure of a spherical droplet, Eq. (5.5-16), using the Laplace equation, Eq. (5.5-14), and the relation between pressure on the liquid phase and the vapor pressure, Eq. (5.3-18).

5.6 Surfaces in Multicomponent Systems

In Example 5.10 we estimated the surface energy of a one-component liquid–vapor surface as though a single layer of molecules had the normal liquid on one side and the vapor on the other side. A solid surface might resemble this crude model, but a liquid surface is more disordered and it is perhaps appropriate to call it a surface region or a surface phase. Figure 5.19a shows schematically an average density profile through a one-component liquid–vapor surface at equilibrium. The thickness of a liquid–vapor interfacial region might be equal to several molecular diameters.

We assume that the surface is planar and horizontal and that the surface region extends from z_1 to z_2. We place a dividing plane at a location z_0 inside the surface region. The volume of each phase is assigned to be the volume that extends to the

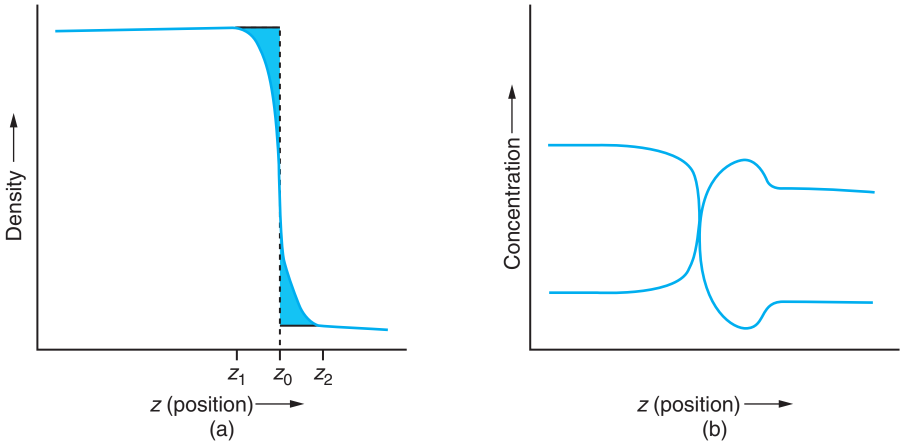

Figure 5.19 A Typical Density Profile Through a Surface Region (Schematic). (a) A one-component system. (b) A two-component system.

dividing plane, so that no volume is ascribed to the surface. The concentration in the homogeneous portion of each phase (the "bulk" portion) is extrapolated up to the surface plane as shown in Figure 5.19a for a single component. The amount of substance in each phase is assigned to be the amount that would occur if the concentration obeyed this extrapolation. The shaded area to the right of the surface plane in Figure 5.19a represents the amount of substance that is present but is not ascribed to phase II by this convention. The shaded area to the left of the surface plane represents the amount of substance that is ascribed to phase I by the convention, but which is actually not present. For a one-component system it is possible to place the plane in the interfacial region so that the two shaded areas are equal in size and no amount of the substance is ascribed to the surface.

In a multicomponent system, this cancellation can generally be achieved for only one substance. Figure 5.19b shows a schematic concentration profile for a two-component system. There is no placement of the plane that will produce equal areas for both substances. We choose to place the plane so that the cancellation occurs for the solvent. The same extrapolation is carried out for each other substance (a solute) as was carried out for a one-component system, and we denote the amount of substance i thus assigned to phase I by $n_i^{(\mathrm{I})}$ and the amount assigned to phase II by $n_i^{(\mathrm{II})}$. We define the *surface excess* of substance number i, denoted by $n_i^{(\sigma)}$:

$$n_i^{(\sigma)} = n_i - n_i^{(\mathrm{I})} - n_i^{(\mathrm{II})} \quad \text{(definition)} \tag{5.6-1}$$

where n_i is the total amount of substance number i (a solute). For a solute that accumulates at the surface, the surface excess is positive, and for a substance that avoids the surface, the surface excess is negative.

The thermodynamic variables of each phase are defined as though the phase were uniform up to the dividing plane. They obey all of the equations of thermodynamics without surface contributions. For phase I,

$$dG^{(\mathrm{I})} = -S^{(\mathrm{I})}dT + V^{(\mathrm{I})}dP + \sum_{i=1}^{c} \mu_i dn_i^{(\mathrm{I})} \tag{5.6-2}$$

with a similar equation for phase II. The phases are at equilibrium so that T, P, and the μ's have the same values in all phases and require no superscripts.

Let us subtract Eq. (5.6-2) for phase I and for phase II from the expression for dG in the version of Eq. (5.5-3) that applies to a multicomponent system:

$$dG - G^{(\mathrm{I})} - G^{(\mathrm{II})} = -S - S^{(\mathrm{I})} - S^{(\mathrm{II})}dT + V - V^{(\mathrm{I})} - V^{(\mathrm{II})}dP + \gamma d\mathscr{A} + \sum_{i=1}^{c} \mu_i d\left[n_i - n_i^{(\mathrm{I})} - n_i^{(\mathrm{II})}\right] \tag{5.6-3}$$

which we rewrite as

$$dG^{(\sigma)} = -S^{(\sigma)}dT + \gamma d\mathscr{A} + \sum_{i=1}^{c} \mu_i dn_i^{(\sigma)} \tag{5.6-4}$$

In Eq. (5.6-4), we have used the fact that $V^{(\mathrm{I})} + V^{(\mathrm{II})} = V$, so that the dP term vanishes. The quantity $G^{(\sigma)}$ is called the *surface Gibbs energy*:

$$G^{(\sigma)} = G - G^{(\mathrm{I})} - G^{(\mathrm{II})} \tag{5.6-5}$$

and $S^{(\sigma)}$ is called the *surface entropy*:

$$S^{(\sigma)} = S - S^{(\mathrm{I})} - S^{(\mathrm{II})} \tag{5.6-6}$$

The surface tension γ is an intensive variable, depending only on T, P, and the composition of the phases of the system. Although $\mathscr{A}$ is not proportional to the size of the system, we assume that there is a contribution to G equal to $\gamma\mathscr{A}$ so that Euler's theorem, instead of the version in Eq. (4.6-4), is

$$G = \gamma\mathscr{A} + \sum_{i=1}^{c} \mu_i n_i \tag{5.6-7}$$

Each phase obeys Euler's theorem without a surface term, so that

$$G^{(\mathrm{I})} = \sum_{i=1}^{c} \mu_i n_i^{(\mathrm{I})} \tag{5.6-8}$$

with an analogous equation for phase II. When Eq. (5.6-8) and its analogue for phase II are subtracted from Eq. (5.6-7), we obtain

$$G^{(\sigma)} = \gamma\mathscr{A} + \sum_{i=1}^{c} \mu_i n_i^{(\sigma)} \tag{5.6-9}$$

We can write an expression for $dG^{(\sigma)}$ from Eq. (5.6-9):

$$dG^{(\sigma)} = \gamma d\mathscr{A} + \mathscr{A} d\gamma + \sum_{i=1}^{c} n_i^{(\sigma)} du_i + \sum_{i=1}^{c} \mu_i dn_i^{(\sigma)} \tag{5.6-10}$$

Equating Eq. (5.6-4) and Eq. (5.6-10), canceling equal terms, and dividing by $\mathscr{A}$, we obtain a surface version of the Gibbs–Duhem equation:

$$0 = \frac{S^{(\sigma)}}{\mathscr{A}}dT + d\gamma + \sum_{i=1}^{c} \Gamma_i^{(\sigma)} d\mu_i \tag{5.6-11}$$

The surface excess per unit area, $\Gamma_i^{(\sigma)}$, is defined by

$$\Gamma_i^{(\sigma)} = \frac{n_i^{(\sigma)}}{\mathscr{A}} \quad \text{(definition)} \tag{5.6-12}$$

and is called the *surface concentration*. If the temperature is constant,

$$d\gamma = -\sum_{i=1}^{c} \Gamma_i^{(\sigma)} d\mu_i \quad \text{(constant temperature)} \tag{5.6-13}$$

This equation can be interpreted as follows: If adding substance i (which raises μ_i) decreases the surface tension, then $\Gamma_i^{(\sigma)}$ is positive and substance i accumulates at the interface. A substance that significantly lowers the surface tension and accumulates at the surface is called a *surfactant*. If raising the chemical potential of substance i increases the surface tension, then $\Gamma_i^{(\sigma)}$ is negative, and substance i avoids the interface.

We will see in Chapter 6 that for a solute in a dilute solution we can write to an adequate approximation

$$\mu_i = \mu_i^\circ + RT \ln(c_i/c^\circ) \tag{5.6-14}$$

where μ_i° is a constant at constant T and P, where c_i is the molar concentration of substance i expressed in mol L^{-1}, and where c° is defined to equal exactly 1 mol L^{-1}. For a two-component solution, we position the surface dividing the phases so that Γ_1, the surface concentration of the solvent, is zero. It can be shown that

$$\Gamma_2 = -\frac{1}{RT}\left(\frac{\partial\gamma}{\partial \ln(c_2)}\right)_{T,P} \tag{5.6-15}$$

and

$$\Gamma_2 = -\frac{c_2}{RT}\left(\frac{\partial\gamma}{\partial c_2}\right)_{T,P} \tag{5.6-16}$$

where the solute is called substance number 2.

Exercise 5.17

Show that Eq. (5.6-15) and Eq. (5.6-16) follow from Eqs. (5.6-13) and (5.6-14).

There are many kinds of systems with interfacial effects that are of practical interest. Such systems have a large surface area per unit mass and either consist of very small particles or have an extremely irregular surface. Surface effects can dominate in determining the behavior of such systems. *Colloids* are suspensions of small solid particles in a liquid medium. *Aerosols* are suspensions of fine solid or liquid particles in a gas and are important in atmospheric chemistry and physics. A number of solids with large surface areas act as *heterogeneous catalysts* that allow adsorbed reactants to react on their surfaces.

PROBLEMS

Section 5.6: Surfaces in Multicomponent Systems

5.48 The following measurements of the surface tension of aqueous sodium chloride solutions at 25.0°C were taken by a student in a physical chemistry laboratory:

$c/\mathrm{mol\,L^{-1}}$	0.00	1.00	2.00	3.00	4.00
$\gamma/\mathrm{N\,m^{-1}}$	0.0720	0.0809	0.0821	0.0841	0.0904

Using Eq. (5.6-16), find the surface concentration of sodium chloride at 1.00 mol L^{-1} and at 2.00 mol^{-1}. What does the sign of this quantity tell you?

5.49 The following measurements of the surface tension of aqueous 1-butanol solutions at 25.0°C were taken by a student in a physical chemistry laboratory:

$c/\mathrm{mol\,L^{-1}}$	0.00	0.110	0.140	0.190
$\gamma/\mathrm{N\,m^{-1}}$	0.0720	0.0595	0.0574	0.0515
$c/\mathrm{mol\,L^{-1}}$	0.250	0.450	0.600	
$\gamma/\mathrm{N\,m^{-1}}$	0.0475	0.0412	0.0354	

Using Eq. (5.6-15), find the surface concentration of 1-butanol at 0.100 mol L^{-1} and at 0.200 mol L^{-1}. What does the sign of this quantity tell you? Calculate the surface area per molecule of 1-butanol for each of these two molar concentrations.

Summary of the Chapter

The fundamental fact of phase equilibrium is that at equilibrium

$$\mu_i^{(\alpha)} = \mu_i^{(\beta)}$$

where the subscript i denotes the substance and the superscripts α and β denote two different phases.

The Gibbs phase rule is

$$f = c - p + 2$$

where f is the number of independent intensive variables, c is the number of components, and p is the number of phases. The fundamental fact of phase equilibrium and the Gibbs phase rule can be used to understand phase diagrams and the experimental facts related to a given phase equilibrium. There are several kinds of phase transitions, including first-order phase transitions, second-order phase transitions, and lambda transitions. Their properties were discussed using the fundamental fact of phase equilibrium.

The Clapeyron equation governs the curves in one-component pressure–temperature phase diagrams:

$$\frac{dP}{dT} = \frac{\Delta S_\mathrm{m}}{\Delta V_\mathrm{m}}$$

where P is the pressure at which two phases can coexist at equilibrium, ΔS_m is the molar entropy change of the phase transition, and ΔV_m is the molar volume change of the transition.

The Clausius–Clapeyron equation gives the vapor pressure of a liquid or solid phase:

$$\ln(P) = \frac{-\Delta H_{\mathrm{m}}}{RT} + \text{constant}$$

where ΔH_{m} is assumed to be temperature-independent.

Inclusion of surface effects leads to the expression for dU

$$dU = TdS - PdV + \gamma d\mathscr{A} + \mu dn$$

where γ is the surface tension and where $\mathscr{A}$ is the interfacial surface area of the system. In most systems the effects of the surface energy are negligible, but the effects are significant in systems with large surface areas per unit mass, such as small droplets, which are found to have a larger vapor pressure than larger droplets.

In a multicomponent system, some substances tend to accumulate at a surface, and others tend to avoid the surface. These phenomena were related to the surface Gibbs energy.

ADDITIONAL PROBLEMS

5.50 The molar enthalpy change of vaporization of water is equal to 44.01 kJ mol^{-1} at 298.15 K, and the vapor pressure of water at this temperature is equal to 23.756 torr.

a. Use the Clausius–Clapeyron equation to estimate the vapor pressure of water at 100°C. Compare your result with the actual value, 760.0 torr.

b. Use the modified Clausius–Clapeyron equation derived in Problem 5.27 to revise your estimate of the vapor pressure at 100°C, assuming that the heat capacities are constant. Comment on your result.

c. Assume that the heat capacities of the liquid and vapor phases are constant and equal to their values at 298.15 K. Find the value of $\Delta H_{\mathrm{m,vap}}$ at 100.0°C, and compare your value with the correct value, 40.66 kJ mol^{-1}.

d. Use the Clausius–Clapeyron equation to estimate the vapor pressure of water at the critical temperature, 647.4 K. The actual critical pressure is equal to 218.3 atm. Explain any discrepancy.

e. Use the modified Clausius–Clapeyron equation derived in Problem 5.27 to estimate the vapor pressure of water at 647.4 K. Comment on your result.

5.51 **a.** Consider a coexistence curve in a pressure–temperature phase diagram of a single pure substance. Show that the phase on the high-temperature side of the curve is the phase of higher molar entropy and that the phase on the high-pressure side of the curve is the phase of smaller molar volume.

b. Interpret the three curves in the water phase diagram in terms of this result.

c. Interpret the curves in the ^{3}He phase diagram in terms of this result.

5.52 **a.** The vapor pressure of mercury at 260°C is equal to 100 torr, and at 330°C it is equal to 400 torr. Find the enthalpy change of vaporization of mercury.

b. Find the normal boiling temperature of mercury and compare it with the experimental value, 356.9°C.

5.53 Label each of the following statements as either true or false. If a statement requires some special condition to make it true, label it as false.

a. At equilibrium, a substance that occurs in two phases will have the same concentration in both phases.

b. Two phases at equilibrium must have the same pressure.

c. The Clapeyron equation applies only to a phase transition involving a vapor phase.

d. The Clapeyron equation is an exact thermodynamic equation.

e. The Clausius–Clapeyron equation is an exact thermodynamic equation.

f. The Clausius–Clapeyron equation can be used for a solid–liquid phase transition.

g. The Clapeyron equation cannot be used for a liquid–vapor phase transition.

h. The surface tension of liquid water is greater than that of liquid benzene because the intermolecular attraction of water molecules is larger than that of benzene, due to hydrogen bonding.

i. It is impossible for four phases of a single substance to coexist at equilibrium.

j. It is impossible for four phases of a mixture of two components to coexist at equilibrium.

k. The maximum number of phases in a system of four components is equal to six.

l. Two phases at equilibrium must have the same temperature.

5.54 The stable crystalline form of sulfur at room temperature is called rhombic sulfur, and another crystalline form is called monoclinic sulfur. The standard-state enthalpy change of formation of monoclinic sulfur at 298.15 K is 0.33 kJ mol^{-1}, and the standard-state Gibbs energy change of formation of monoclinic sulfur is 0.096 kJ mol^{-1}. Assume that both $\Delta H°$ and $\Delta G°$ for the conversion of rhombic sulfur to monoclinic sulfur are temperature-independent. Estimate the temperature of coexistence of these rhombic sulfur and monoclinic sulfur at standard pressure. Compare your result with the experimental temperature, 95°C.

6

The Thermodynamics of Solutions

PRINCIPAL FACTS AND IDEAS

1. A solution is a homogeneous mixture of two or more substances.
2. An ideal solution is a model system in which every component has its chemical potential given for all compositions by

$$\mu_i = \mu_i^* + RT\ln(x_i)$$

where μ_i^* is the chemical potential of the pure substance i, R is the ideal gas constant, T is the absolute temperature, and x_i is the mole fraction of the substance in the solution.
3. Every component in an ideal solution at equilibrium with an ideal vapor phase very nearly obeys Raoult's law

$$P_i = P_i^* x_i$$

where P_i is the partial pressure of gaseous substance i at equilibrium with the solution and P_i^* is the partial pressure of substance i in the gas phase at equilibrium with pure substance i (the vapor pressure of the pure substance).
4. Mixtures of substances with similar molecules form nearly ideal solutions.
5. Nonelectrolyte solutes in dilute solutions very nearly obey Henry's law:

$$P_i = k_i x_i$$

where k_i is a function of temperature called the Henry's law constant and x_i is the mole fraction of substance i in the solution.
6. Activities and activity coefficients describe deviations from ideal or dilute behavior.
7. The activities of strong electrolyte solutes require special treatment. The Debye–Hückel theory provides an accurate limiting law for activity coefficients of electrolyte solutes.
8. Phase diagrams can be used to show the phase equilibria of multicomponent systems and can be understood through the phase rule of Gibbs.
9. Colligative properties depend on concentrations of solutes, but not on their identities.

6.1 Ideal Solutions

A *solution* is a homogeneous mixture of two or more components (substances whose amounts can be independently varied). We ordinarily apply the name only to solid and liquid mixtures, although a gaseous mixture is also homogeneous. We begin with *ideal solutions*, which are defined to be solutions in which the chemical potential of each component is given for all compositions by the formula

$$\boxed{\mu_i(T, P) = \mu_i^*(T, P) + RT\ln(x_i)} \tag{6.1-1}$$

where $\mu_i^*(T, P)$ is the chemical potential of the pure component i when it is at the same temperature, T, and pressure, P, as the solution and where x_i is the mole fraction of component i in the solution.

Raoult's Law

Raoult's law is an empirical law nearly obeyed by some solutions:

$$\boxed{P_i = P_i^* x_i \quad \text{(Raoult's law)}} \tag{6.1-2}$$

where P_i is the *partial vapor pressure* of substance i, defined as the partial pressure of substance i in the vapor phase that is at equilibrium with the solution. The equilibrium vapor pressure of the pure substance i at the temperature and pressure of the solution is denoted by P_i^*, and the mole fraction of substance i in the solution is denoted by x_i. If the solution is liquid and if substance i is a solid at equilibrium at the temperature of the solution, P_i^* must represent the vapor pressure of the supercooled liquid substance.

Raoult's law is named for Francois Marie Raoult, 1830–1901, a French chemist who was one of the founders of physical chemistry.

We now show that a component of an ideal solution obeys Raoult's law if the solution is at equilibrium with an ideal gas mixture. From the fundamental fact of phase equilibrium the chemical potential of component i has the same value in the solution and in the vapor:

$$\mu_i^*(T, P) + RT\ln(x_i) = \mu_i^{\circ(g)} + RT\ln\left(\frac{P_i}{P^\circ}\right) \tag{6.1-3}$$

where we now label the chemical potential of the gas in its standard state as $\mu_i^{\circ(g)}$. We will have additional standard states, so we specify which one we are using.

Equations (6.1-1) and (6.1-3) contain $\mu_i^*(T, P)$, the chemical potential of pure substance i at temperature T and pressure P. The chemical potential of a pure substance is equal to its molar Gibbs energy. It was shown in Chapter 4 that the molar Gibbs energy of a pure solid or liquid is nearly pressure-independent. We will assume that μ_i^* is independent of pressure.

EXAMPLE 6.1

The density of ethanol (substance 1) is equal to 0.7885 g cm^{-3} at 19.0°C. Its equilibrium vapor pressure at 19.0°C is equal to 40.0 torr. Find the change in its chemical potential at 19.0°C if the total pressure is changed from 40.0 torr to 1.000 atm. Compare the value of this quantity with the value of $RT\ln(P_i^* x_i/P^\circ)$, assuming that $x_i = 0.500$.

$$V_{\mathrm{m}}^* = \frac{46.069\ \mathrm{g\ mol^{-1}}}{0.7885\ \mathrm{g\ cm^{-3}}} = 58.437\ \mathrm{cm^3\ mol^{-1}}$$

$$\begin{aligned}\Delta\mu &= V_{\mathrm{m}1}^*(P_1^* - P)\\ &= (58.437 \times 10^{-6}\ \mathrm{m^3\ mol^{-1}})(760\ \mathrm{torr} - 40.0\ \mathrm{torr})\left(\frac{101325\ \mathrm{Pa}}{760\ \mathrm{torr}}\right)\\ &= 5.609\ \mathrm{J\ mol^{-1}}\end{aligned}$$

$$\begin{aligned}RT\ln\left(\frac{P_i^* x_i}{P^\circ}\right) &= (8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(292.15\ \mathrm{K})\ln\left(\frac{(40.0\ \mathrm{torr})(0.500)}{750\ \mathrm{torr}}\right)\\ &= -8804\ \mathrm{J\ mol^{-1}}\end{aligned}$$

where we have used the fact that 1.000 bar is equal to 750 torr. $\Delta\mu$ is 0.064% as large as $RT\ln(P_i^* x_i/P^\circ)$.

At equilibrium the chemical potential of pure component i is equal to the chemical potential of gaseous component i at pressure P_i^*, so that

$$\mu_i^*(T, P) \approx \mu_i^*(T, P_i^*) = \mu_i^{\circ(\mathrm{g})} + RT\ln\left(\frac{P_i^*}{P^\circ}\right) \qquad (6.1\text{-}4)$$

When Eq. (6.1-4) is substituted into Eq. (6.1-3), we obtain

$$\mu_i^{\circ(\mathrm{g})} + RT\ln(P_i^*/P^\circ) + RT\ln(x_i) = \mu_i^\circ(g) + RT\ln(P_i/P^\circ) \qquad (6.1\text{-}5)$$

After canceling and combining terms,

$$RT\ln(P_i^* x_i/P^\circ) = RT\ln(P_i/P^\circ) \qquad (6.1\text{-}6)$$

We divide by RT and take antilogarithms:

$$P_i = P_i^* x_i \qquad (6.1\text{-}7)$$

which is Raoult's law, Eq. (6.1-2). An ideal solution is sometimes defined as a solution in which every substance in the solution obeys Raoult's law for all compositions. If this definition is taken, it can be shown that Eq. (6.1-1) follows as a consequence.

Exercise 6.1

Assuming that Raoult's law holds for component i for all compositions of an ideal solution, show that the chemical potential of this component is given by Equation (6.1-1).

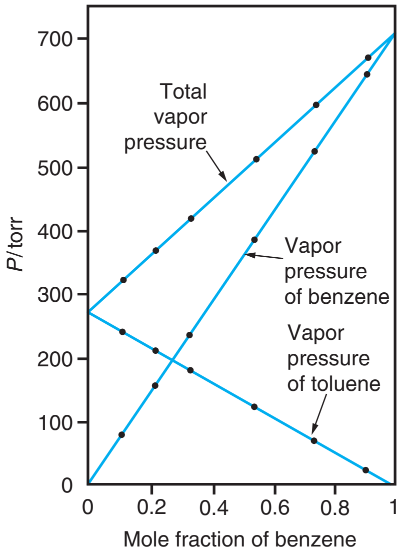

Figure 6.1 The Partial Vapor Pressures of Benzene and Toluene in a Solution at 80°C. Drawn from data of M. A. Rosanoff, C. W. Bacon, and F. W. Schulze, *J. Am. Chem. Soc.*, **36**, 1993 (1914).

Substances with similar molecules usually form nearly ideal solutions. Toluene and benzene are an example. Figure 6.1 shows the partial vapor pressures of benzene and toluene and the total vapor pressure in a solution at 80°C, plotted as functions of the mole fraction of benzene. The line segments in the figure correspond to Raoult's law, which is very nearly obeyed.

The Thermodynamic Variables of an Ideal Solution

The values of thermodynamic properties are usually specified with reference to a standard state. We have already defined the standard state of gases and pure liquids and solids to correspond to a pressure of P° (exactly 1 bar). We now choose the standard state for a component of an ideal liquid solution to be the pure liquid substance at pressure P°. For a component of an ideal solid solution the standard state is the pure solid at pressure P°. We will define all of our standard states to correspond to a pressure P°. Since we assume that the chemical potential of a pure liquid or solid substance is nearly pressure-independent, Eq. (6.1-1) becomes, to a good approximation,

$$\mu_i(T, P) = \mu_i^\circ(T) + RT\ln(x_i) \tag{6.1-8}$$

The thermodynamic functions of a solution are usually expressed in terms of the quantities of mixing. These quantities are defined as the change in the variable for producing the solution from the unmixed components at the same temperature and pressure. The *Gibbs energy change of mixing* is

$$\Delta - G_{\text{mix}} = G(\text{solution}) - G(\text{unmixed}) = \sum_{i=1}^{c} n_i\mu_i - \sum_{i=1}^{c} n_i\mu_i^* \tag{6.1-9}$$

where we have used Euler's theorem, Eq. (5.6-4), to express $G(\text{solution})$. From Eq. (6.1-1) the Gibbs energy of an ideal solution is

$$G(\text{solution}) = \sum_{i=1}^{c} n_i\left[\mu_i^* + RT\ln(x_i)\right] \quad \text{(ideal solution)} \tag{6.1-10}$$

The Gibbs energy change of mixing is

$$\Delta G_{\text{mix}} = RT\sum_{i=1}^{c} n_i\ln(x_i) \quad \text{(ideal solution)} \tag{6.1-11}$$

This equation is identical to that for the Gibbs energy change of mixing of an ideal gas mixture.

Exercise 6.2

Write a formula for the Gibbs energy change of mixing for a mixture of ideal gases, and show that it is the same as Eq. (6.1-11).

If an expression for one thermodynamic variable is obtained, the expressions for other thermodynamic variables can be obtained by the use of thermodynamic identities. The entropy of a system is given by Eq. (4.2-20):

$$-S = \left(\frac{\partial G}{\partial T}\right)_{P,n} \tag{6.1-12}$$

Using Eq. (6.1-10), the entropy of an ideal solution is

$$S = -\sum_{i=1}^{c} n_i\left[\left(\frac{\partial \mu_i^*}{\partial T}\right)_P + R\ln(x_i)\right] \quad \text{(ideal solution)} \tag{6.1-13}$$

For the unmixed components, using Euler's theorem

$$S(\text{unmixed}) = -\sum_{i=1}^{c} n_i\left(\frac{\partial \mu_i^*}{\partial T}\right)_P \tag{6.1-14}$$

so that

$$\Delta S_{\text{mix}} = -R\sum_{i=1}^{c} n_i \ln(x_i) \quad \text{(ideal solution)} \tag{6.1-15}$$

This is the same as the formula for an ideal gas mixture, Eq. (3.3-20).

The enthalpy change of mixing for a solution is given by

$$\Delta H_{\text{mix}} = \Delta G_{\text{mix}} + T\Delta S_{\text{mix}} \tag{6.1-16}$$

so that

$$\Delta H_{\text{mix}} = RT\sum_{i=1}^{c} n_i[\ln(x_i) - \ln(x_i)] = 0 \quad \text{(ideal solution)} \tag{6.1-17}$$

This is the same formula as for ΔH_{mix} of an ideal gas mixture. It can also be shown that

$$\Delta V_{\text{mix}} = 0 \quad \text{(ideal solution)} \tag{6.1-18}$$

Exercise 6.3

Show that Eq. (6.1-18) is correct.

EXAMPLE 6.2

Calculate the Gibbs energy change of mixing, the entropy change of mixing, the enthalpy change of mixing, and the volume change of mixing for a solution of 1.200 mol of benzene and 1.300 mol of toluene at 20.00°C. Assume the solution to be ideal.

Solution

$$\begin{aligned}\Delta G_{\text{mix}} &= RT\,[(1.200\,\text{mol})\ln(0.4800) + (1.300\,\text{mol})\ln(0.5200)] = -4219\,\text{J}\\ \Delta S_{\text{mix}} &= -R\,[(1.200\,\text{mol})\ln(0.4800) + (1.300\,\text{mol})\ln(0.5200)] = 14.39\,\text{J K}^{-1}\\ \Delta H_{\text{mix}} &= 0\\ \Delta V_{\text{mix}} &= 0\end{aligned}$$

We can obtain expressions for other partial molar quantities from the expression for the chemical potential. For example, Eq. (4.5-14) for the partial molar entropy is

$$\bar{S}_i = -\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n} \tag{6.1-19}$$

Application of this equation to Eq. (6.1-1) gives

$$\bar{S}_i = -\left(\frac{\partial \mu_i^*}{\partial T}\right)_{P,n} - R\ln(x_i)$$

$$\bar{S}_i = S_{\text{m},i}^* - R\ln(x_i) \quad \text{(ideal solution)} \tag{6.1-20}$$

where $S_{\text{m},i}^*$ is the molar entropy of pure substance i.

Exercise 6.4

In the same way that Eq. (6.1-20) was derived, obtain the relations for the partial molar volume and partial molar enthalpy of components of an ideal solution:

$$\bar{V}_i = V_{\text{m},i}^* \quad \text{(ideal solution)} \tag{6.1-21}$$

$$\bar{H}_i = H_{\text{m},i}^* \quad \text{(ideal solution)} \tag{6.1-22}$$

Molecular Structure and Ideal Solutions

It is found experimentally that Raoult's law applies most nearly to liquid solutions in which the substances have molecules of similar size, shape, and polarity. The explanation for this fact is that if two substances have similar molecules, a molecule of one substance attracts or repels molecules of the other substance in much the same way as molecules of the same substance. The similarity of interaction allows the molecules to mix randomly in a solution without changing the volume or the enthalpy just as noninteracting molecules mix randomly in a dilute gas mixture.

Exercise 6.5

From the following list, pick pairs of substances that you think will probably form nearly ideal liquid solutions:

o-xylene
p-xylene
ethyl benzene
2-propanol
anthracene
3-methyl pentane
3-pentanone
propanal
m-xylene
toluene
1-propanol
naphthalene
phenanthrene
2-methyl pentane
2-pentanone
propanone

Solid Solutions

In a solid solution the molecules of two or more substances must fit into a single crystal lattice. Gold and platinum atoms are nearly the same size and can do this, as can gold and silver atoms. These elements are completely miscible and form solid solutions that are nearly ideal. However, most substances cannot fit into the crystal lattices of other substances and are nearly insoluble in the solid state, even if they form nearly ideal liquid solutions.

Phase Diagrams of Two-Component Ideal Solutions

The phase diagram for a pure substance requires only two axes corresponding to T and P. In an equilibrium one-phase system with two components, Gibbs' phase rule gives

$$f = c - p + 2 = 2 - 1 + 2 = 3 \quad \text{(one phase, two components)}$$

so that there are three independent intensive variables, which we choose to be T and P and one mole fraction. The phase diagram requires three axes. To make a two-dimensional phase diagram, we must specify a fixed value for one variable.

Pressure–Composition Phase Diagrams

In this kind of phase diagram the temperature has a fixed value. The mole fraction of one component is plotted on the horizontal axis and the pressure is plotted on the vertical axis. For a two-component ideal solution the partial pressure of both components is given by Eq. (6.1-2), so that the total vapor pressure is

$$P_{\text{tot}} = P_1^* x_1 + P_2^* x_2 = P_2^* + \left(P_1^* - P_2^*\right) x_1 \quad \text{(two-component ideal solution)} \tag{6.1-23}$$

where we have used the relationship $x_2 = 1 - x_1$. This equation is represented by a line segment in the pressure–composition phase diagram.

Exercise 6.6

Show that the intercepts of the function in Eq. (6.1-23) at $x_1 = 0$ and $x_1 = 1$ are equal to P_2^* and P_1^*.

The composition of the vapor phase at equilibrium with a liquid solution is not the same as the composition of the liquid solution. If an ideal gas mixture is at equilibrium with a two-component ideal solution, the mole fraction of component 1 in the gaseous phase is given by Dalton's law of partial pressures:

$$y_1 = \frac{P_1}{P_{\text{tot}}} = \frac{P_1^* x_1}{P_1^* x_1 + P_2^* x_2} = \frac{P_1^* x_1}{P_2^* + (P_1^* - P_2^*)x_1} \quad \text{(ideal solution)} \qquad (6.1\text{-}24)$$

where we denote mole fractions in the vapor phase by y_1 and y_2 and mole fractions in the solution phase by x_1 and x_2.

EXAMPLE 6.3

The vapor pressure of pure benzene (component 1) at 20.0°C is equal to 74.9 torr, and that of pure toluene at this temperature is 21.6 torr. Assuming ideality, find the partial vapor pressure of each component, the total vapor pressure, and the mole fractions in the vapor at equilibrium with the solution of Example 6.2.

Solution

Call benzene component 1 and toluene component 2:

$$P_1 = (0.480)(74.9\ \text{torr}) = 36.0\ \text{torr}$$

$$P_2 = (0.520)(21.6\ \text{torr}) = 11.2\ \text{torr}$$

$$P_{\text{tot}} = P_1 + P_2 = 47.2\ \text{torr}$$

$$y_1 = \frac{P_1}{P_{\text{tot}}} = \frac{36.0\ \text{torr}}{47.2\ \text{torr}} = 0.763$$

$$y_2 = \frac{P_2}{P_{\text{tot}}} = \frac{11.2\ \text{torr}}{47.2\ \text{torr}} = 0.237$$

The formula giving the total pressure as a function of y_1 is

$$P_{\text{tot}} = \frac{P_1^* P_2^*}{P_1^* + y_1(P_2^* - P_1^*)} \qquad (6.1\text{-}25)$$

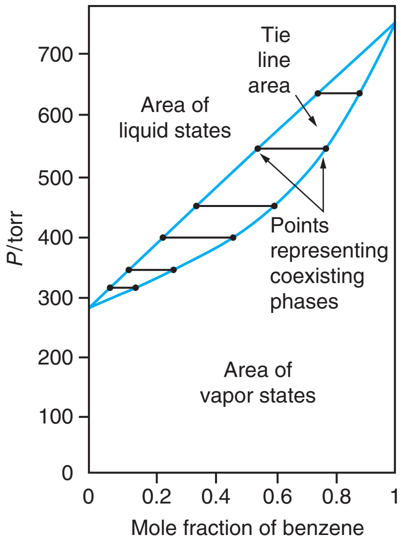

Figure 6.2 The Liquid–Vapor Pressure–Composition Phase Diagram of Benzene and Toluene at 80°C. Drawn from data of M. A. Rosanoff, C. W. Bacon, and F. W. Schulze, *J. Am. Chem. Soc.*, **36**, 1993 (1914).

The derivation of this formula is assigned in Problem 6.1. Figure 6.2 shows the liquid–vapor pressure–composition phase diagram of benzene and toluene at a constant temperature of 80°C. The lower curve represents the total pressure as a function of the mole fraction of benzene in the vapor phase at equilibrium with the liquid phase. The area below this curve represents possible equilibrium intensive states of the system when it is a one-phase vapor. The upper curve (a line segment) represents Eq. (6.1-24), giving the total pressure as a function of the benzene mole fraction in the liquid. The area above this line represents possible equilibrium states of the system when it is a one-phase liquid.

With two phases and two substances there are two independent intensive variables. In Figure 6.2 the temperature is fixed, so there is only one additional independent variable. A horizontal line segment, or *tie line*, between the two curves connects the state points for the two phases at equilibrium with each other at a given pressure. If the mole fraction in one phase is an independent variable, the pressure is a dependent variable given by the height of the curve for that phase, and the mole fraction of the other phase is a dependent variable given by the other end of the tie line at that pressure.

If the pressure is taken as an independent variable, the mole fractions in the two phases, represented by the ends of the tie line, are dependent variables.

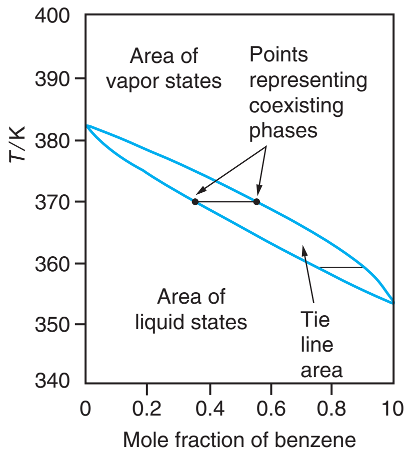

Figure 6.3 The Liquid–Vapor Temperature–Composition Phase Diagram of Benzene and Toluene at 1.000 atm. Drawn from data of M. A. Rosanoff, C. W. Bacon, and F. W. Schulze, *J. Am. Chem. Soc.*, **36**, 1993 (1914).

Temperature–Composition Phase Diagrams

In this type of phase diagram the pressure is held fixed. For two components the mole fraction of one component is plotted on the horizontal axis and the temperature is plotted on the vertical axis. Figure 6.3 shows the liquid–vapor temperature–composition diagram of benzene and toluene at 1.000 atm. The upper curve gives the boiling temperature at the given pressure as a function of the mole fraction of benzene in the vapor phase, and the lower curve gives the boiling temperature at the given pressure as a function of the mole fraction of benzene in the liquid phase. The tie lines drawn between the two curves connect values of the mole fraction in the two phases at equilibrium with each other, giving the composition of one phase as a function of the composition of the other phase at the temperature given by the height of the tie line. Each tie line in this diagram must be the same as the tie line in a pressure–composition diagram corresponding to the temperature of this diagram.

In order to represent the full equilibrium pressure-temperature-composition behavior of a two-component system, a three-dimensional graph is required, as schematically represented in Figure 6.4 for a nearly ideal liquid solution. There are two surfaces in this diagram, and they coincide at the edges of the graph. A pressure–composition diagram is created by passing a plane of constant temperature through the three-dimensional

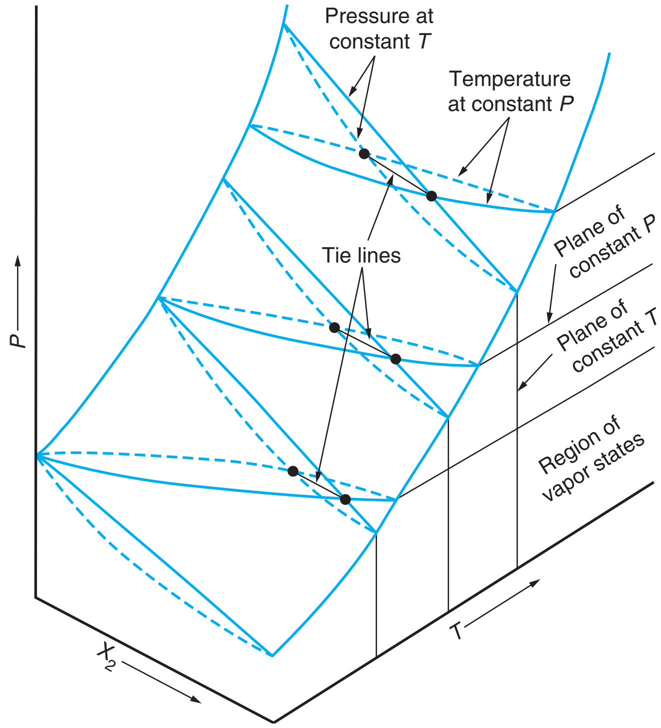

Figure 6.4 Perspective View of the Three-Dimensional Liquid–Vapor Phase Diagram for an Ideal Solution (Schematic).

graph, and a temperature–composition diagram is created by passing a plane of constant pressure though the three-dimensional graph. The intersection of these two planes contains the common tie line of the two diagrams, as shown in the figure.

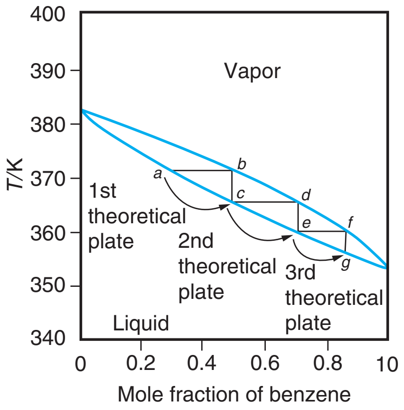

Figure 6.5 Diagram Representing a Constant-Pressure Distillation Process. Each theoretical plate corresponds to one step in the "staircase."

A constant-pressure *distillation* process can be described using the temperature–composition phase diagram, as depicted in Figure 6.5. Point a on the diagram in this figure represents the composition of a liquid solution that is being boiled in the still. Point b, at the other end of the tie line, represents the composition of the vapor at equilibrium with this liquid. This vapor condenses at the temperature represented by point c. A simple still in which this process can be carried out is said to have one *theoretical plate*. A still can be made to produce a greater separation of the components by packing its column with glass beads or other objects. The liquid condenses on the glass beads part way up the column and then evaporates again, making this part of the column equivalent to one theoretical plate. For the process beginning at point a, a second evaporation at point c leads to a vapor with the composition at point d, and this vapor can condense still further up the column, giving a liquid corresponding to point e. This process corresponds to two theoretical plates. Three theoretical plates lead to a liquid with the composition at point g. A still with a large number of theoretical plates can lead to a condensate that is almost entirely made up of the more volatile component. A "spinning-band" still has a rotating helical wire screen that wipes the walls of the column and can provide several hundred theoretical plates.

Exercise 6.7

Estimate from Figure 6.5 the composition and boiling temperature of the condensate produced from the liquid at point a by a still with three theoretical plates.

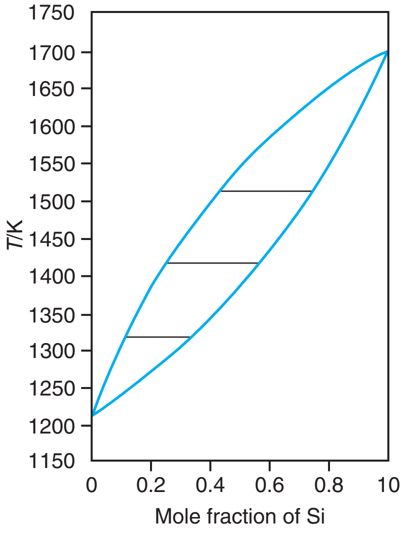

Figure 6.6 The Solid–Liquid Temperature–Composition Phase Diagram of Silicon and Germanium. Since both the solid and liquid phases are nearly ideal solutions, this diagram resembles the liquid–vapor phase diagram of an ideal liquid solution. From C. D. Thurmond, *J. Phys. Chem.*, **57**, 827 (1953).

A two-component solid–liquid phase diagram is similar to a liquid–vapor phase diagram if the solids are miscible. Figure 6.6 shows the temperature–composition phase diagram of silicon and germanium, which form a nearly ideal solid solution and a nearly ideal liquid solution. The area below the lower curve represents one-phase solid solutions, and the area above the upper curve represents one-phase liquid solutions. The area between the curves is a tie-line region, with the two ends of a tie line representing the compositions of the solid phase and the liquid phase at equilibrium with each other. A continuation of the silicon–germanium diagram to higher temperatures leads to the liquid–vapor transition region, giving a diagram with two areas of tie lines, as shown in Figure 6.7.

Maximum Solubilities in Ideal Solutions

Benzene and naphthalene form a nearly ideal liquid solution. However, these two substances are nearly insoluble in each other's solid phase since they cannot both fit into a single crystal lattice. Figure 6.8 schematically shows the vapor pressure and chemical potential of naphthalene in a liquid solution with benzene near room temperature. The standard state of naphthalene for the liquid solution is supercooled liquid naphthalene, which has a higher chemical potential than solid naphthalene. There is a range of mole fractions of naphthalene near unity in which the chemical potential of naphthalene in the solution would exceed that of the solid naphthalene. The mole fraction of naphthalene at which its chemical potential equals that of the solid represents the *maximum solubility* of naphthalene in a solution with benzene. A solution with this composition is said

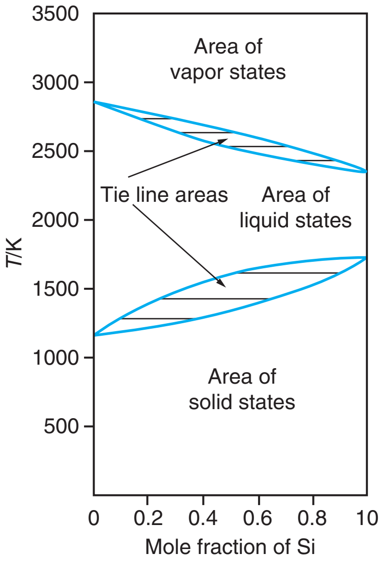

Figure 6.7 The Solid–Liquid and Liquid–Vapor Phase Diagram of Silicon and Germanium (Schematic).

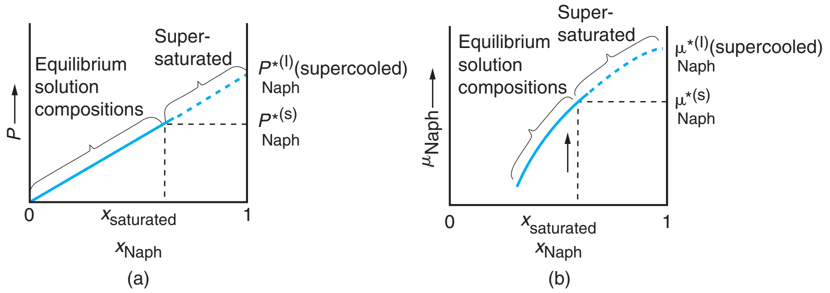

Figure 6.8 Naphthalene in an Ideal Solution (Schematic). (a) The vapor pressure as a function of composition. (b) The chemical potential as a function of composition.

to be *saturated*. If a metastable solution occurs with a greater mole fraction of naphthalene than this, it is called a *supersaturated solution*. The maximum solubility of a solid such as naphthalene in a liquid solvent is independent of the identity of the liquid solvent if the two substances form an ideal solution and are insoluble in the solid phases.

PROBLEMS

Section 6.1: Ideal Solutions

6.1 Derive Eq. (6.1-25).

6.2 Show that an ideal solution obeys the Gibbs–Duhem relation.

6.3 A bulb contains an ideal solution of a nonvolatile substance A and a volatile substance S. This bulb is connected to another bulb containing a solution of another nonvolatile substance B and S so that the two solutions can equilibrate with the same vapor phase. After equilibration, it is found that for any set of compositions, the mole fraction of S in the first bulb is proportional to the mole fraction of S in the second bulb. Prove that the solution of B in S is also ideal.

6.4 Find ΔS_{mix}, ΔG_{mix}, ΔH_{mix}, and ΔV_{mix} if 125.0 g of benzene and 25.0 g of naphthalene are mixed at 60.0°C. State any assumptions.

6.5 A solution is made from 2.50 mol of benzene and 1.50 mol of deuterobenzene at 25°C and 1.00 atm. Find ΔS_{mix}, ΔG_{mix}, ΔH_{mix}, ΔU_{mix}, and ΔV_{mix}.

6.6 Assume that carbon tetrachloride and 1,1,1-trichloroethane (methyl chloroform) form an ideal solution. Look up the vapor pressures of the pure compounds at 25°C and plot a pressure–composition phase diagram for this temperature (four points besides the end points should give an adequate plot).

6.7 Assume that toluene and ethyl benzene form a nearly ideal liquid solution.

a. Construct an accurate graph of the entropy of mixing of a solution of these two substances as a function of x if 1.000 mol of toluene and x mol of ethyl benzene are mixed at a constant temperature of 25°C.

b. Construct an accurate graph of the Gibbs energy of mixing of the solution of part a as a function of x.

6.8 Benzene and toluene form a nearly ideal solution.

a. At 25.00°C, the vapor pressure of benzene is 73.0 torr, and that of toluene is 27.0 torr. Calculate the total vapor pressure and the mole fraction of benzene in the vapor phase that is at equilibrium at 25.00°C with a solution of benzene and toluene having a mole fraction of benzene equal to 0.500.

b. Calculate the Gibbs energy of mixing, the enthalpy of mixing, the volume change of mixing, and the entropy of mixing of the solution in part c if the total amount of substances in the solution is equal to 3.500 mol.

6.9 Assume that carbon tetrachloride and 1,1,1-trichloroethane form an ideal solution. Look up the normal boiling temperatures and the enthalpy changes of vaporization of the pure substances and plot a temperature–composition phase diagram for 1.000 atm. (Four points besides the end points should give an adequate plot.) Assume that the enthalpy changes of vaporization are temperature-independent.

6.10 At 35.2°C, the equilibrium vapor pressure of acetone is 25.9 kPa, and that of carbon disulfide is 68.3 kPa.

a. Assume that Raoult's law is obeyed. Find the partial vapor pressures of each substance at equilibrium with a liquid solution that has a mole fraction of acetone equal to 0.400.

b. The actual equilibrium partial pressure of acetone is 30.7 kPa and that of carbon disulfide is 56.7 kPa. Find the activity and activity coefficient of each substance, using convention I.

6.11 Calculate ΔS for the process of mixing the following: 2.00 mol of an ideal solution of substance 1 and substance 2 with $x_1 = 0.500$ plus 4.00 mol of an ideal solution of substance 1 and substance 2 with $x_1 = 0.75$ plus 1.00 mol of pure substance 1 plus 0.5 mol of pure substance 2.

6.12 Assume that toluene and *ortho*-xylene form an ideal solution at all compositions. At 298.15 K, the vapor pressure of pure toluene is 26.987 torr and the vapor pressure of pure *o*-xylene is 6.609 torr. A solution is formed from 0.500 mol of toluene and a solution of toluene and *o*-xylene containing 0.500 mol of each substance.

a. Find ΔS, ΔG, ΔH, ΔV, and ΔU for this process.

b. Find the total vapor pressure of the resulting solution and the mole fraction of each substance in the vapor phase at equilibrium with the solution.

6.2

Henry's Law and Dilute Nonelectrolyte Solutions

Most solutions are not well described by Raoult's law for all compositions. Figure 6.9 shows the partial vapor pressures and total vapor pressure of a liquid solution of diethyl ether (component 1) and ethanol (component 2) at 20°C. The partial vapor pressures of both components are greater for all compositions than the prediction of Raoult's law, which is represented by broken lines. This behavior is called *positive deviation* from Raoult's law. It corresponds to greater repulsions and/or lesser attractions between unlike molecules than between like molecules. In the case of *negative deviation*, the vapor pressure is smaller than predicted by Raoult's law. It is also possible (but less likely) for the deviation to be positive for one component and negative for another, as is the case with acetone and nitromethane at 318.5 K. However, it is not possible for one component to have positive deviation and the other to have negative deviation over the entire composition range.[1]

Exercise 6.8

At 318.15 K, acetone (component 1) has a negative deviation from Raoult's law in a solution with nitromethane (component 2), and nitromethane has a positive deviation from Raoult's law over part of the range of compositions. What conclusions can you draw about 1-1, 1-2, and 2-2 molecular interactions?

There is a feature of Figure 6.9 that is typical of nonionic substances. For small values of x_1 the curve representing P_1 is nearly linear and for small values of x_2 the

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[1] See M. L. McGlashan, *J. Chem. Educ.*, **40**, 516 (1963).

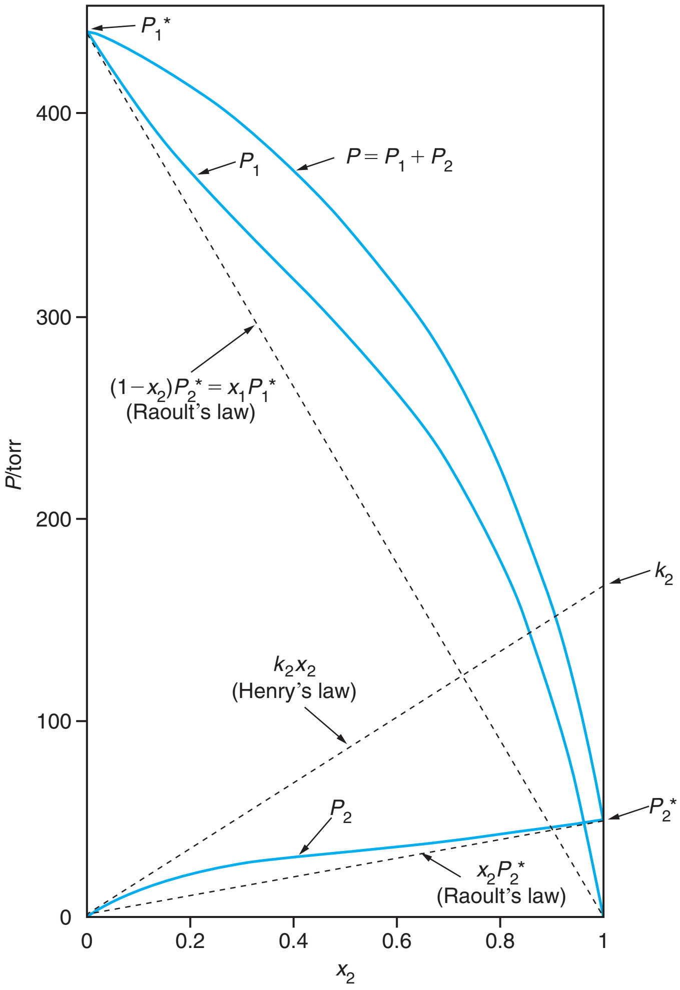

Figure 6.9 Partial Vapor Pressures of Ethanol (Component 2) and Diethyl Ether in a Solution at 20˚C, Showing Positive Deviation from Raoult's Law. Drawn from data of J. Timmermans, *Physicochemical Constants of Binary Systems*, Vol. 2, Interscience Publishers, Inc., New York, 1959, p. 401.

curve representing P_2 is nearly linear. This behavior corresponds to *Henry's law*, which is written:

$$P_i = k_i x_i \quad \text{(Henry's law, valid for } x_i \ll 1) \tag{6.2-1}$$

Henry's law is named for William Henry, 1774–1836, an English chemist who was a friend and colleague of John Dalton and who influenced Dalton's formulation of his atomic theory.

where k_i is called the *Henry's law constant* for substance i. The Henry's law constant is not a true constant. It does not depend on the mole fraction but it depends on temperature and on the identities of all substances present.

There is another feature of Figure 6.9 that is typical of nonionic substances: The curve representing P_1 nearly coincides with the line representing Raoult's law for values of x_1 near unity, and similarly for the P_2 curve near $x_2 = 1$. If one component in a solution is present in a larger amount than the others, it is called the *solvent*. We will generally assign the solvent to be substance number 1. The other substances are called *solutes*. A *dilute solution* is one in which all solutes have small mole fractions. We can generalize the behavior in Figure 6.9 as follows: *In sufficiently dilute solutions nonionic solutes obey Henry's law and the solvent obeys Raoult's law.*

The line in Figure 6.9 that represents Henry's law for ethanol in diethyl ether approximately represents the vapor pressure of ethanol for small values of its mole fraction (near the left edge of the diagram). This extrapolated line has an intercept of approximately 160 torr at the right edge of the diagram, which is the value of the Henry's law constant for ethanol in diethyl ether at the temperature of the figure.

EXAMPLE 6.4

At 40°C, a solution of ethanol (component 2) in benzene (component 1) having a mole fraction of ethanol equal to 0.0200 has a partial vapor pressure of ethanol equal to 30.2 torr. Assuming that Henry's law holds at this composition, find the value of the Henry's law constant for ethanol in benzene.

Solution

$$k_2 = \frac{P_2}{x_2} = \frac{30.2\ \text{torr}}{0.0200} = 1.51 \times 10^3\ \text{torr}$$

Exercise 6.9

Find the value of the Henry's law constant for benzene in ethanol at 40°C. The partial vapor pressure of benzene is equal to 12.8 torr if the mole fraction of benzene is equal to 0.0130.

The Chemical Potential in a Dilute Solution

Physical chemists always want to write a single equation that applies to as many different cases as possible. We would like to write equations similar to Eq. (6.1-8) for the chemical potential of every component of every solution. Consider a dilute solution in which the solvent and the solute are volatile. We equilibrate the solution with a vapor phase, which we assume to be an ideal gas mixture. Using Henry's law, Eq. (6.2-1), for the partial vapor pressure of substance number i (a solute) and using the fundamental fact of phase equilibrium:

$$\mu_i^{(\text{soln})} = \mu_i^{(\text{g})} = \mu_i^{\circ(\text{g})} + RT\ln\left(\frac{k_i x_i}{P^\circ}\right) \quad \text{(dilute solute)}$$

In order to make this equation resemble Eq. (6.1-8), we write this equation as

$$\mu_i^{(\text{soln})} = \mu_i^{\circ(\text{H})} + RT\ln(x_i) \quad \text{(dilute solute)} \tag{6.2-2}$$

where we let

$$\mu_i^{\circ(\text{H})} = \mu_i^{\circ(\text{g})} + RT\ln\left(\frac{k_i}{P^\circ}\right) \tag{6.2-3}$$

The chemical potential $\mu_i^{\circ(\text{H})}$ corresponds to a new standard state for a solute, which we call the *Henry's law standard state*. It is equal to the chemical potential that the pure liquid would have if it had a vapor pressure equal to k_i instead of P_i^*. We specify a pressure of exactly 1 bar, for this standard state. If the pressure on the solution is greatly different from 1 bar, this would require a small correction term like that in Eq. (6.1-5), which we neglect. Since the solvent obeys Raoult's law if the solute obeys Henry's law, the standard state for the solvent in a dilute solution is the same as for a component of an ideal solution. It is the pure solvent at a pressure equal to P°.

Distribution of a Dilute Solute between Two Solvents. Extraction

Consider the equilibration of two solutions containing the same solute but with different solvents that are nearly insoluble in each other. For example, if I_2 is dissolved in water most of the I_2 can be extracted from the water by equilibrating this phase with carbon tetrachloride. For dilute solutions, it is found experimentally that the equilibrium mole fraction of I_2 in the water phase is proportional to the mole fraction of I_2 in the carbon tetrachloride phase. This fact is called *Nernst's distribution law*. For a solute i and two phases denoted by A and B, this empirical law is given by

$$K_{\mathrm{d}} = \frac{x_{i,\mathrm{eq}}^{(\mathrm{B})}}{x_{i,\mathrm{eq}}^{(\mathrm{A})}} \quad \text{(Nernst's distribution law)} \tag{6.2-4}$$

where $x_{i,\mathrm{eq}}^{(\mathrm{A})}$ is the equilibrium mole fraction of the solute in phase A and $x_{i,\mathrm{eq}}^{(\mathrm{B})}$ is the equilibrium mole fraction of the solute in phase B. The constant K_{d} is called the *distribution constant* or *distribution coefficient*. For a given solute, the value of K_{d} depends on temperature and on the identities of the two solvents.

We now show that Nernst's distribution law is valid for solutions that obey Henry's law and obtain a formula for the distribution coefficient. The chemical potential of the solute in the two phases is given by

$$\mu_i^{(\mathrm{A})} = \mu_i^{\circ(\mathrm{H,A})} + RT\ln(x_{i,\mathrm{eq}}^{(\mathrm{A})}) \tag{6.2-5a}$$

and

$$\mu_i^{(\mathrm{B})} = \mu_i^{\circ(\mathrm{H,B})} + RT\ln(x_{i,\mathrm{eq}}^{(\mathrm{B})}) \tag{6.2-5b}$$

At equilibrium,

$$\mu_i^{(\mathrm{A})} = \mu_i^{(\mathrm{B})} \tag{6.2-5c}$$

We solve Eq. (6.2-5a) for $x_{i,\mathrm{A}}$ and solve Eq. (6.2-5b) for $x_{i,\mathrm{B}}$, and after using Eq. (6.2-3), we can write

$$K_{\mathrm{d}} = \frac{x_{i,\mathrm{eq}}^{(\mathrm{B})}}{x_{i,\mathrm{eq}}^{(\mathrm{A})}} = \exp\left[\frac{\mu_i^{\circ(\mathrm{H,A})} - \mu_i^{\circ(\mathrm{H,B})}}{RT}\right] = \frac{k_i^{(\mathrm{A})}}{k_i^{(\mathrm{B})}} \tag{6.2-6}$$

where $k_{i,\mathrm{A}}$ and $k_{i,\mathrm{B}}$ are the Henry's law constants for substance i in phases A and B, respectively. The mole fraction of the solute is greater in the phase in which its Henry's law constant is smaller. Equilibrating the two phases allows the solute to be extracted from the other phase.

Exercise 6.10

Carry out the steps to obtain Eq. (6.2-6).

EXAMPLE 6.5

The value of the distribution coefficient for I_2 between water (phase B) and carbon tetrachloride (phase A) is approximately equal to 0.0022 at 25.0°C. If a solution containing 0.0100 mol of I_2 and 1.000 mol of water is equilibrated with 1.000 mol of carbon tetrachloride at this temperature, find the final mole fraction of iodine in each phase.

Solution

Denote I_2 by the subscript i. Since the mole fractions of I_2 are small, we can write to a good approximation

$$x_i^{(\mathrm{H_2O})} + x_i^{(\mathrm{CCl_4})} \approx 0.0100$$

$$\frac{x_i^{(\mathrm{H_2O})}}{x_i^{(\mathrm{CCl_4})}} = \frac{x_i^{(\mathrm{H_2O})}}{0.0100 - x_i^{(\mathrm{H_2O})}} = 0.0022$$

$$x_i^{(\mathrm{H_2O})} = (0.0022)(0.0100 - x_i^{(\mathrm{H_2O})}) = 0.00022 - (0.0022)x_i^{(\mathrm{H_2O})}$$

$$1.0022x_i^{(\mathrm{H_2O})} = 0.000022$$

$$x_i^{(\mathrm{H_2O})} = \frac{0.000022}{1.0022} = 0.000022$$

$$x_i^{(\mathrm{CCl_4})} = 0.0100 - 0.000022 = 0.009978$$

Other Measures of Composition

The *molality* of component i (a solute) in a solution is defined by

$$\boxed{m_i = \frac{n_i}{w_1} \quad \text{(definition of molality)}} \tag{6.2-7}$$

where n_i is the amount of component i in moles and w_1 is the mass of the solvent (component 1) in kilograms. The units of molality are mol kg^{-1}, sometimes referred to as "molal." If M_1 is the molar mass of the solvent, then

$$w_1 = n_1 M_1 \tag{6.2-8}$$

so that the mole fraction of component i is given by

$$x_i = \frac{n_i}{n_1 + n_2 + \cdots + n_c} = \frac{n_i}{(w_1/M_1) + n_2 + \cdots + n_c} \tag{6.2-9}$$

For a dilute solution n_1 is much larger than the other amounts, and the molality is nearly proportional to the mole fraction:

$$x_i \approx \frac{n_i M_1}{w_1} = m_i M_1 \quad \text{(dilute solution)} \tag{6.2-10}$$

For a dilute solution Henry's law can be expressed in terms of the molality:

$$\boxed{P_i = k_i m_i M_1 = k_i^{(\mathrm{m})} m_i \quad \text{(dilute solution)}} \tag{6.2-11}$$

where $k_i^{(\mathrm{m})} = k_i M_1$ is called the *molality Henry's law constant* for substance i. For a sufficiently dilute solution it is independent of the molality but depends on the identities of all substances present and on the temperature.

EXAMPLE 6.6

a. From the value of k_2 for ethanol (substance 2) in Example 6.4, find the value of $k_2^{(\mathrm{m})}$.

b. Find the vapor pressure of a 0.0500 mol kg^{-1} solution of ethanol in benzene, assuming the molality version of Henry's law to hold.

Solution

a. $k_2^{(\mathrm{m})} = (1.51 \times 10^3\ \text{torr})(0.07812\ \text{kg mol}^{-1}) = 118\ \text{torr}(\text{mol kg}^{-1})^{-1}$

b. $P_2 = \left[118\ \text{torr}(\text{mol kg}^{-1})^{-1}\right]\left(0.0500\ \text{mol kg}^{-1}\right) = 5.90\ \text{torr}$

For a dilute solution, the chemical potential of a solute can be expressed in terms of the molality in an equation similar to Eqs. (6.2-2) and (6.1-8). Using Eqs. (6.2-2) and (6.2-10),

$$\mu_i = \mu_i^{\circ(\mathrm{H})} + RT\ln(m_i M_1) \quad \text{(dilute solution)}$$

$$\boxed{\mu_i = \mu_i^{\circ(\mathrm{m})} + RT\ln(m_i/m^\circ) \quad \text{(dilute solution)}} \tag{6.2-12}$$

where

$$\mu_i^{\circ(\mathrm{m})} = \mu_i^{\circ(\mathrm{H})} + RT\ln(M_1 m^\circ) \tag{6.2-13}$$

and where m° is defined to equal 1 mol kg^{-1} (exactly).

The quantity $\mu_i^{\circ(\mathrm{m})}$ is the chemical potential of substance i in its *molality standard state*. This standard state is component i in a hypothetical solution with m_i equal to m° (exactly 1 mol kg^{-1}) and with Henry's law in the form of Eq. (6.2-11) valid at this molality. Again we specify a pressure of exactly 1 bar for this standard state. Since the standard state is a hypothetical solution, the actual 1-molal solution is not required to obey Henry's law.

Exercise 6.11

Show that $\mu_i^{\circ(\mathrm{m})}$ is equal to the chemical potential of substance i in the vapor phase at equilibrium with a 1.000 mol kg^{-1} solution if Eq. (6.2-11) is valid at this molality.

The *molar concentration* of component i is defined by

$$c_i = \frac{n_i}{V} \tag{6.2-14}$$

where n_i is the amount of the solute in moles and V is the volume of the solution. In SI units the molar concentration is measured in moles per cubic meter (mol m^{-3}). If the molar concentration is measured in moles per liter (mol L^{-1}, sometimes abbreviated as M), it is called the *molarity*. A common symbol for the molarity is the formula for the substance inside square brackets:

$$c_i = [\mathscr{F}_i] \tag{6.2-15}$$

where $\mathscr{F}_i$ is an abbreviation for the formula of substance i. The molar concentration depends on the temperature because of thermal expansion, although the molality does not.

EXAMPLE 6.7

Assuming that the coefficient of thermal expansion of an aqueous solution is the same as that of water, $2.07 \times 10^{-4}\,\mathrm{K}^{-1}$, find the molarity at 25.0°C of a solution that has a molarity of $0.1000\,\mathrm{mol\,L^{-1}}$ at 20.0°C.

Solution

Consider a quantity of solution that has a volume at 20°C of 1.000 L. The amount of solute is

$$n_2 = (0.1000\,\mathrm{mol\,L^{-1}})(1.000\,\mathrm{L}) = 0.1000\,\mathrm{mol}$$

At 25°C, the volume of the solution is

$$V = (1.000\,\mathrm{L})\left[1 + (2.0661 \times 10^{-4}\,\mathrm{K}^{-1})(5.0\,\mathrm{K})\right] = 1.0010\,\mathrm{L}$$

The molarity (molar concentration) at 25.0°C is

$$c_2 = \frac{0.1000\,\mathrm{mol}}{1.0010\,\mathrm{L}} = 0.0999\,\mathrm{mol\,L^{-1}}$$

In a dilute solution, the amounts of solutes are small and the volume of the solution is nearly equal to the volume of the solvent used to make the solution

$$V \approx n_1 V_{\mathrm{m},1}^{*} \tag{6.2-16}$$

where $V_{\mathrm{m},1}^{*}$ is the molar volume of the pure solvent (substance number 1). In this case

$$c_i \approx \frac{n_i}{n_1 V_{\mathrm{m},1}^{*}} \approx \frac{x_i}{V_{\mathrm{m},1}^{*}} \quad \text{(dilute solution)} \tag{6.2-17}$$

EXAMPLE 6.8

Show that for a dilute solution, Henry's law becomes

$$P_i = k_i V_{\mathrm{m},1}^{*} c_i = k_i^{(\mathrm{c})} c_i \tag{6.2-18}$$

Solution

For a dilute solution,

$$c_i = \frac{n_i}{V} \approx \frac{n_i}{n_1 V_{\mathrm{m},1}} \approx \frac{x_i}{V_{\mathrm{m},1}}$$

$$x_i \approx c_i V_{\mathrm{m},1}$$

Henry's law is

$$P_i = k_i x_i \approx k_i V_{\mathrm{m},1} c_i = k_i^{(\mathrm{c})} c_i$$

This equation becomes more nearly exact as the concentration becomes smaller.

For a dilute solution, the chemical potential can be expressed in terms of the molar concentration. We begin with the relation in terms of the mole fraction:

$$\mu_i = \mu_i^{\circ(\mathrm{H})} + RT\ln(x_i)$$

Expressing the mole fraction in terms of the molar concentration,

$$\mu_i = \mu_i^{\circ(\mathrm{H})} + RT\ln(c_i V_{\mathrm{m},1}) = \mu_i^{\circ(\mathrm{H})} + RT\ln(c_i^{\circ} V_{\mathrm{m},1}) + RT\ln(c_i/c^{\circ})$$

where $c^{\circ} = 1\ \mathrm{mol\,L^{-1}}$ or $1\ \mathrm{mol\,m^{-3}}$ (exactly). We let

$$\mu_i^{\circ(\mathrm{c})} = \mu_i^{\circ(\mathrm{H})} + RT\ln(c_i^{\circ} V_{\mathrm{m},1})$$

and obtain the result

$$\mu_i = \mu_i^{\circ(\mathrm{c})} + RT\ln(c_i/c^{\circ}) \quad \text{(dilute solution)} \tag{6.2-19}$$

In addition to the mole fraction, molality, and concentration, the composition of a solution can be represented by the mass percentage, by parts per million by mass, or by volume percentage. For dilute solutions, Henry's law can be expressed in terms of any of these composition measures, since all of them are proportional to the mole fraction in a dilute solution.

Exercise 6.12

Find the expressions for the Henry's law constants using parts per million, percentage by volume, and percentage by mass.

The Solubility of a Gas in a Liquid

At equilibrium the amount of a gas that dissolves in a liquid is very nearly proportional to the partial pressure of the gas, thus obeying Henry's law. Instead of thinking of a solution producing a vapor phase at equilibrium with the solution, we think of a gas dissolving to produce a dilute liquid solution at equilibrium with the gas.

EXAMPLE 6.9

At 25°C, water at equilibrium with air at 1.000 atm contains about 8.3 ppm (parts per million) of dissolved oxygen by mass. Compute the Henry's law constant.

Solution

The mole fraction of oxygen in air saturated with water vapor at 25°C is 0.203. The mole fraction of oxygen in the water phase is

$$x_2 = \left(\frac{8.3\ \text{g}}{32.0\ \text{g mol}^{-1}}\right)\left(\frac{18.0\ \text{g mol}^{-1}}{1 \times 10^6\ \text{g}}\right) = 4.7 \times 10^{-6}$$

The Henry's law constant is

$$\begin{aligned} k_2 &= \frac{0.203\ \text{atm}}{4.7 \times 10^{-6}} = 4.3 \times 10^4\ \text{atm} \\ &= 4.3 \times 10^4\ \text{atm}\left(\frac{101325\ \text{Pa}}{1\ \text{atm}}\right) = 4.4 \times 10^9\ \text{Pa} \end{aligned}$$

The Solvent in a Dilute Solution Obeys Raoult's Law

We now show from thermodynamics that if the solute in a two-component solution obeys Henry's law for some dilute range of composition, the solvent obeys Raoult's law over this range of composition. We begin with the Gibbs–Duhem relation for constant pressure and temperature:

$$x_1\left(\frac{\partial \mu_1}{\partial x_2}\right)_{T,P} + x_2\left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P} = 0 \tag{6.2-20}$$

The vapor phase must have an additional gas or gases (such as air) present to keep the pressure constant if the mole fractions are changed. The small amount of air that dissolves in the solution can be ignored, and the small effect of the change in pressure on the vapor pressures is negligible (see Example 5.7).

Assume that component 2 obeys Henry's law over the range of composition from $x_2 = 0$ to $x_2 = x_2'$. In this range

$$\left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P} = RT\left(\frac{d\ln(x_2)}{dx_2}\right) = \frac{RT}{x_2} \tag{6.2-21}$$

Since $x_1 + x_2 = 1$, $dx_2 = -dx_1$, and $\partial\mu_1/\partial x_1 = -\partial\mu_1/\partial x_2$. Using this fact and Eq. (6.2-20), we obtain

$$-x_1\left(\frac{\partial \mu_1}{\partial x_2}\right)_{T,P} = x_1\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} = x_2\left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P} = \frac{x_2 RT}{x_2} = RT \tag{6.2-22}$$

Dividing this equation by x_1 and multiplying by dx_1, we obtain

$$\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} dx_1 = \left(\frac{RT}{x_1}\right) dx_1 \tag{6.2-23}$$

Integrating this equation from $x_1 = 1$ to $x_1 = x_1' = 1 - x_2'$, we obtain

$$\mu_1(x_1') - \mu_1(1) = RT\ln(x_1') - \ln(1) \tag{6.2-24a}$$

which is the same as

$$\mu_1(x_1) = \mu_1^* + RT \ln(x_1) \tag{6.2-24b}$$

where we drop the prime symbol (′) on x_1. This is the same as Eq. (6.1-1), which leads to Raoult's law as in Section 6.1. If a dilute solution contains several solutes that all obey Henry's law, the solvent obeys Raoult's law just as in the case of one solute. The proof of this assertion is assigned in Problem 6.20.

PROBLEMS

Section 6.2: Henry's Law and Dilute Nonelectrolyte Solutions

6.13 A certain volatile solvent has a vapor pressure of 300.0 torr when pure at 298.15 K. When 6.40 g of a solute is dissolved in 1.000 mol of the solvent, the partial vapor pressure of the solvent at 298.15 K is 285.7 torr. Assuming that the solute obeys Henry's law and that the solvent obeys Raoult's law, find the molar mass of the solute.

6.14 Deep-sea divers can suffer a condition known as the "bends" if they breathe ordinary air at a pressure equal to the ambient hydrostatic pressure, because nitrogen gas dissolves in blood at high pressure and is released as bubbles in the bloodstream when the diver decompresses.

a. Calculate the amount of nitrogen dissolved in 5.000 L of blood (roughly the volume in an adult human) at equilibrium with air (78 mol% nitrogen) at a depth of 200 m, assuming that Henry's law constant for nitrogen in blood is equal to 7.56×10^4 atm, the value for nitrogen in water at 20.0°C.

b. Calculate the volume of this amount of nitrogen as a gas at 1.000 atm and 20.0°C.

6.15 **a.** Find the value of the distribution coefficient for iodine between water and carbon tetrachloride at 25°C, using the concentration description. The density of carbon tetrachloride is 1.59 g cm^{-3}.

b. Iodine is equilibrated between water and carbon tetrachloride at 25°C. The final concentration of iodine in the carbon tetrachloride phase is equal to 0.0734 mol L^{-1}. Find the volume of a sodium thiosulfate solution with 0.0100 mol L^{-1} required to titrate 25.00 mL of the aqueous phase. (2 mol of thiosulfate is required to react with 1 mol of I_2.)

6.16 Find the value of the distribution coefficient for iodine between water and carbon tetrachloride at 25°C, using the molality description.

6.17 From the value of the Henry's law constant for ethanol in benzene at 40°C, calculate the value of the Henry's law constant for ethanol in benzene at this temperature if mass fractions are used instead of mole fractions to describe the system.

6.18 When water is saturated with air at sea level and 298 K, there are 8.3 ppm (parts per million) of oxygen by mass dissolved. Find the equilibrium mole fraction of oxygen dissolved in water at 298 K if the partial pressure of oxygen is equal to 10.0 atm.

6.19 At 25°C, the Henry's law constant for nitrogen in water is 8.68×10^9 Pa and the Henry's law constant for nitrogen in benzene is 0.239×10^9 Pa. A solution of nitrogen in water at 25°C with 6.00 ppm (parts per million) of nitrogen by mass is at equilibrium with a solution of nitrogen in benzene. Find the mole fraction of nitrogen in the benzene solution.

6.20 Show that the solvent in a solution of several solutes obeys Raoult's law at a certain composition if all solutes obey Henry's law for all compositions between this composition and the pure solvent. *Hint:* Carry out the integration for fixed proportions of solutes, so that the mole fractions of the solutes remain proportional to each other.

6.21 Find the activity of water in a 0.0250 mol kg^{-1} solution of sucrose in water at 298.15 K. Assume dilute solution behavior.

6.22 The Henry's law constant for methane in benzene is equal to 481 atm. Find the molality of methane dissolved in benzene if the equilibrium partial pressure of methane is 0.250 atm.

6.3 Activity and Activity Coefficients

We have obtained several relations for the chemical potential that look quite similar. For an ideal gas, either pure or in a mixture,

$$\mu_i = \mu_i^\circ + RT\ln\left(\frac{P_i}{P^\circ}\right) \quad \text{(ideal gas)} \tag{6.3-1}$$

For a component of an ideal solution or for the solvent in a dilute solution,

$$\mu_i = \mu_i^* + RT\ln(x_i) \quad \begin{array}{l}\text{(component of an ideal solution}\\ \text{or solvent in a dilute solution)}\end{array} \tag{6.3-2}$$

For a solute in a dilute solution we had a choice of three relations:

$$\mu_i = \mu_i^{\circ(\mathrm{H})} + RT\ln(x_i) \quad \text{(solute in a dilute solution)} \tag{6.3-3}$$

$$\mu_i = \mu_i^{\circ(\mathrm{m})} + RT\ln(m_i/m^\circ) \quad \text{(solute in a dilute solution)} \tag{6.3-4}$$

$$\mu_i = \mu_i^{\circ(\mathrm{c})} + RT\ln(c_i/c^\circ) \quad \text{(solute in a dilute solution)} \tag{6.3-5}$$

The Definition of the Activity

In each of the preceding five equations the chemical potential is equal to a standard-state chemical potential plus a term that consists of RT times the logarithm of a composition variable. We now want to write a single equation that will apply to all cases:

$$\mu_i = \mu_i^\circ + RT\ln(a_i) \quad \text{(defines the activity } a_i\text{)} \tag{6.3-6}$$

where μ_i° is the chemical potential of substance i in the appropriate standard state and where this equation defines a_i, the *activity* of substance i.

Comparison of Eq. (6.3-6) with the preceding five equations shows that

$$a_i = \frac{P_i}{P^\circ} \quad \text{(ideal gas)} \tag{6.3-7}$$

$$a_i = x_i \quad \begin{array}{l}\text{(component of an ideal solution}\\ \text{or solvent in a dilute solution)}\end{array} \tag{6.3-8}$$

$$a_i = x_i \quad \text{(dilute solute, mole fraction description)} \tag{6.3-9}$$

$$a_i = \frac{m_i}{m^\circ} \quad \text{(dilute solute, molality description)} \tag{6.3-10}$$

$$a_i = \frac{c_i}{c^\circ} \quad \text{(dilute solute, concentration description)} \tag{6.3-11}$$

The activity is a dimensionless quantity that is equal to unity if the substance is in its standard state. Each measure of the activity corresponds to a different standard state. For example, the standard state for a component in an ideal solution or a solvent in an arbitrary solution is the pure substance. The standard state for a solute that obeys Henry's law is the hypothetical pure substance that has a vapor pressure equal to k_i, the Henry's law constant. The standard state of a dilute solute in the molality description is a hypothetical solute with a molality of 1 mol kg^{-1} such that Henry's law is obeyed at this composition. The standard state of a dilute solute in the concentration description is a hypothetical solute with a molar concentration of 1 mol m^{-3} or 1 mol L^{-1} such that Henry's law is obeyed at this composition.

The Activity of a Pure Solid or Liquid

The standard state of a pure solid or liquid is the pure substance at pressure $P°$. If the substance is at a pressure P' not equal to $P°$,

$$\mu_i(P') = G^*_{\mathrm{m},i}(P') = G^{\circ}_{m,i} + \int_{P°}^{P'} V^*_{\mathrm{m},i}dP \approx \mu_i^\circ + V^*_{\mathrm{m},i}\left(P' - P°\right) \tag{6.3-12}$$

where we assume that the solid or liquid has a nearly constant volume. By comparison with Eq. (6.3-6),

$$RT\ln(a_i) = V^*_{\mathrm{m},i}\left(P - P°\right) \tag{6.3-13}$$

where we drop the prime label (′) on the P. The activity of a pure liquid or solid at pressure P is given by

$$\boxed{a_i = \exp\left(\frac{V^*_{\mathrm{m},i}\,(P - P°)}{RT}\right) \quad \text{(pure solid or liquid)}} \tag{6.3-14}$$

The exponent in Eq. (6.3-14) is generally quite small unless P differs greatly from $P°$. For ordinary pressures we will assume that the activity of a pure solid or liquid is equal to unity.

EXAMPLE 6.10

Find the activity of pure liquid water at a pressure of 2.000 bar and a temperature of 298.15 K.

Solution

$$\ln(a) = \frac{\left(1.805\times 10^{-6}\,\mathrm{m^3\,mol^{-1}}\right)(1.00\,\mathrm{atm})\left(101325\,\mathrm{N\,m^{-2}\,atm^{-1}}\right)}{\left(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}\right)(298.15\,\mathrm{K})} = 0.0007378$$

$$a = e^{0.0007378} = 1.000728$$

Exercise 6.13

Find the pressure such that the activity of liquid water is equal to 1.0100 at 298.15 K.

The Activity and Activity Coefficient of a Nonideal Gas

The standard state for a nonideal gas is defined to be the hypothetical ideal gas at the standard-state pressure P°. From Eq. (5.4-6) we see that Eq. (6.3-6) applies to a nonideal gas if we define the activity of a nonideal gas to be the ratio of the fugacity to P°:

$$a_i = f_i/P^\circ \quad \text{(nonideal gas)} \tag{6.3-15}$$

We define the *activity coefficient* γ_i of a nonideal gas as

$$\gamma_i = \frac{a_i(\text{real})}{a_i(\text{ideal})} \tag{6.3-16}$$

so that the activity coefficient of a gas equals the ratio of the fugacity to the pressure:

$$\gamma_i = \frac{f_i/P^\circ}{P_i/P^\circ} = \frac{f_i}{P_i} \tag{6.3-17}$$

The activity coefficient of an ideal gas equals unity. The chemical potential of a nonideal gas can be written

$$\mu_i = \mu_i^\circ + RT\ln(a_i) = \mu_i^\circ + RT\ln\left(\frac{f_i}{P^\circ}\right) = \mu_i^\circ + RT\ln\left(\frac{\gamma_i P_i}{P^\circ}\right) \tag{6.3-18}$$

The activity coefficient of a gas is also known as the *fugacity coefficient* and is sometimes denoted by ϕ_i instead of by γ_i. If the value of the activity coefficient of a real gas is greater than unity, the gas has a greater activity and a greater chemical potential than if it were ideal at the same temperature and pressure. If the value of the activity coefficient is less than unity, the gas has a lower activity and a lower chemical potential than if it were ideal.

Activities and Activity Coefficients in Solutions

We now obtain formulas for solutions that are neither ideal nor dilute. The activities are specified in different ways, depending on whether one of the components is designated as the solvent and depending on the composition variables used. There are two different schemes that use mole fractions as composition variables, called convention I and convention II.

Convention I

In this treatment all of the components are treated in the same way, with no substance designated as the solvent. The standard state for each component is the pure substance at pressure P° and at the temperature of the solution, just as with an ideal solution. As before, we obtain working formulas for volatile substances by assuming that the solution is at equilibrium with an ideal gas mixture. The chemical potential of substance i in the solution is equal to its chemical potential in the vapor phase. If we write the chemical potential in the solution in terms of the activity as in Eq. (6.3-6),

$$\mu_i = \mu_i^{\circ(\text{I})} + RT\ln a_i^{(\text{I})} = \mu_i^{(\text{g})} = \mu_i^{\circ(\text{g})} + RT\ln\left(\frac{P_i}{P^\circ}\right) \tag{6.3-19}$$

where we attach the superscript (I) to specify that we are using convention I. Since $\mu_i^{\circ(\mathrm{I})}$ is the chemical potential of the pure liquid, μ_i^*, it is equal to the chemical potential of the gaseous substance at a partial pressure equal to the equilibrium vapor pressure P_i^*:

$$\mu_i^* = \mu_i^{\circ(\mathrm{I})} = \mu_i^{\circ(\mathrm{g})} + RT\ln\left(\frac{P_i^*}{P^\circ}\right) \tag{6.3-20}$$

We are ignoring a small correction in $\mu_i^{\circ(\mathrm{I})}$ due to the fact that the standard state is at $P = P^\circ = 1$ bar, whereas μ_i^* pertains to pressure P_i^*. The relation of Eq. (6.3-19) becomes

$$\mu_i^{\circ(\mathrm{g})} + RT\ln\left(\frac{P_i^*}{P^\circ}\right) + RT\ln a_i^{(\mathrm{I})} = \mu_i^{\circ(\mathrm{g})} + RT\ln\left(\frac{P_i}{P^\circ}\right) \tag{6.3-21}$$

Canceling equal terms and taking antilogarithms in Eq. (6.3-21), we obtain

$$P_i = P_i^* a_i^{(\mathrm{I})} \tag{6.3-22}$$

which resembles Raoult's law except that the activity $a_i^{(\mathrm{I})}$ occurs instead of the mole reaction x_i. The activity acts as an "effective" mole fraction in determining the partial vapor pressure of the substance. Equation (6.3-22) is equivalent to

$$\boxed{a_i^{(\mathrm{I})} = \frac{P_i}{P_i^*}} \tag{6.3-23}$$

The *activity coefficient* in convention I is defined as the ratio of the activity to the mole fraction:

$$\boxed{\gamma_i^{(\mathrm{I})} = \frac{a_i^{(\mathrm{I})}}{x_i} \quad \text{(definition of the activity coefficient)}} \tag{6.3-24}$$

It is equal to the actual vapor pressure divided by the value of the vapor pressure that is predicted by Raoult's law:

$$\boxed{\gamma_i^{(\mathrm{I})} = \frac{P_i/P^\circ}{P_{i,\mathrm{ideal}}/P^\circ} = \frac{P_i}{P_i^* x_i}} \tag{6.3-25}$$

The activity coefficient specifies how the substance deviates from Raoult's law. If $\gamma_i > 1$, the partial vapor pressure of substance i is higher than predicted by Raoult's law, and if $\gamma_i < 1$, it is lower than predicted by Raoult's law.

EXAMPLE 6.11

Find the value of the activity and the activity coefficient of 2,2,4-trimethyl pentane (component 2) in ethanol at 25°C at a mole fraction of 0.2748, according to convention I. The partial vapor pressure is equal to 48.31 torr and the vapor pressure of the pure liquid is equal to 59.03 torr.

Solution

$$a_2^{(\mathrm{I})} = \frac{48.31\ \mathrm{torr}}{59.03\ \mathrm{torr}} = 0.8184$$

$$\gamma_2^{(\mathrm{I})} = \frac{0.8184}{0.2748} = 2.978$$

Exercise 6.14

Find the value of the activity and the activity coefficient of ethanol in the solution of the previous example according to convention I. The partial vapor pressure is 46.91 torr and the vapor pressure of pure ethanol at 25°C is equal to 49.31 torr.

Convention II

The mole fractions of all components are used as composition variables in convention II, as in convention I. One substance, component number 1, is designated as the solvent and is treated just as in convention I:

$$a_1^{(\mathrm{II})} = a_1^{(\mathrm{I})} = \frac{P_1}{P_1^*} \quad \text{(component 1 = solvent)} \tag{6.3-26}$$

$$\gamma_1^{(\mathrm{II})} = \gamma_1^{(\mathrm{I})} = \frac{a_1^{(\mathrm{I})}}{x_1} = \frac{P_1/P^\circ}{P_{1(\mathrm{ideal})/P^\circ}} = \frac{P_1}{P_1^* x_1} \quad \text{(component 1 = solvent)} \tag{6.3-27}$$

Solutes are treated differently from convention I. The standard state for a solute in convention II is the same as that for a dilute solute: the hypothetical pure substance that obeys Henry's law. The chemical potential of the solute in its standard state is equal to the chemical potential of an ideal gas at pressure equal to k_i, which is the same as the Henry's law standard state:

$$\mu_i^{\circ(\mathrm{II})} = \mu_i^{\circ(\mathrm{H})} = \mu_i^{\circ(\mathrm{g})} + RT\ln\left(\frac{k_i}{P^\circ}\right) \quad \text{(component } i = \text{solute)} \tag{6.3-28}$$

The activity takes on the value that is needed to produce a version of Eq. (6.3-6):

$$\mu_i = \mu_i^{\circ(\mathrm{II})} + RT\ln(a_i^{(\mathrm{II})}) \tag{6.3-29}$$

Equation (6.3-28) is substituted into Eq. (6.3-29) and the chemical potential of substance i in the solution is equated to its chemical potential in the gas phase, which is assumed to be an ideal gas mixture. This gives

$$\mu_i^{\circ(\mathrm{g})} + RT\ln\left(\frac{k_i}{P^\circ}\right) + RT\ln\left(a_i^{(\mathrm{II})}\right) = \mu_i^{\circ(\mathrm{g})} + RT\ln\left(\frac{P_i}{P^\circ}\right) \tag{6.3-30}$$

Cancellation and taking antilogarithms lead to

$$P_i = k_i a_i^{(\mathrm{II})} \quad \text{(component } i = \text{solute)} \tag{6.3-31}$$

This equation is the same as Henry's law except for the occurrence of the activity instead of the mole fraction. The activity is an "effective" mole fraction in expressing the chemical potential and the partial vapor pressure. Equation (6.3-31) is equivalent to

$$a_i^{(\mathrm{II})} = \frac{P_i}{k_i} \quad (\text{component } i = \text{solute}) \tag{6.3-32}$$

The *activity coefficient* in convention II is again defined as the ratio of the activity to the mole fraction. It is equal to the actual vapor pressure divided by the vapor pressure predicted by Henry's law and describes how the substance deviates from Henry's law:

$$\gamma_i^{(\mathrm{II})} = \frac{a_i^{(\mathrm{II})}}{x_i} = \frac{P_i}{k_i x_i} \quad (\text{component } i = \text{solute}) \tag{6.3-33}$$

Equation (6.3-29) can now be written

$$\mu_i = \mu_i^{\circ(\mathrm{II})} + RT\ln(\gamma_i^{(\mathrm{II})} x_i) \quad (\text{component } i = \text{solute}) \tag{6.3-34}$$

Convention II is sometimes referred to as the application of the *solute standard state* to the solutes and the application of the *solvent standard state* to the solvent. Convention I is called the application of the solvent standard state to every component. The reason for having two conventions is that we would like to have activity coefficients nearly equal to unity as often as possible. In convention I we describe the deviation of each substance from Raoult's law. If Raoult's law is approximately obeyed by all substances, the use of convention I gives an activity coefficient approximately equal to unity for each substance. In convention II we describe the deviation of the solvent from Raoult's law and the deviation of a solute from Henry's law. If Henry's law is approximately obeyed by a solute, the use of convention II gives an activity coefficient approximately equal to unity for that solute, as well as an activity coefficient approximately equal to unity for the solvent, which would approximately obey Raoult's law.

EXAMPLE 6.12

Henry's law constant for ethanol in diethyl ether at 20°C is equal to 160 torr. Find the activity and activity coefficient of ethanol (component 2) in diethyl ether (component 1) at 20°C for a mole fraction of ethanol equal to 0.100, using both convention I and convention II. The partial pressure of ethanol at this composition and temperature is equal to 12.45 torr, and the vapor pressure of pure ethanol at this temperature is equal to 44.40 torr.

Solution

By convention I:

$$a_2^{(\mathrm{I})} = \frac{P_2}{P_2^*} = \frac{12.45\ \text{torr}}{44.40\ \text{torr}} = 0.280$$

$$\gamma_2^{(\mathrm{I})} = \frac{0.280}{0.100} = 2.80$$

By convention II:

$$a_2^{(\mathrm{II})} = \frac{P_2}{k_2} = \frac{12.45\,\mathrm{torr}}{160\,\mathrm{torr}} = 0.0778$$

$$\gamma_2^{(\mathrm{II})} = \frac{a_2}{x_2} = \frac{0.0778}{0.100} = 0.778$$

The activity coefficient $\gamma_2^{(\mathrm{II})}$ is closer to unity than is $\gamma_2^{(\mathrm{I})}$. The activity coefficient of the solvent is the same in both conventions.

Exercise 6.15

Since diethyl ether is designated as the solvent in the previous example its activity and activity coefficient are the same in convention II as in convention I. Find the activity and the activity coefficient of diethyl ether in the previous example. The partial vapor pressure of diethyl ether at this composition and pressure is equal to 408.6 torr and the vapor pressure of pure diethyl ether at this temperature is equal to 442.6 torr.

The Molality Description

Activities and activity coefficients of solutes are also defined for the molality description. The molality of solute number i is given by

$$m_i = \frac{n_i}{w_1} = \frac{n_i}{n_1 M_1} = \frac{x_i}{x_1 M_1} \tag{6.3-35}$$

where M_1 is the molar mass of the solvent and w_1 is the mass of the solvent in kilograms. Once again, we want to have a version of Eq. (6.3-6). Using the relation of Eq. (6.3-35) in Eq. (6.3-34), we write

$$\mu_i = \mu_i^{\circ(\mathrm{II})} + RT\ln(M_1 m^\circ) + RT\ln\left(\frac{\gamma_i^{(\mathrm{II})} x_1 m_i}{m^\circ}\right) \tag{6.3-36}$$

where m° is defined to equal 1 mol kg^{-1} (exactly). This equation is in the form of Eq. (6.3-6) if

$$a_i^{(\mathrm{m})} = \frac{\gamma_i^{(\mathrm{II})} x_1 m_i}{m^\circ} \tag{6.3-37}$$

and

$$\mu_i^{\circ(\mathrm{m})} = \mu_i^{\circ(\mathrm{II})} + RT\ln(M_1 m^\circ) \tag{6.3-38}$$

The standard state is the same as for the molality description of a dilute solute that obeys Henry's law: the hypothetical solution with molality equal to 1 mol kg^{-1} and obeying the molality version of Henry's law, Eq. (6.2-11).

We define the *molality activity coefficient*

$$\gamma_i^{(\mathrm{m})} = \gamma_i^{(\mathrm{II})} x_1 \tag{6.3-39}$$

so that Eq. (6.3-36) can be written

$$\boxed{\mu_i = \mu_i^{\circ(\mathrm{m})} + RT \ln\left(\frac{\gamma_i^{(\mathrm{m})} m_i}{m^\circ}\right)} \tag{6.3-40}$$

Since $x_1 \approx 1$ in dilute solutions, the molality activity coefficient and the mole fraction activity coefficient are nearly equal to each other in a dilute solution.

Equation (6.3-40) is the same as Eq. (6.2-12) except for the presence of the activity coefficient. All that is needed to convert an expression for a dilute solution into one for an arbitrary solution is to insert the activity coefficient.

The Concentration Description

The molar concentration is given by

$$c_i = \frac{n_i}{V} = \frac{n_i}{nV_\mathrm{m}} = \frac{x_i}{V_\mathrm{m}} \tag{6.3-41}$$

where $V_\mathrm{m} = V/n$ is the *mean molar volume* (n is the total amount of all substances). We want to write an equation of the form

$$\boxed{\mu_i = \mu_i^{\circ(\mathrm{c})} + RT \ln\left(\frac{\gamma_i^{(\mathrm{c})} c_i}{c^\circ}\right)} \tag{6.3-42}$$

so that the activity in the concentration description is

$$a_i^{(\mathrm{c})} = \frac{\gamma_i^{(\mathrm{c})} c_i}{c^\circ} \tag{6.3-43}$$

where c° is defined to be exactly equal to $1\ \mathrm{mol\,L^{-1}}$ or $1\ \mathrm{mol\,m^{-3}}$. Equation (6.3-42) is valid if

$$\mu_i^{\circ(\mathrm{c})} = \mu_i^{(\mathrm{II})} + RT \ln(V_{\mathrm{m},1}^* c^\circ) \tag{6.3-44}$$

and

$$\boxed{\gamma_i^{(\mathrm{c})} = \frac{\gamma_i^{(\mathrm{II})} V_\mathrm{m}}{V_{\mathrm{m},1}^*}} \tag{6.3-45}$$

The standard-state chemical potential is that of a solute with a concentration equal to $1\ \mathrm{mol\,L^{-1}}$ or $1\ \mathrm{mol\,m^{-3}}$ and obeying Henry's law in the concentration description, as in Eq. (6.2-16).

In all of our descriptions, a solvent is treated in the same way as in convention I. Its activity is always its mole fraction times its activity coefficient and its standard state is the pure liquid:

$$a_1 = \gamma_1 x_1 \quad (1 = \text{solvent, all descriptions}) \tag{6.3-46}$$

Since the activities and activity coefficients of a solute in two different descriptions are not necessarily equal to each other, we have attached superscripts to specify which description is being used. We will sometimes omit these superscripts, relying on the context to make clear which description is being used. In a sufficiently dilute solution, the activity coefficients in all of these descriptions approach each other in value.

PROBLEMS

Section 6.3: Activity and Activity Coefficients

6.23 Assume that a 1.000 mol kg^{-1} solution of naphthalene in benzene is ideal. Calculate the value of the activity coefficient of naphthalene in the molality description and in the concentration description.

6.24 Find the activity of pure liquid water at 1250 bar and 25°C.

6.25 Find the activity coefficient of gaseous nitrogen at 298.15 K and 20.00 atm, using whatever information you need from earlier chapters of this book.

6.26 Find the activity of graphite and that of diamond at the coexistence pressure at 298.15 K. Assume that the molar volumes are constant.

6.27 In a certain binary mixture, the vapor pressure of substance 2 is given by

$$\begin{aligned} P_2 &= (0.689\ \text{atm})x_2 \text{ if } x_2 \le 0.100 \\ P_2 &= (0.754\ \text{atm})x_2 \text{ if } 0.95 \le x_2 \\ P_2 &= 0.435\ \text{atm if } x_2 = 0.600 \end{aligned}$$

a. Find the Henry's law constant k_2.

b. Find the vapor pressure of pure substance 2.

c. Find the activity and activity coefficient of substance 2 at $x_2 = 0.0500, 0.600$, and 0.95 by convention I and by convention II, treating substance 2 as a solute.

6.28 Naphthalene is a solid near room temperature, but it forms a nearly ideal liquid solution with benzene or with toluene. Show that the mole fraction of naphthalene in a solution that is equilibrated with solid naphthalene (a saturated solution) has the same mole fraction of naphthalene, whether the solvent is benzene or toluene.

6.29 **a.** From data on enthalpy changes of formation in Table A.8, find the standard-state differential heat of solution of KOH at 298.15 K.

b. From data on Gibbs energy changes of formation in Table A.8, find the value of $\mu_i^{\circ(\text{m})} - G_m^{*(\text{solid})}$ for KOH at 298.15 K.

6.30 **a.** From data in Problem 6.39, find the activity coefficient of chloroform in acetone for the solution of Problem 6.39, using the molality description and regarding acetone as the solvent.

b. Find the activity coefficient of acetone in the solution of Problem 6.39, using the molality description and regarding acetone as the solvent.

6.31 A *regular solution* is one for which the Gibbs energy is given by

$$G(T, P, n_1, n_2) = n_1 G^{\circ}_{\text{m},1} + n_2 G_{\text{m},2^{\circ}} + RTn_1 \ln(x_1) + n_2 \ln(x_2) + w\frac{n_1 n_2}{n_1 + n_2}$$

where w depends only on P and T.

a. Find the expression for μ_1, the chemical potential of substance 1. Write the expression for μ_2 by analogy with your expression for μ_1.

b. Show that your expressions conform to Euler's theorem.

6.32 The maximum solubility of I_2 in water at 1.000 atm and 298.15 K is equal to 1.42×10^{-3} mol kg^{-1}. Find the value of $\mu_i^{\circ(\text{m})} - \mu^{*(\text{solid})}$ for I_2. State any assumptions.

6.33 Assume that the activity of the solvent in a two-component solution obeys the formula

$$\ln(a_1) = \ln(x_1) + \sum_{n=1}^{\infty} C_n x_2^n$$

where the C's are constants. Derive an expression for the activity coefficient of substance 2, using convention II.

6.34 In a certain solution, the activity of substance 1 (the solvent) is given by

$$\ln(a_1) = \ln(x_1) + Bx_2^2$$

where B is a constant. Derive an expression for a_2 using convention II.

6.4 The Activities of Nonvolatile Solutes

For a nonvolatile substance we must find a way to determine its activity coefficient that does not depend on measuring its vapor pressure. We will discuss three different methods. The first is through integration of the Gibbs–Duhem equation. The second is through a theory due to Debye and Hückel, which can be applied to electrolyte solutes. The third method for electrolyte solutes is an electrochemical method, which we will discuss in Chapter 8. Published data are available for common electrolytes, and some values are included in Table A.11 in Appendix A.

The Gibbs–Duhem Integration

For a two-component solution with a volatile solvent such as water and a nonvolatile solute, values of the activity of the solvent can be determined for several values of the solvent mole fraction between unity and the composition of interest. Integration of the Gibbs–Duhem relation can then give the value of the activity coefficient of the solute. The activity of the solvent is usually determined using the *isopiestic method*. The solution of interest and a solution of a well-studied nonvolatile reference solute in the same solvent are placed in a closed container at a fixed temperature. A solution of KCl is usually used as the reference solute for aqueous solutions, since accurate water activity coefficient data are available for KCl solutions. The solutions are left undisturbed at constant temperature until enough solvent has evaporated from one solution and condensed into the other solution to equilibrate the solvent in the two solutions.

At equilibrium, the activity of solvent (substance 1) in the solution of interest (solution B) is equal to the activity of solvent in the reference solution (solution A), so that

$$\gamma_1^{(B)} = \frac{a_1^{(B)}}{x_1^{(B)}} = \frac{a_1^{(A)}}{x_1^{(B)}} = \frac{\gamma_1^{(A)} x_1^{(A)}}{x_1^{(B)}} \tag{6.4-1}$$

The solutions are analyzed to determine the mole fractions of the solvent in the two solutions, and the activity of the solvent in the reference solution is determined from tabulated values. The activity of the solvent in the unknown solution is equal to this value. The experiment is repeated several times for a range of compositions of solution B beginning with pure solvent and extending to $x_2 = x_2'$, the composition at which we want the value of γ_2.

For constant pressure and temperature, the Gibbs–Duhem relation for two components is given by Eq. (4.6-11). When we substitute Eq. (6.3-6) into this equation, we obtain

$$x_1 RTd\ln(a_1) + x_2 RTd\ln(a_2) = 0 \tag{6.4-2}$$

Using convention II, $a_1 = \gamma_1 x_1$ and $a_2 = \gamma_2 x_2$, where we omit the superscript (II). Using the fact that $x_i d\ln(x_i) = dx_i$, we obtain

$$x_1 RTd\ln(\gamma_1) + RTdx_1 + x_2 RTd\ln(\gamma_2) + RTdx_2 = 0$$

Since $x_1 + x_2 = 1$, $dx_1 + dx_2 = 0$, and two terms cancel. We divide by x_2RT and obtain the equation

$$d\ln(\gamma_2) = -\frac{x_1}{x_2}d\ln(\gamma_1) = -\frac{x_1}{1 - x_1}d\ln(\gamma_1) \tag{6.4-3}$$

We integrate Eq. (6.4-3) from $x_1 = x_1''$ to $x_1 = x_1'$ (the composition we are interested in). The lower limit x_1'' cannot be taken equal to unity, because the denominator $1 - x_1$ goes to zero in this case. We choose a value of x_1'' close enough to unity that Raoult's law is obeyed by the solvent. At this composition the solute obeys Henry's law and γ_2 is equal to unity. Integration of Eq. (6.4-3) gives

$$\ln\gamma_2(x_1') = -\int_{x_1=x_1''}^{x_1=x_1'} \frac{x_1}{1 - x_1}d\ln(\gamma_1) \tag{6.4-4}$$

where we consider both γ_2 and γ_1 to be functions of x_1. Unless the data are fit to some formula this integral is approximated numerically.

In the case of an electrolyte solute the Gibbs–Duhem integration is carried out in a slightly different way. Consider an electrolyte solute represented by the formula $M_{\nu_+}X_{\nu_-}$, where ν_+ and ν_- represent the numbers of cations and anions in its formula. In the case of $CaCl_2$, $\nu_+ = 1$ and $\nu_- = 2$. The total number of ions in the formula is denoted by ν, equal to $\nu_+ + \nu_-$. The substance must be electrically neutral:

$$\nu_+z_+ + \nu_-z_- = 0 \tag{6.4-5}$$

where z_+ is the valence of the cation and z_- is the *valence* of the anion. The valence is the number of proton charges on an ion. It is positive for a cation and negative for an anion.

It is impossible to measure the chemical potential of an ion since ions of one charge cannot be added without adding ions of the opposite charge at the same time. The (unmeasurable) chemical potential of the cation is given by

$$\mu_+ = \mu_+^\circ + RT\ln(\gamma_+m_+/m^\circ)$$

and that of the anion is given by

$$\mu_- = \mu_-^\circ + RT\ln(\gamma_-m_-/m^\circ)$$

Since these chemical potentials cannot be measured, we must define the chemical potential of the neutral electrolyte solute. This is discussed in Chapter 7, but we anticipate the result, which is that the chemical potential of the neutral electrolyte solute (substance number 2) is given by

$$\begin{aligned}\mu_2 &= \nu_+\mu_+ + \nu_-\mu_- \\ &= \nu_+\mu_+^\circ + RT\ln(\gamma_+m_+/m^\circ) + \nu_-\mu_-^\circ + RT\ln(\gamma_-m_-/m^\circ) \\ &= \nu_+\mu_+^\circ + \nu_-\mu_-^\circ + RT\ln\left(\gamma_+^{\nu_+}\gamma_-^{\nu_-}m_+^{\nu_+}m_-^{\nu_-}/m^{\circ\nu}\right)\end{aligned}$$

This is a measurable quantity since the neutral electrolyte substance can be added while keeping the amounts of all other substances fixed.

In order to write equations that apply to all electrolyte solutes, we define the *mean ionic activity coefficient*

$$\gamma_\pm = \left(\gamma_+^{\nu_+}\gamma_-^{\nu_-}\right)^{1/\nu} \tag{6.4-6}$$

and the *mean ionic molality*

$$m_\pm = \left(m_+^{\nu_+} m_-^{\nu_-}\right)^{1/\nu} \tag{6.4-7}$$

These are examples of *geometric means*. For a 1-3 electrolyte such as $CrCl_3$, $m_\pm$ is equal to $(27)^{1/4} m_2 = 2.2795 m_2$, where m_2 is the *stoichiometric molality* of the solute (the molality that would occur if no dissociation occurred). The chemical potential of the neutral electrolyte solute is given by

$$\begin{aligned} \mu_2 &= \nu_+\mu_+^\circ + \nu_-\mu_-^\circ + RT\ln(\gamma_\pm^\nu (m_\pm/m^\circ)^\nu) \\ &= \nu_+\mu_+^\circ + \nu_-\mu_-^\circ + \nu RT\ln(\gamma_\pm m_\pm/m^\circ) \end{aligned} \tag{6.4-8}$$

The activity of the solvent can be expressed in terms of the *osmotic coefficient* ϕ, defined by

$$\phi = -\frac{\ln(a_1)}{M_1 \nu m_2} = \frac{\mu_1^\circ - \mu_1}{RTM_1 \nu m_2} \quad \text{(definition)} \tag{6.4-9}$$

where a_1 is the activity of the solvent, and M_1 is the molar mass of the solvent. If the solute dissociates completely, νm_2 is equal to the sum of the molalities of the ions. From Eq. (6.4-9)

$$\mu_1 = \mu_1^\circ - RTM_1 \nu m_2 \phi \tag{6.4-10}$$

The chemical potential of the solute can be written

$$\mu_2 = \mu_2^\circ + \nu RT \ln(\gamma_\pm \nu_\pm m_2/m^\circ) \tag{6.4-11}$$

where

$$\gamma_\pm = \left(\gamma_+^{\nu_+} \gamma_-^{\nu_-}\right)^{1/\nu} \tag{6.4-12}$$

For constant pressure and temperature, the Gibbs–Duhem relation for a two-component system is written in the form

$$n_1 d\mu_1 + n_2 d\mu_2 = 0 \tag{6.4-13}$$

Since the molality m_2 is equal to the amount of substance 2 divided by the mass of the solvent (substance 1),

$$n_2 = m_2 n_1 M_1 \tag{6.4-14}$$

where M_1 is the molar mass of the solvent. Use of Eqs. (6.4-10), (6.4-11), and (6.4-14) in Eq. (6.4-13) gives

$$-n_1 \nu RTM_1 m_2 d\phi + \phi dm_2 + m_2 n_1 M_1 \nu RT d\ln(\gamma_2) + d\ln(m_2/m^\circ) = 0$$

Cancellation of the common factor and use of the identity

$$d\ln(m) = (1/m)dm$$

gives

$$-m_2 d\phi - \phi dm_2 + m_2 d\ln(\gamma_2) + dm_2 = 0 \tag{6.4-15}$$

which is the same as

$$d\ln(\gamma_2) = d\phi + \frac{\phi - 1}{m_2}dm_2 \tag{6.4-16}$$

If data for the osmotic coefficient are available over this molality range, Eq. (6.4-16) can be integrated from $m_2 = 0$ to $m_2 = m_2'$, a particular value of m_2:

$$\int_{m_2=0}^{m_2=m_2'} d\ln(\gamma_2) = \int_{m_2=0}^{m_2=m_2'} d\phi + \int_0^{m_2'} \frac{\phi - 1}{m_2}dm_2 \tag{6.4-17}$$

The integral on the left-hand side of this equation yields zero at its lower limit, since the activity coefficient approaches unity as m_2 approaches 0. It can be shown that ϕ approaches unity as m_2 approaches zero, so that the integral converges and we can write

$$\ln(\gamma_2(m_2')) = \phi(m_2') - 1 + \int_0^{m_2'} \frac{\phi - 1}{m_2}dm_2 \tag{6.4-18}$$

The integral is approximated numerically from the data, giving the value of γ_2 at m_2'.

Exercise 6.16

Using the relation $x_1 = 1 - x_2 = 1 - n_2/n_1$ at high dilution, show that ϕ approaches 1 as m_2 approaches 0.

The Debye–Hückel Theory

This is a theory for the activity coefficients of dilute electrolyte solutes. Ions exert large forces on each other, and these forces are called *long-range forces* because they act over large distances compared with other intermolecular forces. The electrostatic force on a charge Q_1 due to a charge Q_2 is given by *Coulomb's law*,

Coulomb's law is named for Charles Augustin de Coulomb, 1736–1806, the French physicist who discovered the law.

$$\mathbf{F}_{12} = \mathbf{e}_r \frac{Q_1 Q_2}{4\pi\varepsilon r_{12}^2} \tag{6.4-19}$$

where r_{12} is the distance between the charges and where the unit vector $\mathbf{e}_r$ points from object 1 toward object 2. If the two charges have the same sign the force is a repulsion, and if they have opposite signs the force is an attraction. The quantity ε is the *permittivity* of the medium between the charges. The permittivity of a vacuum is denoted by ε_0 and is equal to 8.854519×10^{-12} C^2 N^{-1} m^{-2}. The ratio of the permittivity of a given material to that of a vacuum is called the *dielectric constant* and is denoted by ε_{rel}:

$$\varepsilon_{\text{rel}} = \frac{\varepsilon(\text{material})}{\varepsilon_0} \tag{6.4-20}$$

The dielectric constant of water is larger than that of most substances and at 25°C is equal to 78.54. Even though the electrostatic forces between ions in an aqueous solution are weaker than those in a vacuum by the reciprocal of this factor, the electrostatic forces between ions in a solution are strong compared with other intermolecular forces, and they act over a large distance compared to other intermolecular forces.

Debye and Hückel devised a theory for the activity coefficients of ionic solutes. Their theory begins with the expression for the force between a pair of ions in Eq. (6.4-19), assuming a constant value of the permittivity of the solvent. It is also assumed that the centers of two ions cannot approach each other more closely than some distance of closest approach, called a. The solution is assumed to behave like an ordinary dilute solution except for the effects of the electrostatic forces.

The Debye–Hückel theory was devised by Peter J. W. Debye, 1884–1966, a Dutch-American physicist and chemist who received the Nobel Prize for chemistry in 1936 for his work on the dipole moments of molecules, and Erich Hückel, 1896–1980, a German chemist who is also known for an approximation scheme used in molecular quantum mechanics.

We will not discuss the details of the Debye–Hückel theory.[2] The main idea of the theory was to pretend that the ions in a solution could have their charges varied reversibly from zero to their actual values. This charging process created an *ion atmosphere* around a given ion with an excess of ions of the opposite charge. The reversible net work of creating the ion atmosphere was calculated from electrostatic theory. According to Eq. (4.1-32) the reversible net work is equal to ΔG, which leads to equations for the electrostatic contribution to the chemical potential and the activity coefficient for the central ion. The principal result of the Debye–Hückel theory is a formula for the activity coefficient of ions of type i:

$$\ln(\gamma_i) = -\frac{z_i^2 \alpha I^{1/2}}{1 + \beta a I^{1/2}} \tag{6.4-21}$$

where z_i is the valence of the ion (the number of proton charges on the ion). The quantities α and β are functions of temperature, and of the properties of the solvent:

$$\alpha = (2\pi N_{\mathrm{Av}} \rho_1)^{1/2} \left(\frac{e^2}{4\pi\varepsilon k_{\mathrm{B}} T} \right) \tag{6.4-22}$$

$$\beta = e \left[\frac{2 N_{\mathrm{Av}} \rho_1}{\varepsilon k_{\mathrm{B}} T} \right] \tag{6.4-23}$$

where e is the charge on a proton, N_{Av} is Avogadro's constant, ρ_1 is the density of the solvent, k_{B} is Boltzmann's constant (equal to R/N_{Av}), T is the absolute temperature, and ε is the permittivity of the solvent. The quantity I is the *ionic strength*, defined as a sum over all of the s different charged species in the solution:

$$I = \frac{1}{2} \sum_{i=1}^{s} m_i z_i^2 \quad \text{(definition of ionic strength)} \tag{6.4-24}$$

where m_i is the molality of species i and z_i is its valence. All of the ions in the solution must be included in the ionic strength. The formula in Eq. (6.4-21) is for the activity coefficient in the molality description, but for a relatively dilute solution it can be used for the activity coefficient in the concentration description.

EXAMPLE 6.13

Calculate the ionic strength of a solution that is 0.100 mol kg^{-1} in NaCl and 0.200 mol kg^{-1} in $\mathrm{CaCl_2}$. Assume complete dissociation.

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[2] An account of the development is found in T. L. Hill, *Statistical Thermodynamics*, Addison-Wesley, Reading, MA, 1960, pp. 321ff. The original reference is P. Debye and E. Hückel, *Physik. Z.*, **24**, 185 (1923).

Solution

$$\begin{aligned} I &= \frac{1}{2}\left[m\left(\mathrm{Na}^{+}\right)(+1)^2 + m(\mathrm{Ca}^{2+})(+2)^2 + m(\mathrm{Cl}^{-})(-1)^2\right] \\ &= \frac{1}{2}\left(0.100\,\mathrm{mol\,kg^{-1}}\right) + \left(0.200\,\mathrm{mol\,kg^{-1}}\right)\left(2^2\right) + \left(0.500\,\mathrm{mol\,kg^{-1}}\right) \\ &= 0.700\,\mathrm{mol\,kg^{-1}} \end{aligned}$$

Notice the large contribution of a multiply charged ion such as Ca^{2+}.

Exercise 6.17

Calculate the ionic strength of a solution that is $0.150\,\mathrm{mol\,kg^{-1}}$ in K_2SO_4 and $0.050\,\mathrm{mol\,kg^{-1}}$ in Na_2SO_4. Assume complete dissociation.

Exercise 6.18

Show that for water at 298.15 K, the value of α is

$$\alpha = 1.171\,\mathrm{kg^{1/2}\,mol^{-1/2}} \quad \text{(in water, 298.15 K)} \tag{6.4-25}$$

The density of water at 298.15 K is equal to $997.14\,\mathrm{kg\,m^{-3}}$.

Exercise 6.19

Show that for water at 298.15 K,

$$\beta = 3.281 \times 10^9\,\mathrm{kg^{1/2}\ mol^{-1/2}\,m^{-1}} \quad \text{(in water, 298.15 K)} \tag{6.4-26}$$

The density of water at 298.15 K is equal to $997.14\,\mathrm{kg\,m^{-3}}$.

We must convert Eq. (6.4-21) to an equation for the activity coefficient of a neutral electrolyte. Using the definition of the mean ionic activity coefficient and the requirement of electrical neutrality, we write Eq. (6.4-21) once for the cation and once for the anion and combine them using Eq. (6.4-6) to obtain

$$\ln(\gamma_{\pm}) = -z_{+}|z_{-}|\frac{\alpha I^{1/2}}{1 + \beta a I^{1/2}} \tag{6.4-27}$$

Exercise 6.20

Carry out the algebraic steps to obtain Eq. (6.4-27).

EXAMPLE 6.14

Calculate the value of $\gamma_{\pm}$ for a 0.0100 mol kg^{-1} solution of NaCl in water at 298.15 K. Assume that the distance of closest approach is 3.05×10^{-10} m, which gives a value of βa equal to 1.00 kg$^{1/2}$ mol$^{-1/2}$.

Solution

$$\ln(\gamma_{\pm}) = -\frac{\left(1.171\ \mathrm{kg}^{1/2}\ \mathrm{mol}^{-1/2}\right)\left(0.01\ \mathrm{mol\ kg}^{-1}\right)^{1/2}}{1+\left(1.00\ \mathrm{kg}^{1/2}\ \mathrm{mol}^{-1/2}\right)\left(0.01\ \mathrm{mol\ kg}^{-1}\right)^{1/2}} = -0.1065$$

$$\gamma_{\pm} = 0.899$$

The Debye–Hückel result has been shown experimentally to be an accurate *limiting law*. That is, it becomes more nearly exact as the concentration approaches zero. In practice, it is sufficiently accurate for ionic strengths up to 0.01 mol kg^{-1}, but is not necessarily accurate for larger ionic strengths. Figure 6.10 shows experimental values of the mean ionic activity coefficient of several electrolyte solutes in water at 298.15 K as a function of $\sqrt{m}$. The correct limiting behavior is shown by the fact that the curves of each set of ions with the same value of $z_+|z_-|$ approach unity with the slope that is given by the Debye–Hückel theory.

If $a \approx 3.0 \times 10^{-10}$ m, then $\beta a \approx 1.00$ kg$^{1/2}$ mol$^{-1/2}$ and we can write an approximate equation

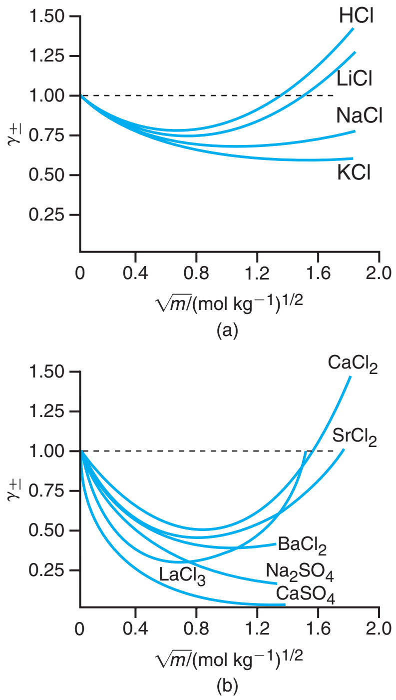
$$\ln(\gamma_{\pm}) = -z_+|z_-|\frac{\alpha I^{1/2}}{1+(I/m^{\circ})^{1/2}} \tag{6.4-28}$$

where $m^{\circ} = 1$ mol kg^{-1}(exactly). For small values of the ionic strength the $\beta a I^{1/2}$ term in the denominator of Eq. (6.4-27) is relatively small compared with unity and can be neglected. The resulting equation is similar to the first term in an empirical equation of Brønsted that predated the theory of Debye and Hückel.[3] For a 1-1 electrolyte like NaCl, this equation is

$$\ln(\gamma_{\pm}) = -am^{1/2} + bm \quad \text{(1-1 electrolyte)} \tag{6.4-29}$$

where m is the molality of the solute (note that $m = I$ for a 1-1 electrolyte) and where a and b are constants.

Much of the disagreement of the Debye–Hückel result with experiment for moderate concentrations has been attributed to the formation of *ion pairs*, which consist of two ions of opposite charge held together by electrostatic attraction.[4] These ion pairs are not chemically bonded like complex ions such as $AgCl_2^-$, and the two ions can have solvent molecules between them. Much work has been done to extend the Debye–Hückel theory, beginning in 1926 with a theory of Bjerrum[5] that explicitly included ion pairing. Some later research is based on theoretical work of Mayer,[6] in which



(a)

(b)

Figure 6.10 The Mean Ionic Activity Coefficients of Several Electrolyte Solutes as a Function of the Square Root of the Ionic Strength.

Johannes Nicolas Brønsted, 1879–1947, was a Danish physical chemist who made various contributions, including the Brønsted–Lowry definition of acids and bases. He was elected to the Danish parliament in 1947, but died before taking office.

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[3] J. N. Brønsted, *J. Am. Chem. Soc.*, **44**, 938 (1922).

[4] See R. W. Clark and J. M. Bonicamp, *J. Chem. Educ.*, **75**, 1182 (1998) for a discussion of the inclusion of this and other factors in solubility equilibria.

[5] N. Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, 9 (1926).

[6] J. E. Mayer, *J. Chem. Phys.*, **18**, 1426 (1950); K. S. Pitzer, *Acc. Chem. Res.*, 1**0**, 317, (1977).

the Debye–Hückel result appears as the leading term of a series containing powers and logarithms of the ionic strength. The work of Mayer gives some credibility to the Brønsted equation and to an equation of Guggenheim:[7]

$$\ln(\gamma_\pm) = -z_+|z_-|\frac{\alpha I^{1/4}}{1+(I/m^\circ)^{1/2}} + \frac{2v_+v_-}{v}bm \tag{6.4-30}$$

Joseph E. Mayer, 1904–1983, was a prominent American physical chemist who was well known for a textbook in statistical mechanics that he coauthored with his wife, Maria Goeppert Mayer, 1906–1972, who was one of the 1963 Nobel Prize winners in physics for her work on the shell theory of nuclei.

where b is a parameter that is evaluated experimentally for each electrolyte solute, not necessarily equal to the constant in Brønsted's theory. The *Davies equation*[8] is a generalized version of Guggenheim's equation. For water as the solvent and for a temperature of 298.15 K, the Davies equation is

$$\boxed{\log_{10}(\gamma_\pm) = -0.510z_+|z_-|\left[\frac{(I/m^\circ)^{1/2}}{1+(I/m^\circ)^{1/2}} - 0.30\frac{I}{m^\circ}\right]} \tag{6.4-31}$$

This equation can be used when no experimental information is available. In some cases it can give usable results for activity coefficients up to ionic strengths of 0.5 mol kg^{-1} or beyond, but it is ordinarily in error by several percent in this region. Table A.11 in Appendix A gives experimental values of the mean ionic activity coefficients of several aqueous electrolytes at various concentrations. It also gives the predictions of the Debye–Hückel formula with βa taken equal to 1.00 kg$^{1/2}$ mol$^{-1/2}$, and of the Davies equation.

EXAMPLE 6.15

Calculate the activity coefficient for the solution of Example 6.14 using the Davies equation. Find the percent difference between the result of the Davies equation and that of the Debye–Hückel limiting law.

$$\log_{10}(\gamma_\pm) = -0.510\left(\frac{(0.0100)^{1/2}}{1+(0.0100)^{1/2}} - (0.30)(0.0100)\right) = 4.48\times10^{-2}$$

$$\gamma_\pm = 0.902$$

$$\%\text{ difference} = \frac{0.902-0.899}{0.899}\times 100\% = 0.3\%$$

Exercise 6.21

Calculate the activity coefficient for an aqueous solution of NaCl with molality 0.250 mol kg^{-1} at 298.15 K using the Davies equation. Find the percent difference between the result of the Davies equation and that of the Debye–Hückel limiting law.

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[7] E. A. Guggenheim, *Phil. Mag.*, **19**, 588 (1935); E. A. Guggenheim and J. C. Turgeon, *Trans. Faraday Soc.*, **51**, 747 (1955).

[8] C. W. Davies, *Ion Association*, Butterworth, London, 1962, pp. 35–52.

PROBLEMS

Section 6.4: The Activities of Nonvolatile Solutes

6.35 **a.** Look up the value of the dielectric constant and density for methanol. Calculate the values of the Debye–Hückel parameters α and β for methanol as the solvent at 298.15 K.

b. Calculate the value of $\gamma_{\pm}$ for a 0.0100 mol kg^{-1} NaCl solution in methanol at 298.15 K. Calculate the percent difference between this value and that in water at the same temperature and molality.

6.36 **a.** Calculate the value of $\gamma_{\pm}$ for a 0.0075 mol kg^{-1} KCl solution at 298.15 K using the Debye–Hückel formula, Eq. (6.4-27), and using a value of βa equal to 1.00 kg$^{1/2}$ mol$^{-1/2}$. Repeat the calculation for a 0.0075 mol kg^{-1} FeSO$_4$ solution at the same temperature, using the same value of βa.

b. Repeat the calculations of part a using the Davies equation. Calculate the percent difference between each value in part a and the corresponding value in part b.

6.37 **a.** Make a plot of $\gamma_{\pm}$ as a function of the molality for a 1-1 electrolyte at 298.15 K, using the Davies equation. Compare your graph with that of Figure 6.10 and comment on any differences.

b. Make a plot of $\gamma_{\pm}$ as a function of the molality for a 1-2 electrolyte at 298.15 K, using the Davies equation. Compare your graph with that of Figure 6.10 and comment on any differences.

c. Make a plot of $\gamma_{\pm}$ as a function of the molality for a 2-2 electrolyte at 298.15 K, using the Davies equation. Compare your graph with that of Figure 6.10 and comment on any differences.

6.38 Find the activity coefficient of a 0.200 mol kg^{-1} solution of NaCl in water at 298.15 K, using (a) the Debye–Hückel equation and (b) the Davies equation. Which is more nearly correct for this molality? The experimental value is found in Table A.11 of the appendix.

6.5

Thermodynamic Functions of Nonideal Solutions

We begin with the expression for the chemical potential of a component of a nonideal solution, using convention I:

$$\mu_i = \mu_i^* + RT\ln(a_i) = \mu_i^* + RT\ln\left(\gamma_i^{(\mathrm{I})}x_i\right) \tag{6.5-1}$$

Manipulation of this equation allows us to obtain formulas for all of the thermodynamic variables for a nonideal solution.

Partial Molar Quantities in Nonideal Solutions

An expression for the partial molar entropy can be obtained by use of Eq. (4.5-14):

$$\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n'} = \overline{S}_i = -\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n} \tag{6.5-2}$$

$$\overline{S}_i = -\left(\frac{\partial \mu_i^*}{\partial T}\right)_{P,n} - R\ln\left(\gamma_i^{(\mathrm{I})}x_i\right) - RT\left(\frac{\partial \ln\left(\gamma_i^{(\mathrm{I})}x_i\right)}{\partial T}\right)_{P,n}$$

$$= S^*_{\mathrm{m},i} - R\ln(x_i) - R\ln\left(\gamma_i^{(\mathrm{I})}\right) - RT\left(\frac{\partial \ln\left(\gamma_i^{(\mathrm{I})}\right)}{\partial T}\right)_{P,n}$$

$$= \overline{S}_i^{(\mathrm{ideal})} - R\ln\left(\gamma_i^{(\mathrm{I})}\right) - RT\left(\frac{\partial \ln\left(\gamma_i^{(\mathrm{I})}\right)}{\partial T}\right)_{P,n} \tag{6.5-3}$$

The partial molar enthalpy is given by

$$\overline{H}_i = \mu_i + T\overline{S}_i$$

$$= \mu_i^* + RT\ln\left(\gamma_i^{(\mathrm{I})}x_i\right) + T\left[S^*_m(i) - R\ln\left(x_i\gamma_i^{(\mathrm{I})}\right) - RT\left(\frac{\partial \ln\left(\gamma_i^{(\mathrm{I})}\right)}{\partial T}\right)_{P,n}\right]$$

$$= H^*_{\mathrm{m},i} - RT^2\left(\frac{\partial \ln\left(\gamma_i^{(\mathrm{I})}\right)}{\partial T}\right)_{P,n} \tag{6.5-4}$$

An expression for the partial molar volume is

$$\overline{V}_i = V^*_{\mathrm{m},i} + RT\left(\frac{\partial \ln\left(\gamma_i^{(\mathrm{I})}\right)}{\partial P}\right)_{T,n} \tag{6.5-5}$$

Exercise 6.22

Carry out the steps to obtain Eq. (6.5-5).

The partial molar quantities can also be expressed in terms of the activity coefficients using convention II, the molality description, or the concentration description.

Exercise 6.23

Write an expression for the partial molar entropy of a component of a solution using the molality description.

Thermodynamic Functions of Nonideal Solutions

The thermodynamic functions of solutions are generally expressed in terms of the changes produced by mixing the pure components to form the solution at constant temperature and pressure. From Euler's theorem and Eq. (6.3-6), the Gibbs energy of a nonideal solution is given by

$$G(\mathrm{soln}) = \sum_{i=1}^{c} n_i\left[\mu_i^{\circ(\mathrm{I})} + RT\ln\left(a_i^{(\mathrm{I})}\right)\right] \tag{6.5-6}$$

For convention I the standard states are the pure components, so that

$$G(\text{unmixed}) = \sum_{i=1}^{c} n_i \mu_i^* = \sum_{i=1}^{c} n_i \mu_i^{\circ(\mathrm{I})} \tag{6.5-7}$$

where we neglect a small difference between μ_i^* and μ_i° due to a possible difference of the pressure from P°. The change in Gibbs energy for producing the solution (the *Gibbs energy change of mixing*) is

$$\Delta G_{\mathrm{mix}} = \sum_{i=1}^{c} n_i \mu_i^* + RT \sum_{i=1}^{c} n_i \ln\left(a_i^{(\mathrm{I})}\right) - \sum_{i=1}^{c} n_i \mu_i^*$$

$$\Delta G_{\mathrm{mix}} = RT \sum_{i=1}^{c} n_i \ln\left(a_i^{(\mathrm{I})}\right) = RT \sum_{i=1}^{c} n_i \ln(x_i) + RT \sum_{i=1}^{c} n_i \ln\left(\gamma_i^{(\mathrm{I})}\right) \tag{6.5-8}$$

The first sum in the right-hand side of the final version of this equation is the same as for an ideal solution, and the second sum represents a correction for the nonideality of the solution. This contribution is called the *excess Gibbs energy* and is denoted by G^{E}:

$$\Delta G_{\mathrm{mix}} = \Delta G_{\mathrm{mix}}^{(\mathrm{ideal})} + G^{\mathrm{E}} \tag{6.5-9}$$

so that

$$G^{\mathrm{E}} = RT \sum_{i=1}^{c} n_i \ln\left(\gamma_i^{(\mathrm{I})}\right) \tag{6.5-10}$$

The *excess entropy* can be defined for a nonideal solution:

$$S^{\mathrm{E}} = \Delta S_{\mathrm{mix}} - \Delta S_{\mathrm{mix}}^{(\mathrm{ideal})} \tag{6.5-11}$$

The *excess enthalpy* and the *excess volume* are equal to the mixing quantities, since ΔH_{mix} and ΔV_{mix} both vanish for an ideal solution.

Exercise 6.24

a. Show that

$$S^{\mathrm{E}} = -R \sum_{i=1}^{c} n_i \ln \gamma_i^{(\mathrm{I})} - RT \sum_{i=1}^{c} n_i \left(\frac{\partial \ln\left(\gamma_i^{(\mathrm{I})}\right)}{\partial T}\right)_{P,n} \tag{6.5-12}$$

b. Show that

$$H^{\mathrm{E}} = \Delta H_{\mathrm{mix}} = -RT^2 \sum_{i=1}^{c} n_i \left(\frac{\partial \ln\left(\gamma_i^{(\mathrm{I})}\right)}{\partial T}\right)_{P,n} \tag{6.5-13}$$

c. Show that

$$V^{\mathrm{E}} = \Delta V_{\mathrm{mix}} = RT \sum_{i=1}^{c} n_i \left(\frac{\partial \ln\left(\gamma_i^{(\mathrm{I})}\right)}{\partial P}\right)_{T,n} \tag{6.5-14}$$

The expressions for ΔG_{mix}, ΔS_{mix}, and ΔV_{mix} can be expressed in terms of the activity coefficients using convention II, the molality description, or the concentration description.

Exercise 6.25

Write an expression for ΔG_{mix} using convention II activity coefficients.

The enthalpy change of mixing is often expressed in terms of the *heat of solution* or *enthalpy change of solution*. For a two-component solution, the *molar integral heat of solution* of component 1 in a solution with component 2 is defined by

$$\Delta H_{\text{int},1} = \frac{\Delta H_{\text{mix}}}{n_1} \tag{6.5-15}$$

and the molar integral heat of solution of component 2 is defined by

$$\Delta H_{\text{int},2} = \frac{\Delta H_{\text{mix}}}{n_2} \tag{6.5-16}$$

The same enthalpy change of mixing occurs in both equations, but it is divided by the amount of a different substance in each case.

EXAMPLE 6.16

If 2.000 mol of ethanol (substance 2) and 10.000 mol of water (substance 1) are mixed at a constant temperature of 298.15 K and a constant pressure of 1.000 atm, the enthalpy change is equal to −9.17 kJ. Find the molar integral heat of solution of ethanol in 5.000 mol of water and the molar integral heat of solution of water in 0.200 mol of ethanol.

Solution

$$\Delta H_{\text{int},2} = -\frac{9.17\,\text{kJ}}{2.00\,\text{mol}} = -4.58\,\text{kJ mol}^{-1}$$
$$\Delta H_{\text{int},1} = -\frac{9.17\,\text{kJ}}{10.00\,\text{mol}} = -0.917\,\text{kJ mol}^{-1}$$

Using Euler's theorem for a two-component system,

$$\Delta H_{\text{mix}} = n_1\bar{H}_1 + n_2\bar{H}_2 - \left(n_1 H^*_{\text{m},1} + n_2 H^*_{\text{m},2}\right) \tag{6.5-17}$$

the integral heat of solution of a component of a two-component solution can be written in terms of the partial molar enthalpies:

$$\begin{aligned}\Delta H_{\text{int},2} &= \frac{1}{n_2}\left[n_1\left(\bar{H}_1 - H^*_{\text{m},1}\right) + n_2\left(\bar{H}_2 - H^*_{\text{m},2}\right)\right]\\ &= \frac{n_1}{n_2}\left(\bar{H}_1 - H^*_{\text{m},1}\right) + \bar{H}_2 - H^*_{\text{m},2}\end{aligned} \tag{6.5-18}$$

This integral heat of solution is the enthalpy change per mole of substance 2 for the process of making the solution, starting with the pure substances. A similar equation can be written for $\Delta H_{\text{int},1}$.

The *differential heat of solution* of component 2 is defined by

$$\Delta H_{\text{diff},2} = \left(\frac{\partial \Delta H_{\text{mix}}}{\partial n_2}\right)_{T,P,n'} \quad \text{(definition)} \tag{6.5-19}$$

This differential heat of solution is the enthalpy change per mol of substance 2 for adding an infinitesimal amount of substance 2 to the solution. It is also equal to the enthalpy change of adding 1 mol of solute to a very large solution of the given composition. The idea is that the addition changes the composition only infinitesimally. From Eqs. (6.5-17) and (6.5-19),

$$\Delta H_{\text{diff},i} = \overline{H}_i - H^*_{\text{m},i} \tag{6.5-20}$$

Equation (6.5-20) is valid for any number of components, whereas Eq. (6.5-18) is valid only for a two-component solution.

Exercise 6.26

Write the version of Eq. (6.5-18) that applies to a solution of c components.

Tabulated Thermodynamic Properties for Solutes

In Chapter 2 we discussed enthalpy changes of formation for gases and pure substances. The enthalpy change of formation of substance i in a solution is defined as the enthalpy change to produce 1 mol of substance i from the necessary elements in their most stable forms and then to dissolve the 1 mol of substance i in a large amount of the solution of the specified composition, not changing the composition of the solution. The enthalpy change of formation therefore includes the differential heat of solution. The standard-state enthalpy change of formation of substance i is given by

$$\Delta H^\circ_{\text{f}}(i,\ \text{in soln}) = \overline{H}^\circ_i - H^\circ \quad \text{(elements)} \tag{6.5-21}$$

The molality description is generally used, which means that the value pertains to a hypothetical 1 mol kg^{-1} solution with activity coefficient equal to unity.

The Gibbs energy change of formation is similar to the enthalpy change of formation. It is the change in Gibbs energy to produce 1 mol of the substance from the necessary elements in their most stable forms. The standard-state Gibbs energy of formation for a solute is given by

$$\Delta G^\circ_{\text{f}}(i,\ \text{in soln}) = \mu^\circ_i - G^\circ \quad \text{(elements)} \tag{6.5-22}$$

It includes the Gibbs energy change to dissolve 1 mol of the solute in a large amount of the solution of the specified composition. Tabulated values of enthalpy changes and Gibbs energy changes of formation for several solutes are given in Table A.8, using the molality description. The notation (ao) means that the value is for an aqueous solute that is not ionized. The notation (ai) is for an aqueous electrolyte solute that is completely ionized or dissociated.

EXAMPLE 6.17

The following are values for ethanol at 298.15 K:

	$\Delta_f H°/\text{kJ mol}^{-1}$	$\Delta_f G°/\text{kJ mol}^{-1}$
liquid	−277.69	−174.78
ao	−288.3	−181.64

a. Find the value of the differential heat of solution in the standard state.
b. Find the value of $\mu_2^{\circ(\text{m})} - G^*_{\text{m},2}(\text{liq})$ for ethanol in H_2O at 298.15 K.

Solution

a. Call ethanol component number 2:

$$\Delta H_{\text{diff},2°} = H^{\circ(m)}_{\text{m},2°} - H^*_{\text{m},2}(\text{liq}) = \Delta_f H^\circ(2,\text{ao}) - \Delta_f H_2^\circ(\text{liq})$$
$$= -288.3\,\text{kJ mol}^{-1} - (-277.69\,\text{kJ mol}^{-1}) = -10.6\,\text{kJ mol}^{-1}$$

Note the difference in value between this quantity and the integral heat of solution in Example 6.16.

b. $$\mu_2{}^{\circ(\text{m})} - G^*_{\text{m},2}(\text{liq}) = \Delta_f G°(2,\text{ao}) - \Delta_f G°(2,\text{liq})$$
$$= -181.64\,\text{kJ mol}^{-1} - (-174.78\,\text{kJ mol}^{-1}) = -6.86\,\text{kJ mol}^{-1}$$

PROBLEMS

Section 6.5: Thermodynamic Functions of Nonideal Solutions

6.39 At 35.2°C, the vapor pressure of pure acetone is equal to 344.5 torr, and that of pure chloroform is equal to 293 torr. At this temperature, a solution of 0.7090 mol of acetone and 0.2910 mol of chloroform has a total vapor pressure of 286 torr and a mole fraction of acetone in the vapor of 0.8062.

- **a.** Using convention I, find the activity and activity coefficient of each component.
- **b.** Find the Gibbs energy change of mixing and the excess Gibbs energy for the solution.
- **c.** The Henry's law constant for chloroform in acetone at this temperature is equal to 145 torr. Considering acetone to be the solvent, find the activity and activity coefficient for each component according to convention II.

6.40 A solution of acetone (substance 2) and diethyl ether (substance 1) has $x_2 = 0.500$. At 30°C, this solution is at equilibrium with a vapor phase that has partial pressures $P_2 = 168$ torr and $P_1 = 391$ torr. The vapor pressures of the pure substances at this temperature are $P_2^* = 283$ torr and $P_1^* = 646$ torr.

- **a.** Using convention I, find the activity and activity coefficient of each substance.
- **b.** Find ΔG_{mix} for a solution containing 1.000 mol of acetone and 1.000 mol of diethyl ether.

6.41 At 35.2°C, the equilibrium vapor pressure of chloroform is 293 torr and that of acetone is 344.5 torr. A liquid solution with acetone mole fraction equal to 0.5061 has an equilibrium total vapor pressure of 255 torr and an acetone mole fraction in the vapor of 0.5625. Assume the vapor to be an ideal gas mixture.

- **a.** Using convention I, find the activity and activity coefficient of each substance.
- **b.** Find the Gibbs energy change of mixing for 1.000 mol of solution (that is, 0.4939 mol of chloroform and 0.5061 mol of acetone).

6.42 At 298.15 K, the equilibrium vapor pressure of water is 23.756 torr, and that of *n*-propanol is 21.76 torr. The Henry's law constant for *n*-propanol in water at this temperature is equal to 252 torr. An aqueous solution of *n*-propanol with a mole fraction of *n*-propanol equal to 0.100 has a partial vapor pressure of water equal to 22.7 torr and a partial vapor pressure of *n*-propanol equal to 13.2 torr.

a. Find the mole fraction of *n*-propanol in the vapor phase at equilibrium with the solution at 298.15 K.

b. Using convention II, find the activities and activity coefficients of the two substances in the solution. State any assumptions.

c. Using convention I, find the activities and activity coefficients of the two substances in the solution. State any assumptions.

d. Find the Gibbs energy change of mixing of a solution containing 0.900 mol of water and 0.100 mol of *n*-propanol. Find the excess Gibbs energy of the solution.

6.43 For a mixture of ethylene glycol (substance 1) and methanol (substance 2) at 298.15 K, the excess enthalpy and excess Gibbs energy were found to be

x_2	H^E/cal mol^{-1}	G^E/cal mol^{-1}
0	0	0
0.1	8.2	17.71
0.2	18.63	32.58
0.3	25.67	44.72
0.4	29.62	52.13
0.5	31.47	55.39
0.6	31.70	54.18
0.7	28.40	48.48
0.8	22.35	39.95
0.9	14.07	21.35
1.0	0	0

a. Calculate ΔH_{mix} and ΔG_{mix} for a solution consisting of 0.100 mol of methanol and 0.4 mol of ethylene glycol.

b. Calculate ΔH and ΔG for mixing the solution of part a with a solution consisting of 0.4 mol of methanol and 0.100 mol of ethylene glycol.

6.44 Find the value of ΔG_{mix} and the excess Gibbs energy for the solution of Example 6.12. The partial pressure of ethanol at this composition and temperature is equal to 12.45 torr, and the vapor pressure of pure ethanol at this temperature is equal to 44.40 torr. The partial vapor pressure of diethyl ether at this composition and pressure is equal to 408.6 torr, and the vapor pressure of pure diethyl ether at this temperature is equal to 442.6 torr.

6.45 A solution of ethanol (substance 1) and 2,2,4-trimethyl pentane (substance 2) has $x_2 = 0.2748$ and $a_2 = 0.8184$, using convention I. The value of a_1 is 0.9513.

a. Find the activity coefficient of each substance, using convention I.

b. Find the Gibbs energy change of mixing of a solution with this composition containing a total of 2.000 mol.

6.46 In a liquid solution of tetrachlorosilane, $SiCl_4$, and tetrachloromethane, CCl_4, the mole fraction of $SiCl_4$ is equal to 0.472. At 25°C, the vapor in equilibrium with this solution has a mole fraction of $SiCl_4$ equal to 0.648. At this temperature, the vapor pressure of pure $SiCl_4$ is equal to 238.3 torr, and the vapor pressure of pure CCl_4 is equal to 114.9 torr. The total vapor pressure of the solution is equal to 179.1 torr.

a. Find the total vapor pressure that would be predicted by Raoult's law for this solution at this temperature, and find the activity coefficient of each component, using convention I.

b. Calculate ΔG_{mix} and the excess Gibbs energy of this solution if it contains a total of 1.000 mol of the two substances.

6.47 A liquid solution of acetone (A) and chloroform (C) with liquid mole fraction $x_A = 0.7090$ has a total equilibrium vapor pressure at 308.4 K equal to 286 torr with $y_A = 0.8062$.

a. Using convention I, find the activities and activity coefficients of both components in the liquid phase.

b. Find the Gibbs energy change of mixing for a liquid solution containing 0.7090 mol of A and 0.291 mol of C.

c. The Henry's law constant for C in A at this temperature is $k_C = 145$ torr. Find the activity and activity coefficient of chloroform in the solution of part a using convention II.

6.48 In a solution of diethyl ether (substance 1) and acetone (substance 2) at 30°C with $x_2 = 0.400$, $\gamma_1^{(\text{I})} = 1.14$, $\gamma_2^{(\text{I})} = 1.31$, and $\gamma_2^{(\text{II})} = 0.63$.

a. Find the value of ΔG_{mix} for a solution of 0.800 mol of acetone and 1.200 mol of diethyl ether at 30°C. Find the value of the excess Gibbs energy.

b. Find the activity coefficient of acetone in the solution of part a using the molality description, treating diethyl ether as the solvent.

6.49 Using data in the appendix, find the standard-state differential heat of solution of CO_2 in water at 298.15 K. State in words what this quantity represents, including the definition of the standard state.

6.6 Phase Diagrams of Nonideal Mixtures

A complete two-component phase diagram requires three dimensions to plot T, P, and the mole fraction of one component, as depicted in Figure 6.4. Two-dimensional phase diagrams are produced by passing planes of constant T or constant P through the diagram.

Liquid–Vapor Phase Diagrams

Figure 6.11 shows a pressure–composition liquid–vapor phase diagram of ethanol and diethyl ether for a fixed temperature of 20°C. Compare Figure 6.11 with Figure 6.2, which represents the nearly ideal mixture of benzene and toluene. Figure 6.12 shows the temperature–composition phase diagram of the same mixture for a fixed pressure of 1.84 atm. Compare this figure with Figure 6.3. This system exhibits positive deviation from Raoult's law. The vapor pressure is larger than it would be if the solution were ideal, and the solution boils at a lower temperature than if it were an ideal solution.

Figure 6.13 shows the pressure–composition phase diagram of ethanol and benzene. There is such a large positive deviation from Raoult's law that there is a maximum in the vapor pressure curve. Figure 6.14 shows the temperature–composition phase diagram of acetone and chloroform, which corresponds to a large negative deviation from Raoult's law. Either a maximum or minimum point in a phase diagram is called an *azeotrope*. The two curves representing liquid and vapor compositions must be tangent at an azeotrope, so that the two phases have the same composition. This assertion is proved in Appendix D.

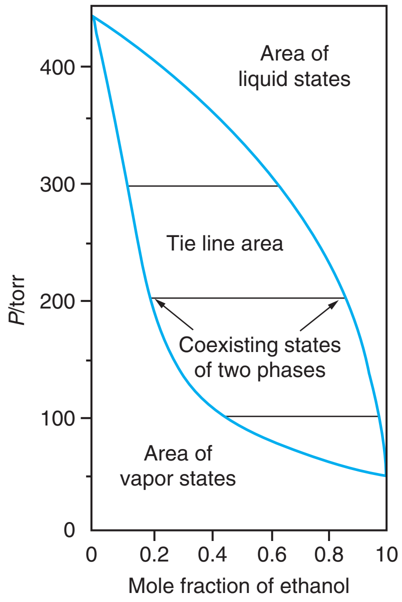

Figure 6.11 Pressure–Composition Phase Diagram for Diethyl Ether–Ethanol at 20°C. The lower curve shows the pressure as a function of mole fraction in the vapor, and the upper curve shows the pressure as a function of mole fraction in the liquid. Drawn from data in J. Timmermans, *Physicochemical Constants of Binary Systems*, Vol. 2, Interscience Publishers, New York, 1959, p. 401.

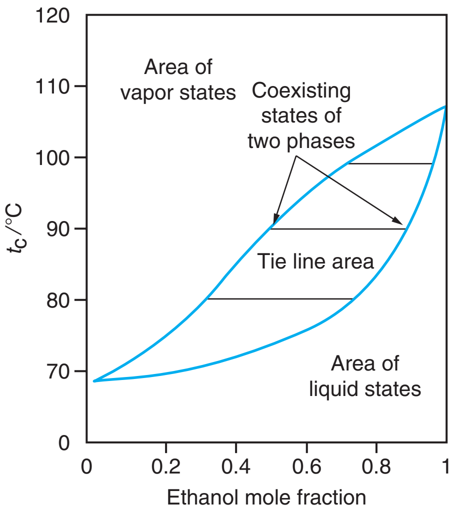

Figure 6.12 Temperature–Composition Phase Diagram for Diethyl Ether–Ethanol at 1.84 atm. The lower curve represents the temperature as a function of mole fraction in the liquid, and the upper curve represents the temperature as a function of mole fraction in the vapor. Drawn from data in J. Timmermans, *Physicochemical Constants of Binary Systems*, Vol. 2, Interscience Publishers, New York, 1959, p. 401.

An *azeotropic mixture* is sometimes called a *constant-boiling mixture*, since it distills without any change in composition. It is impossible to distill from one side of an azeotrope to the other. For example, ethanol and water at 1.00 atm have an azeotrope at an ethanol mole fraction equal to 0.90. Any mixture of ethanol and water can be distilled to this composition, but no further.

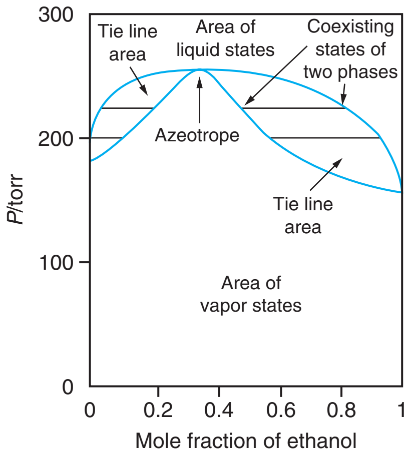

Figure 6.13 Liquid–Vapor Pressure–Composition Phase Diagram of Ethanol and Benzene, Showing an Azeotrope. Drawn from data in J. Timmermans, *Physicochemical Constants of Binary Systems*, Vol. 2, Interscience Publishers, New York, 1959, p. 61.

Exercise 6.27

At 1.000 atm the boiling temperature of water is 100°C and that of ethanol is 78.3°C. The azeotrope boils at 78.17°C at this pressure.

a. Sketch the liquid–vapor temperature–composition phase diagram of ethanol and water.

b. By drawing a "staircase" of line segments representing distillation, as in Figure 6.7, show that a distillation process beginning with a mole fraction of ethanol less than 0.90 cannot give a distillate with an ethanol mole fraction greater than 0.90.

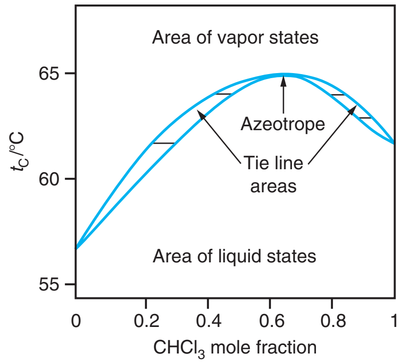

Figure 6.14 Liquid–Vapor Temperature–Composition Phase Diagram of Acetone and Chloroform.

If a binary mixture has a sufficiently large positive deviation from ideality, the system at equilibrium can contain two liquid phases. Figure 6.15 shows schematically the temperature–composition phase diagram of two hypothetical substances, called A and B. Below the temperature labeled T_c there is a region of tie lines. A tie line in this region connects points representing the compositions of the two liquids that can be at equilibrium with each other. The compositions to the right or to the left of this region are possible equilibrium compositions of a single liquid phase.

The highest point in the tie-line region at temperature T_c is called an *upper critical solution point* or an *upper consolute point*. It has a number of properties similar to those of the gas–liquid critical point in Figure 1.5. If a mixture has the same overall composition as that of the consolute point, it will be a two-phase system at a temperature below the consolute temperature. If its temperature is gradually raised, the meniscus between the phases becomes diffuse and disappears, in the same way that the meniscus

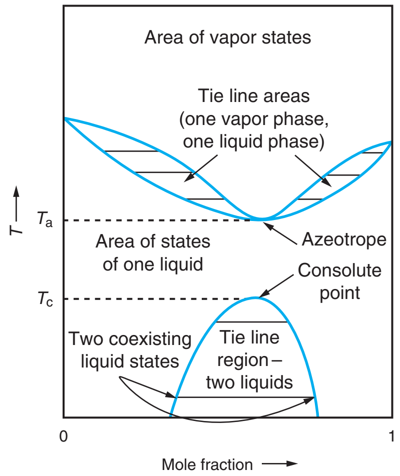

Figure 6.15 Temperature–Composition Phase Diagram of a System with Liquid–Liquid Phase Separation (Schematic).

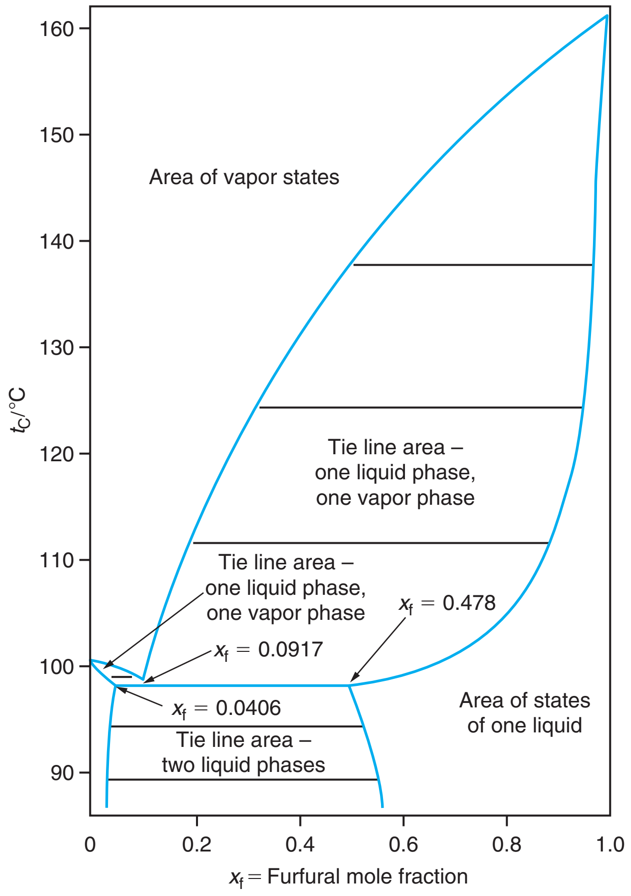

Figure 6.16 Liquid–Vapor Temperature–Composition Phase Diagram of Furfural and Water at 1.000 atm. After G. H. Mains, *Chem. Met. Eng.*, **26**, 779 (1922).

between the liquid and vapor phases disappears as the liquid–vapor critical point is approached, as was shown in Figure 1.6.

There are a few mixtures, such as water and nicotine, that have both an upper and a lower consolute point, so that the boundary of the tie-line region is a closed curve. Below the lower consolute point at 61.5°C water and nicotine mix in all proportions. Above the upper consolute temperature at 233.0°C they also mix in all proportions.[9] Between these temperatures there is a tie-line region in the diagram and the liquids are only partially miscible. Another mixture with both a lower and an upper consolute temperature is butoxyethanol and water, with a lower consolute temperature of 48.01°C and an upper consolute temperature of 130.7°C.[10]

If the positive deviation from ideality is even greater than that of Figure 6.15, the two-phase region can extend to the liquid–vapor region and produce a phase diagram like that of Figure 6.16, which shows the temperature–composition phase diagram of furfural and water at a constant pressure of 1.000 atm. The horizontal tie line at

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[9] A. N. Campbell, E. M. Kartzmark, and W. E. Falconer, *Can. J. Chem.*, **36**, 1475 (1958).

[10] Y. Izumi *et al.*, *J. Physique*, **42**, 544 (1981); H. L. Cox and L. H. Cretcher, *J. Amer. Chem. Soc.*, **48**, 451 (1926).

97.9°C connects three points representing the compositions of two liquid phases and one gas phase that can coexist at equilibrium. By the Gibbs phase rule, only one intensive variable is independent in a system of two components and three phases. Since the pressure is fixed for this diagram, the compositions of all three phases and the temperature are fixed.

To purify furfural by the process of *steam distillation*, water is added to impure furfural and the two-phase mixture is boiled. If the impurities do not change the boiling temperature very much, the two-phase mixture boils near 97.9°C at 1.000 atm. The vapor has a furfural mole fraction equal to 0.092. The vapor is condensed to two liquid phases, and the furfural layer is recovered and dried. At 20°C, this layer has a furfural mole fraction of 0.78 before drying. The advantage of steam distillation is that it can be carried out at a lower temperature than an ordinary distillation. The higher temperature of an ordinary distillation might decompose the organic substance.

Solid–Liquid Phase Diagrams

Figure 6.6 depicted the temperature–composition phase diagram of silicon and germanium, which form a nearly ideal solid solution. Figure 6.17 shows the solid–liquid temperature–composition phase diagram of gold and copper, which are completely miscible in both the solid and liquid phases, but which do not form an ideal solid solution. The lower area represents temperatures and compositions of a one-phase system (a solid solution). The tie-line areas contain tie lines connecting the composition of a solid solution and the composition of the liquid solution at equilibrium with that solid solution. The area above the tie-line region represents a liquid solution.

Just as liquids are purified by distillation, solids are sometimes purified by *zone refining*, in which a rod-shaped piece of the solid is gradually pulled through a ring-shaped furnace. A zone of the solid melts as it moves into the furnace and freezes as it moves out of the furnace. This process is analogous to the vaporization and recondensation of a liquid in distillation, except that the melting process gives a liquid of the same composition as the solid, making the initial process correspond to a vertical line segment in the diagram. In many cases the solid that freezes out approximates the equilibrium composition at the other end of the tie line at the end of the vertical line

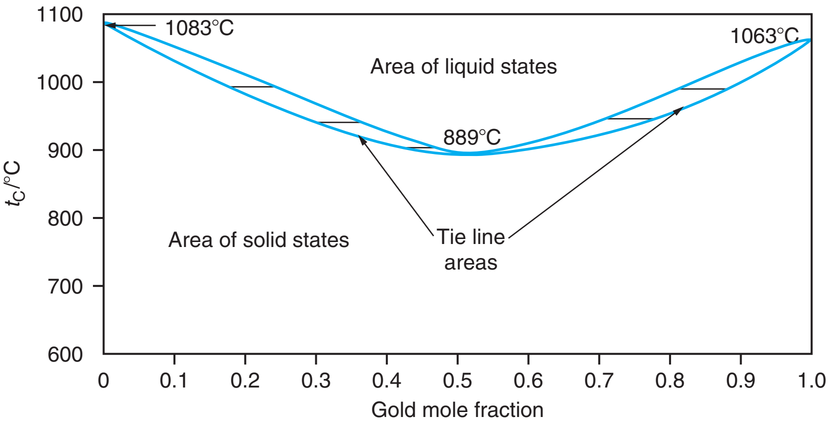

Figure 6.17 Solid–Liquid Temperature–Composition Phase Diagram of Gold and Copper. From M. Hansen, *The Constitution of Binary Alloys*, McGraw-Hill, New York, 1958, p. 199.

segment, being richer in the higher-melting component than the original solid. The lower-melting substance is "swept" to the end of the rod. This process is analogous to distillation in a still with one theoretical plate. A second pass through the furnace can lead to a further purification.

Exercise 6.28

By drawing a "staircase" in Figure 6.17, determine what composition will result from three successive zone refining passes starting with a gold–copper solid solution of gold mole fraction equal to 0.70. What would many successive zone refining passes lead to if the curves had a maximum instead of a minimum?

Figure 6.18 shows the solid–liquid temperature–composition phase diagram of silver and copper at 1.00 atm. There are two one-phase regions of limited solid solubility, labeled α and β. A tie line in the area between the α and β regions represents two coexisting saturated solid solutions, one that is mostly silver and one that is mostly copper. The tie line at 779°C connects the points representing the two solid phases and one liquid phase that can be at equilibrium with the two solid phases. The point representing this liquid phase is called the *eutectic point*. If a liquid that has the same composition as the eutectic is cooled, two solid phases will freeze out when it reaches the eutectic temperature, with compositions represented by the ends of the tie line.

Exercise 6.29

For each one-phase region in the phase diagram of Figure 6.18, give the phase that can occur and give the number of independent intensive variables (excluding the pressure, which is fixed at 1 atm). For each two-phase (tie-line) region, give the phases that can be at equilibrium and give the number of independent intensive variables, excluding the pressure.

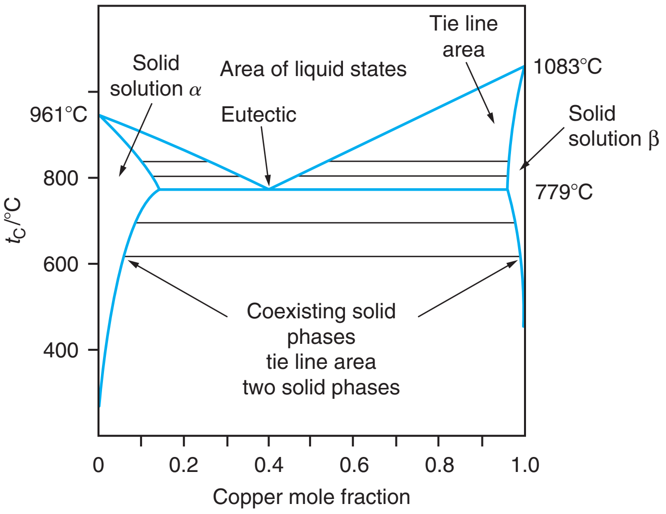

Figure 6.18 Solid–Liquid Temperature–Composition Phase Diagram of Silver and Copper. From R. E. Dickerson, *Molecular Thermodynamics*, W. A. Benjamin, Inc., New York, 1969, p. 371.

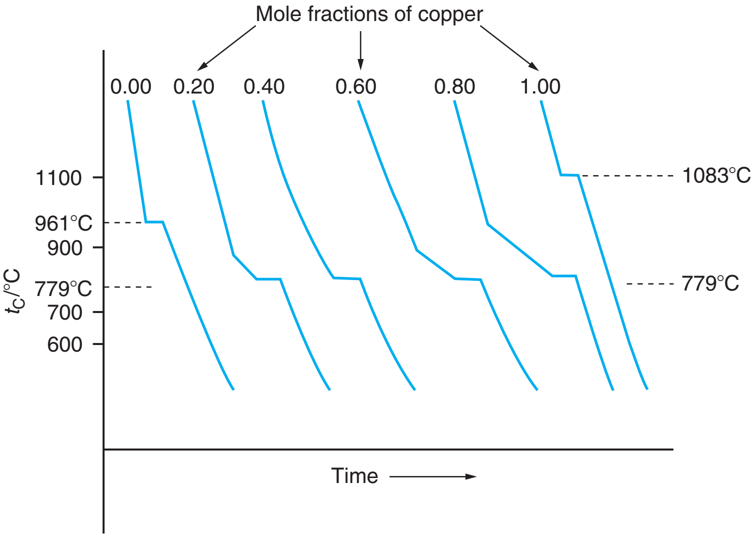

Figure 6.19 Cooling Curves for the Silver–Copper System. From R. E. Dickerson, *Molecular Thermodynamics*, W. A. Benjamin, Inc., New York, 1969, p. 371.

Solid–liquid phase diagrams like that of Figure 6.18 can be constructed by analyzing experiments in which a mixture of known composition is heated above its melting point and then allowed to cool slowly. Figure 6.19 shows *cooling curves* representing the temperature of mixtures of silver and copper as a function of time for various mole fractions of copper. The cooling curves for the pure substances (mole fraction 0.00 and 1.00) exhibit horizontal line segments representing freezing of the substance. The temperature of the pure substance cannot drop below its freezing temperature until all of the liquid has frozen. The cooling curve for copper mole fraction equal to 0.80 drops smoothly until a copper-rich solid solution begins to freeze out at about 950°C. At this point the slope of the curve changes but the cooling curve does not become horizontal. The principal reason for this is that the composition of the liquid changes as the solid solution β is removed since the solid solution is richer in copper than the liquid solution. The slope of the curve is less steep than that of the first portion because the enthalpy change of freezing is being evolved. When the eutectic temperature is reached at 779°C, a second solid solution, mostly silver and saturated in copper, begins to freeze out. With three phases present the temperature must remain constant. A horizontal portion of the cooling curve results, called the *eutectic halt*. Only when the system is entirely frozen can the temperature drop further. The phase diagram is constructed by plotting the points at which the slope of the cooling curve changes.

Phase diagrams can also be constructed from data obtained by the technique of *differential scanning calorimetry* (abbreviated *DSC*). In this technique a sample of the material to be studied is placed in a small pan with a cover, usually made of aluminum, since aluminum has a rather large thermal conductivity. The sample can be as small as 10 mg, which makes the method quite versatile. An identical pan is usually left empty, but could contain a blank substance. Each of the pans is fitted with a temperature-measuring device and an electrical heater. Both of the pans are gradually heated and the amount of electrical energy added to each pan is monitored.

The additional electrical energy required to maintain the sample pan at the same temperature as the blank pan is determined as the temperature is increased. The heat capacity of the sample material can be determined if no phase transition occurs. If a phase transition occurs, the temperature of the phase transition and the enthalpy change of the phase transition can be determined.

Figure 6.20 shows the solid–liquid temperature–composition phase diagram of *p*-xylene and bromobenzene at 1 atm. This diagram is similar to that of silver and copper in Figure 6.18 except that the solids are almost completely insoluble in each other. The regions of solid solubility are too small to show in the figure. The two solids that occur in the diagram are nearly pure substances and the tie lines extend to the edge of the diagram.

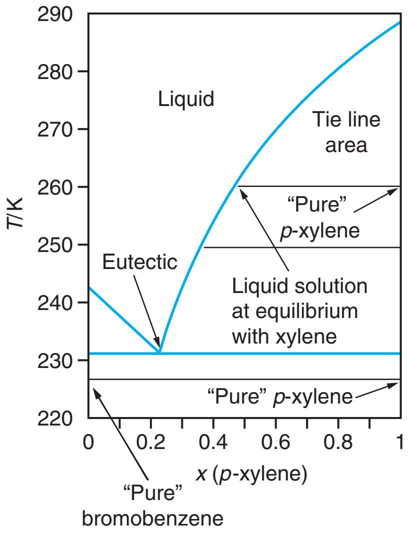

Figure 6.20 Solid–Liquid Temperature–Composition Phase Diagram of *p*-Xylene and Bromobenzene. From M. L. McGlashan, *Chemical Thermodynamics*, Academic Press, New York, 1979, p. 268.

Solid–Liquid Phase Diagrams with Compounds

Sometimes two substances form solid-state compounds. Figure 6.21 shows the solid–liquid temperature–composition phase diagram of aniline (A) and phenol (P), which exhibit a compound $C_6H_5NH_2 \cdot C_6H_5OH$ (abbreviated by AP) in the solid state. Such a compound has a crystal lattice containing both substances in a stoichiometric ratio. This crystal lattice is different from the crystal lattice of either A or P and A, and the three solids, A, P, and AP are almost completely insoluble in each other. The compound

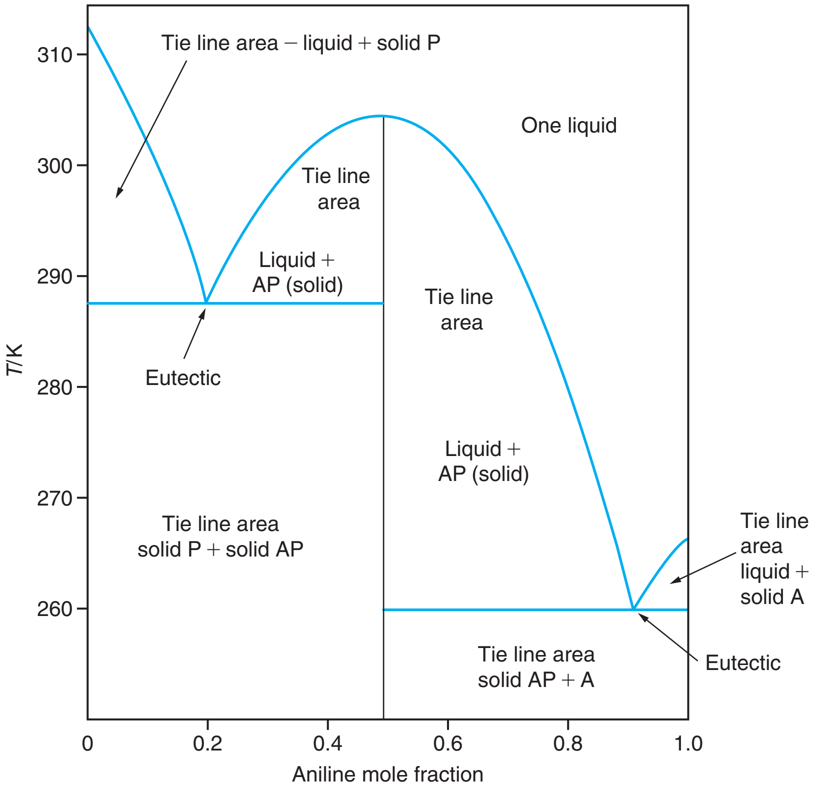

Figure 6.21 Solid–Liquid Temperature–Composition Phase Diagram of Aniline and Phenol.

AP does not exist in the liquid state. When it melts an equimolar liquid solution of aniline and phenol results. This is called *congruent melting*.

The phase diagram resembles two phase diagrams set side by side. The right half of the diagram is the phase diagram for the two substances AP and A. The left half of the diagram is the phase diagram for the two substances *P* and AP. The tie-line area at the lower right represents the coexistence of nearly pure A with nearly pure AP, and the corresponding area on the left represents the coexistence of nearly pure P with nearly pure AP. Solid aniline and phenol cannot coexist with each other at equilibrium because of the occurrence of the compound.

Figure 6.22 shows the temperature–composition phase diagram of copper and lanthanum. There are four different compounds: $LaCu_6$, $LaCu_4$, $LaCu_2$, and LaCu. There are only two maxima in the diagram, corresponding to congruent melting of the compounds $LaCu_2$ and $LaCu_6$. The two compounds LaCu and $LaCu_4$ do not melt to form a single liquid. The compound LaCu melts at 551°C to form two phases: a liquid solution with lanthanum mole fraction equal to 0.57 and solid $LaCu_2$. This phenomenon is called *incongruent melting* because the liquid phase does not have the same composition as the solid phase from which it formed, and another solid phase is formed. Solid $LaCu_2$ and solid LaCu can equilibrate with the liquid solution as indicated by the tie line connecting the points representing the three phases. The point representing the composition of the liquid is called a *peritectic point*. Just as with a

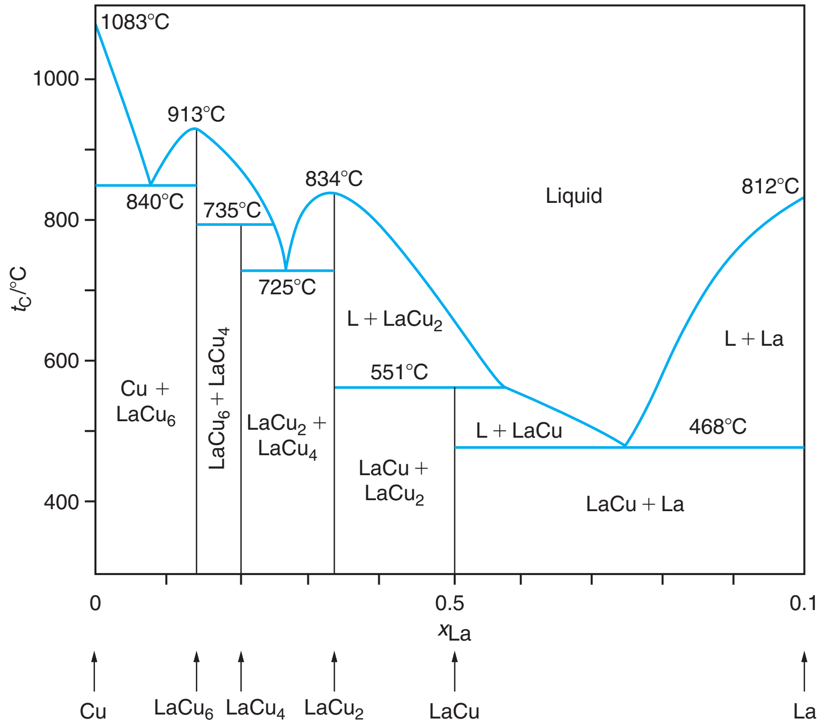

Figure 6.22 solid–liquid temperature–composition Phase Diagram of Copper and Lanthanum. From R. E. Dickerson, *Molecular Thermodynamics*, W. A. Benjamin, Inc., New York, 1969, p. 379.

eutectic point, the compositions of the three phases are not variable at constant pressure.

Exercise 6.30

a. Describe what happens when $LaCu_4$ melts.

b. For each area in Figure 6.22 and for each tie line connecting three phases, tell what phase or phases occur and give the number of independent intensive variables.

Three-Component Phase Diagrams

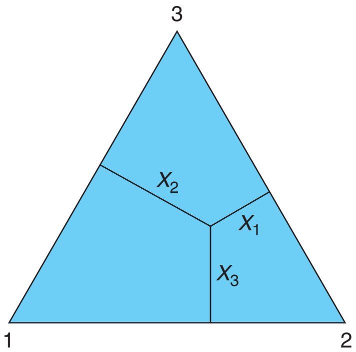

Figure 6.23 Mole Fractions of a Three-Component System Plotted in an Equilateral Triangle.

For three components a complete phase diagram would require four dimensions, representing T, P, and two mole fractions. If the pressure is held fixed, a temperature–composition phase diagram is obtained that requires three dimensions. If the temperature and the pressure are both held fixed we have a composition–composition phase diagram with two independent mole fractions and one dependent mole fraction. Instead of plotting the two independent mole fractions on two perpendicular axes, an equilateral triangle is customarily used to plot the mole fractions, as depicted in Figure 6.23. A theorem of plane geometry asserts that the sum of the three perpendicular distances to the sides of an equilateral triangle has the same value for any point inside the triangle. If the size of the triangle is chosen so that this sum equals unity, these three perpendicular distances can represent the three mole fractions. Each vertex of the triangle represents a pure component.

Figure 6.24 shows the composition–composition phase diagram of water, acetone, and ethyl acetate for a constant temperature of 30°C and a constant pressure of 1.00 atm. There is a one-phase region of complete miscibility and a two-phase region containing tie lines, representing the compositions of two liquid phases that coexist at equilibrium. Since all points in the diagram correspond to the same temperature and pressure, the tie lines must remain in the plane of the diagram but are not required to be parallel to each other. Their directions must be determined experimentally.

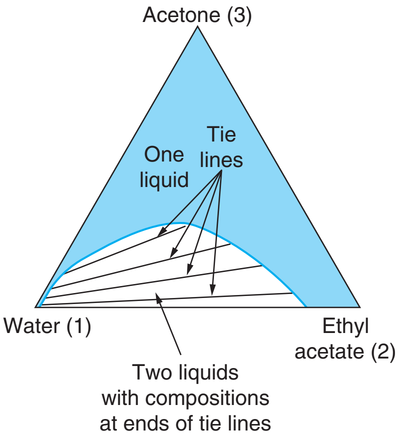

Figure 6.24 Liquid Composition–Composition Phase Diagram of Water, Acetone, and Ethyl Acetate at 1 atm and 30°C.

PROBLEMS

Section 6.6: Phase Diagrams of Nonideal Mixtures

6.50 **a.** Sketch the temperature–composition phase diagram of phenol (substance 1) and p-toluidine (substance 2), using w_1 (the mass fraction of phenol) as the independent variable. The melting temperature of phenol is 40.7°C and that of p-toluidine is 43.7°C. The molar mass of phenol is $94.11\,\mathrm{g\,mol^{-1}}$, and that of p-toluidine is $107.16\,\mathrm{g\,mol^{-1}}$. There is a single compound, which has a mass fraction of phenol equal to 0.4676, and which melts congruently at 30°C. The eutectic between p-toluidine and the compound is at 145°C and the other eutectic is at 10°C.

b. Redraw the phase diagram using the mole fraction as the independent variable. What is the formula of the compound?

6.51 Describe what happens if one begins with a vapor phase containing water and furfural with a water mole fraction equal to 0.500, and gradually cools this mixture from 150°C to 85°C. Give the approximate temperatures at which phase transitions occur.

6.52 Describe what happens if one begins with a small amount of liquid water at 99.0°C and gradually adds liquid furfural to the water at constant temperature until one has a mixture that has a mole fraction of furfural equal to 0.90. Give the approximate mole fractions at which phase transitions occur.

6.53 Draw a sketch of the solid–liquid temperature–composition phase diagram of sodium and potassium. There is a single compound, Na_2K, which melts incongruently at 6.6°C to give essentially pure sodium and a solution with sodium mole fraction equal to 0.42. The melting temperature of sodium is 97.5°C, and that of potassium is 63°C. There is a eutectic at -12.5°C and a sodium mole fraction equal to 0.15. There is some solid solubility, which you should indicate qualitatively. Label each area in the diagram with the number of independent intensive variables corresponding to that phase.

6.54 Sketch cooling curves for mixtures of phenol (P) and aniline (A) with aniline mole fractions equal to 0.26 (at the eutectic between P and the compound AP), 0.35, 0.50, and 0.90. Describe what happens at each break in each curve.

6.55 Sketch the solid–liquid temperature–composition phase diagram of CuCl (copper(I) chloride) and $FeCl_3$ (iron(III) chloride). The melting temperature of CuCl is 430°C and that of $FeCl_3$ is 306°C. There is a single compound, $CuCl \cdot FeCl_3$, which melts near 320°C. There is a eutectic near 300°C and $x = 0.37$, where x is the mole fraction of $FeCl_3$. There is a second eutectic near 260°C and $x = 0.81$. Label each area with the phase or phases present and the number of independent intensive variables.

6.56 Sketch the solid–liquid and liquid–vapor temperature–composition phase diagram of titanium and uranium. The two substances form a nearly ideal liquid solution with a uranium boiling temperature of 1133°C and a titanium boiling temperature of 1660°C. The melting temperature of uranium is 770°C, and that of titanium is 882°C. There is a compound, TiU_2, which melts at 890°C. The eutectic between the compound and uranium is at uranium mole fraction 0.95 and 720°C, and the eutectic between titanium and the compound is at uranium mole fraction 0.28 and 655°C. Label each area with the number of independent intensive variables.[11]

6.57 From the following information, sketch the temperature–composition phase diagram of lanthanum (La) and antimony (Sb) using x_{Sb} (the mole fraction of antimony) on the horizontal axis.

The melting temperature of pure antimony is 631°C and the melting temperature of pure lanthanum is 921°C. There are four compounds: La_2Sb ($x_{Sb} = 0.333$), La_3Sb_2 ($x_{Sb} = 0.400$), LaSb ($x_{Sb} = 0.500$), and $LaSb_2$ ($x_{Sb} = 0.667$). La_2Sb melts incongruently at 1460°C, giving La_3Sb_2(s) and a solution with $x_{Sb} = 0.32$. La_3Sb_2 melts congruently at 1690°C, giving a solution of La and Sb with $x_{Sb} = 0.400$. LaSb melts incongruently at 1540°C, giving La_3Sb_2 and a solution with $x_{Sb} = 0.54$. $LaSb_2$ melts incongruently at 1110°C, giving LaSb and a solution with $x_{Sb} = 0.75$. There is a eutectic between La and La_2Sb at 845°C with $x_{Sb} = 0.04$. There is a eutectic between $LaSb_2$ and Sb at 630°C with $x_{Sb} \approx 0.99$. There is no significant solid solubility between any solid phases.

6.58 **a.** Sketch a cooling curve for a mixture of lanthanum and copper with a mole fraction of lanthanum equal to 0.30. Label each break in the curve and say what phase or phases are freezing out for each portion of the curve.

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[11] The actual diagram might be more complicated. See Hansen, *The Constitution of Binary Alloys*, McGraw-Hill, New York, 1958, pp. 1238ff.

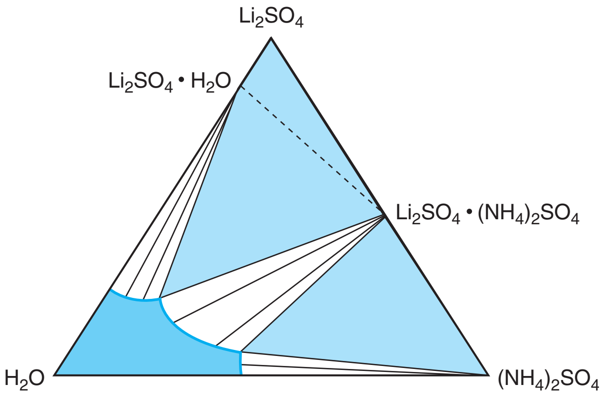

Figure 6.25 Concentration–Concentration Phase Diagram of Lithium Sulfate, Ammonium Sulfate, and Water at 30°C and 1.000 atm. Pure lithium sulfate and ammonium sulfate are solid at this temperature.

b. Repeat part a for a mole fraction of lanthanum equal to 0.53.

6.59 Sketch the titanium–nickel temperature–composition phase diagram. The melting temperature of nickel is equal to 1453°C and that of titanium is equal to 1675°C. There are three compounds, $TiNi_3$, melting near 1370°C, TiNi, melting near 1300°C, and Ti_2Ni, which melts incongruently near 990°C. There are fairly sizable regions of solid solubility except that nothing dissolves in $TiNi_3$. The three eutectics, in order of increasing titanium mole fraction, are near 1300°C, 1110°C, and 940°C. The incongruent melting of Ti_2Ni gives a solid solution that is mostly TiNi and a solution that has a titanium mole fraction near 0.70. Label each area with the phase or phases present and the number of independent intensive variables.

6.60 Figure 6.25 shows a phase diagram of lithium sulfate, ammonium sulfate, and water at constant temperature and pressure. For each area in the diagram, tell what phase or phases are present and give the number of independent intensive variables.

6.61 Consider a hypothetical pair of substances denoted by A and B. Substance A melts at 650°C and substance B melts at 575°C. The two substances form two compounds in the solid state, A_2B and AB_2, but mix in all proportions in the liquid phase. A_2B melts congruently at 550°C. AB_2 melts incongruently to give pure A and a solution with $x_A = 0.40$. Sketch the phase diagram. Label each area with the

phases present and the value of f, the number of degrees of freedom, or number of independent intensive variables.

6.7 Colligative Properties

Colligative properties are properties that depend on the concentration of a solute but not on its identity. The name comes from a Latin word meaning “tied together” and is used because of the common dependence that these properties have on solute concentration. The four principal colligative properties are freezing point depression, boiling point elevation, vapor pressure lowering, and osmotic pressure.

Freezing Point Depression

Consider a solid solute that is soluble in a liquid solvent but insoluble in the solid solvent. Assume that the pure solid solvent (component number 1) is at equilibrium with a liquid solution containing the dilute solute. From the fundamental fact of phase equilibrium,

$$\mu_1^{(\text{liq})} = \mu_1^{*(\text{solid})} \tag{6.7-1}$$

We assume that the solution is sufficiently dilute that the solvent obeys the ideal solution equation:

$$\mu_1^{*(\text{liq})} + RT\ln(x_1) = \mu_1^{*(\text{solid})} \tag{6.7-2}$$

where x_1 is the mole fraction of the solvent in the solution. By the Gibbs phase rule there are two independent intensive variables. If the pressure and temperature are chosen to be independent variables the mole fraction of the solvent in the liquid phase is a dependent variable.

Our strategy is to differentiate Eq. (6.7-2), then to apply thermodynamic relations to it and then to integrate. We divide by T and then differentiate with respect to T at constant P:

$$\left(\frac{\partial(\mu_1^{*(\text{liq})}/T)}{\partial T}\right)_P + R\left(\frac{\partial \ln(x_1)}{\partial T}\right)_P = \left(\frac{\partial \mu_1^{*(\text{solid})}/T}{\partial T}\right)_P \tag{6.7-3}$$

By the use of thermodynamic relations

$$\left(\frac{\partial\left(\mu_1^*/T\right)}{\partial T}\right)_P = \frac{T\left(\partial\mu_1^*/\partial T\right)_P - \mu_1^*}{T^2} = \frac{-TS_{\text{m},1}^* - \mu_1^*}{T^2} = -\frac{H_{\text{m},1}^*}{T^2} \tag{6.7-4}$$

Use of this identity in Eq. (6.7-3) gives

$$R\left(\frac{\partial \ln(x_1)}{\partial T}\right)_P = \frac{H_{\text{m},1}^{*(\text{liq})} - H_{\text{m},1}^{*(\text{solid})}}{T^2} = \frac{\Delta_{\text{fus}} H_{\text{m},1}^*}{T^2} \tag{6.7-5}$$

where $\Delta_{\text{fus}} H_{\text{m},1}^*$ is the enthalpy change of fusion of the pure solvent.

The equilibrium temperature will be lower than the freezing temperature of the pure solvent. We multiply Eq. (6.7-5) by dT and integrate both sides of Eq. (6.7-5) from the normal melting temperature of the pure solvent $T_{\text{m},1}$ to some lower temperature T'.

$$R\int_{T_{\text{m},1}}^{T'} \left(\frac{\partial \ln(x_1)}{\partial T}\right)_P dT = \int_{T_{\text{m},1}}^{T'} \frac{\Delta_{\text{fus}} H_{\text{m},1}^*}{T^2} dT \tag{6.7-6}$$

To a good approximation, $\Delta_{\text{fus}} H_{\text{m},1}^*$ is constant over a small range of temperature. To this approximation

$$R\ln x_1(T') = -\Delta_{\text{fus}} H_{\text{m},1}^* \left[\frac{1}{T'} - \frac{1}{T_{\text{m},1}}\right] \tag{6.7-7}$$

where $x_1(T')$ is the mole fraction of the solvent in the solution that is at equilibrium with the pure solvent at temperature T', and where we have used the fact that $x_1 = 1$ at temperature $T_{\text{m},1}$. Our system (pure solid solvent plus liquid solution) corresponds to one of the curves in a solid–liquid phase diagram such as Figure 6.20, so that Eq. (6.7-7) is the equation for this curve in the case that there is no appreciable solid solubility and the liquid solvent acts ideally. For dilute solutions, Eq. (6.7-7) is simplified by using the first term of a Taylor series

$$\ln(x_1) = \ln(1 - x_2) = -x_2 - \frac{x_2^2}{2} - \cdots \approx -x_2 \tag{6.7-8}$$

Exercise 6.31

a. Write the next two terms in the Taylor series for $\ln(1-x_2)$.
b. Evaluate the two terms of part a for $x_2 = 0.0100$.
c. Find the percentage error for the approximation of Eq. (6.7-8) for $x_2 = 0.100$, 0.0100, 0.00100, and 0.000100.

Use of the approximation of Eq. (6.7-8) gives

$$x_2 \approx \Delta_{\text{fus}} H^*_{\text{m},1} \frac{T_{\text{m},1} - T}{RT_{\text{m},1}T}$$

where we omit the prime superscript ($'$) on T. This equation is accurate only for dilute solutions, in which case T is approximately equal to $T_{\text{m},1}$. We replace T by $T_{\text{m},1}$ in the denominator of this expression:

$$x_2 \approx \left(\frac{\Delta_{\text{fus}} H^*_{\text{m},1}}{RT^2_{\text{m},1}}\right)\Delta T_{\text{f}} \tag{6.7-9}$$

where we use the symbol ΔT_{f} for $T_{\text{m},1} - T$, the freezing point depression.

Equation (6.7-9) is often rewritten in terms of the molality, using Eq. (6.2-10) to relate the molality and the mole fraction for a dilute solution:

$$x_2 = M_1 m_2$$

where M_1 is the molar mass of the solvent (measured in kilograms). The result is

$$\Delta T_{\text{f}} = K_{\text{f},1} m_2 \tag{6.7-10}$$

where m_2 is the molality of the solute. The quantity $K_{\text{f},1}$ is called the *freezing point depression constant* for the specific solvent.

$$K_{\text{f},1} = \frac{M_1 RT^2_{\text{m},1}}{\Delta_{\text{fus}} H_{\text{m},1}} \tag{6.7-11}$$

The freezing point depression constant $K_{\text{f},1}$has a different value for each solvent, but is independent of the identity of the solute. If there are several solutes m_2 is replaced by the sum of the molalities of all solutes. If a solute dissociates or ionizes, the total molality of all solute species must be used, although it might be necessary to account for ion pairing. The freezing point depression can be used to determine the extent of ionization of a weak electrolyte.

Exercise 6.32

The molar enthalpy change of fusion of water is equal to 6.01 kJ mol^{-1}. Show that the value of the freezing point depression constant for water is equal to 1.86 K kg mol^{-1}.

EXAMPLE 6.18

Find the freezing point depression of a solution of 10.00 g of sucrose in 1.000 kg of water.

Solution

$$m_2 = \frac{(10.00\,\text{g sucrose})\left(\dfrac{1\,\text{mol sucrose}}{342.30\,\text{g sucrose}}\right)}{1.000\,\text{kg}} = 0.02921\,\text{mol kg}^{-1}$$

$$\Delta T = \left(1.86\,\text{K kg mol}^{-1}\right)\left(0.02921\,\text{mol kg}^{-1}\right) = 0.0543\,\text{K}$$

Exercise 6.33

At 25°C a solution of acetic acid with a stoichiometric molality of 0.100 mol kg^{-1} is approximately 1.32% ionized. Assuming that this percentage ionization applies at the freezing temperature, find the freezing temperature of this solution.

Boiling Point Elevation

Consider a volatile solvent (component 1) and a nonvolatile solute (component 2) in a solution that is at equilibrium with the gaseous solvent at a constant pressure. We assume that the gas phase is an ideal gas and that the solvent acts as though it were ideal. Our development closely parallels the derivation of the freezing point depression formula earlier in this section. The fundamental fact of phase equilibrium gives

$$\frac{\mu_1^{*(\text{liq})}}{T} + R\ln\left(x_1^{(\text{liq})}\right) = \frac{\mu_1^{(\text{gas})}}{T} \tag{6.7-12}$$

where x_1 is the mole fraction of the solvent in the liquid phase. Use of Eq. (6.7-4) gives

$$R\left(\frac{\ln\left(\partial x_1^{(\text{liq})}\right)}{\partial T}\right)_P = -\frac{H_{\text{m},1}^{(\text{gas})}}{T^2} + \frac{H_{\text{m},1}^{*(\text{liq})}}{T_2} = -\frac{\Delta_{\text{vap}}H_{\text{m},1}^{*}}{T^2} \tag{6.7-13}$$

where $\Delta_{\text{vap}}H_{\text{m},1}^{*}$ is the molar enthalpy change of vaporization of the pure solvent. We now multiply by dT and integrate from $T_{\text{b},1}$, the normal boiling temperature of component 1, to a higher temperature, T'. Over a small interval of temperature, the enthalpy change of vaporization is nearly constant, so that integration gives an equation analogous to Eq. (6.7-7):

$$R\ln\left(x_1^{(\text{liq})}\right) = \Delta_{\text{vap}}H_{\text{m},1}^{*}\left(\frac{1}{T'} - \frac{1}{T_{\text{b},1}}\right) \tag{6.7-14}$$

Equation (6.7-14) can be simplified in the case of small boiling point elevations by using the same approximations as were used in Eq. (6.7-9b), with the result

$$x_2 = \left(\frac{\Delta_{\text{vap}}H_{\text{m},1}^{*}}{RT_{\text{b},1}^2}\right)\Delta T_{\text{b}} \tag{6.7-15}$$

where $\Delta T_{\text{b}} = T - T_{\text{b}}$.

When Eq. (6.7-15) is solved for the boiling point elevation and written in terms of the molality, the result is analogous to Eq. (6.7-10):

$$\Delta T_{\mathrm{b}} = K_{\mathrm{b},1} m_2 \tag{6.7-16}$$

The *boiling point elevation constant* for substance 1 is given by

$$K_{\mathrm{b},1} = \frac{M_1 R T_{\mathrm{b},1}^2}{\Delta_{\mathrm{vap}} H_{\mathrm{m},1}^*} \tag{6.7-17}$$

This quantity has a different value for each solvent, but does not depend on the identity of the solute. If more than one solute is present, the molality m_2 is replaced by the sum of the molalities of all solutes.

EXAMPLE 6.19

Show that the value of the boiling point elevation constant for water is equal to $0.513\ \mathrm{K\,kg\,mol^{-1}}$. At 100°C $\Delta_{\mathrm{vap}} H_{\mathrm{m}}^* = 40.67\ \mathrm{kJ\,mol^{-1}}$.

Solution

$$K_{\mathrm{b},1} = \frac{(0.01801\ \mathrm{kg\,mol^{-1}})(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})(373.15\ \mathrm{K})^2}{40670\ \mathrm{J\,mol^{-1}}} = 0.513\ \mathrm{K\,kg\,mol^{-1}}$$

Exercise 6.34

Find the boiling temperature at 1.000 atm of a solution of 5.00 g of glucose in 1.000 kg of water.

Vapor Pressure Lowering

For a nonvolatile solute and a volatile solvent that obeys Raoult's law, the total vapor pressure is equal to the vapor pressure of the solvent:

$$P_{\mathrm{vap}} = x_1 P_1^* \tag{6.7-18}$$

where $P_{1,\mathrm{vap}}^*$ is the vapor pressure of the pure solvent (component 1) and where x_1 is the mole fraction of the solvent in the liquid phase. The lowering of the vapor pressure is given by

$$\Delta P_{\mathrm{vap}} = P_{1,\mathrm{vap}}^* - P_{\mathrm{vap}} = P_{1,\mathrm{vap}}^* - x_1 P_{1,\mathrm{vap}}^* = P_{1,\mathrm{vap}}^*(1 - x_1) = P_{1,\mathrm{vap}}^* x_2 \tag{6.7-19}$$

Exercise 6.35

a. Calculate the vapor pressure at 100.0°C of the solution in Exercise 6.34.

b. From Eq. (6.7-19), obtain an expression for the vapor pressure lowering of a dilute solution in terms of the molality.

Osmotic Pressure

This colligative property involves the equilibrium of a liquid solution and the pure liquid solvent on opposite sides of a semipermeable membrane that allows only the solvent to equilibrate. The equilibrium is achieved by having different pressures in the two phases. A simple osmometer is shown in Figure 6.26. The left side of this apparatus contains a solution containing a solute (component 2) dissolved in a solvent (component 1), and the right side contains pure solvent. The pressure of the solution is increased above that of the pure solvent by the gravitational (hydrostatic) force on the solution in the left column.

We denote the pressure on the pure solvent by P, and the pressure on the solution by $P + \Pi$. The difference Π is called the *osmotic pressure*. At equilibrium, the value of the chemical potential of the solvent must be the same on both sides of the membrane. If the solvent obeys Raoult's law,

$$\mu_1^*(T, P) = \mu_1(T, P + \Pi) = \mu_1^*(T, P + \Pi) + RT\ln(x_1) \tag{6.7-20}$$

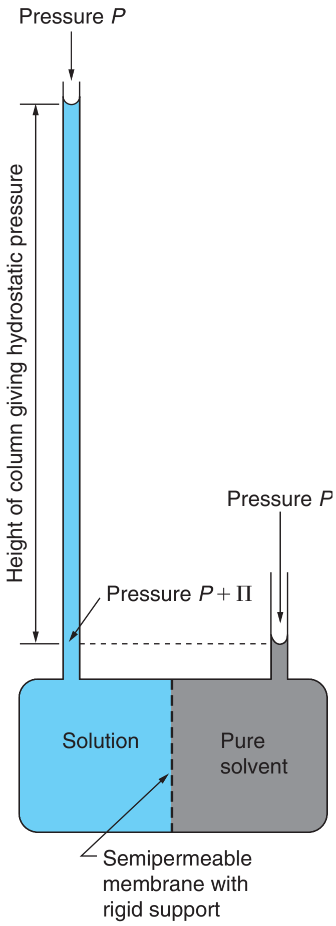

Figure 6.26 An Osmometer (Schematic).

we must abandon our previous approximation that the chemical potential is independent of the pressure. From Eq. (5.4-10), if the molar volume of the pure liquid is nearly independent of pressure (a good approximation),

$$\mu_1^*(T, P + \Pi) - \mu_1^*(T, P) = \int_P^{P+\Pi} V_{\mathrm{m},1}^* dP \approx \Pi V_{\mathrm{m},1}^* \tag{6.7-21}$$

which gives

$$\Pi V_{\mathrm{m},1}^* = -RT\ln(1 - x_2) \approx RTx_2 \tag{6.7-22}$$

It is customary to rewrite Eq. (6.7-22) in another form. For a dilute solution of two components

$$x_2 = \frac{n_2}{n_1 + n_2} \approx \frac{n_2}{n_1}$$

and we can write

$$V = n_1\bar{V}_1 + n_2\bar{V}_2 \approx n_1 V_{\mathrm{m},1}^*$$

Use of these two equations gives

$$\Pi = \frac{n_2 RT}{V} = c_2 RT \tag{6.7-23}$$

where c_2 is the molar concentration of the solute. Equation (6.7-23) is one of two equations known as the *van't Hoff equation*. It is remarkably similar to the ideal gas equation of state.

The van't Hoff equation is named for Jacobus Henricus van't Hoff, 1852–1911, a Dutch physical chemist who won the 1901 Nobel Prize in chemistry for his work on osmotic pressure. He was also the first person to propose the tetrahedral carbon atom.

EXAMPLE 6.20

The osmotic pressure of a moderately dilute solution can be surprisingly large. Find the osmotic pressure at 25°C of an aqueous solution of sucrose with a molar concentration of $0.200\ \mathrm{mol\ L^{-1}}$.

Solution

$$\Pi = (0.200\,\mathrm{mol\,L^{-1}})\left(\frac{1000\,\mathrm{L}}{1\,\mathrm{m^{-3}}}\right)\left(8.3145\,\mathrm{J\,K^{-1}mol^{-1}}\right)(298.15\,\mathrm{K})$$
$$= 4.96 \times 10^5\,\mathrm{Pa} = 4.89\,\mathrm{atm}$$

Exercise 6.36

a. Verify Eq. (6.7-23).

b. Find the osmotic pressure of a solution of 5.00 g of glucose in 1.000 L of aqueous solution at 298.15 K.

c. Calculate the height of the solution required to give a hydrostatic pressure of this size. The density of the solution is 1.002 g $\mathrm{cm^{-3}}$.

PROBLEMS

Section 6.7: Colligative Properties

6.62 The normal melting temperature of phenanthrene is 96.3°C. Its enthalpy change of fusion is 18.6 kJ $\mathrm{mol^{-1}}$. Find the solubility (maximum mole fraction) of phenanthrene in a liquid solution with naphthalene at 82.0°C. Assume that the liquid solution is ideal and that no solid solubility occurs.

6.63 The melting temperature of TNT (2,4,6-trinitrotoluene) is 80.83°C, and its enthalpy change of fusion is 21.23 kJ $\mathrm{mol^{-1}}$. Assume that TNT forms an ideal liquid solution with nitrobenzene. Find the maximum solubility (mole fraction of TNT in the liquid at equilibrium with solid TNT) at 60°C. Assume that the liquid solution is ideal and that no solid solubility occurs. What can you say about the maximum solubility of TNT in some other liquid with which TNT forms an ideal solution?

6.64 **a.** Calculate the freezing temperature at 1.000 atm of a solution of 5.00 g of sucrose in 95.00 g of water, using Eq. (6.7-9).

b. Calculate the freezing temperature of the solution of part a using Eq. (6.7-7).

c. Modify Eq. (6.7-7) by discontinuing the assumption that the solution is dilute, including an activity coefficient for the water. From the actual freezing point depression of 0.29°C, find the value of the activity coefficient of water in the solution of part a.

6.65 Find the freezing point depression of a solution of 1.500 g of KCl in 1.000 kg of water. Assume that the KCl dissociates completely, so that 2 mol of dissolved ions results from 1 mol of KCl.

6.66 A sample of 1.000 g of a solute is dissolved in 15.00 mL of benzene at 20°C. The density of benzene at this temperature is 0.8765 g $\mathrm{mL^{-1}}$. The freezing temperature depression was 3.04°C. Find the molar mass of the solute.

6.67 **a.** Calculate the boiling temperature of the solution of Problem 6.64, using Eq. (6.7-14).

b. Repeat the calculation using Eq. (6.7-15) and calculate the percent difference of the boiling point elevation from that of part a.

c. Repeat the calculation using Eq. (6.7-16) and calculate the difference of the boiling point elevation from that of part a.

6.68 The density of ethylene glycol is 1.1088 g $\mathrm{cm^{-3}}$ and its melting temperature is equal to −11.5°C. Calculate the freezing temperature of a mixture of 0.500 L of ethylene glycol and 9.500 L of water.

6.69 A sample of myoglobin with mass 1.000 g is dissolved in 100.0 mL of aqueous solution. The osmotic pressure of the solution is 11.0 torr at 25.00°C. Find the molar mass of myoglobin.

Summary of the Chapter

For each component of an ideal solution, by definition

$$\mu_i(T, P) = \mu_i^*(T, P) + RT \ln(x_i)$$

Each component of an ideal solution nearly obeys Raoult's law,

$$P_i = P_i^* x_i$$

where x_i is the mole fraction of component i in the solution. In a nonideal solution, the partial vapor pressure of a sufficiently dilute solute is governed by Henry's law:

$$P_i = k_i x_i$$

The activity a_i of substance i in any state is defined by the relation

$$\mu_i = \mu_i^\circ + RT \ln(a_i)$$

where μ_i° is the chemical potential in some standard state. According to two different mole fraction descriptions, called convention I and convention II, the activity is given by

$$a_i = \gamma_i x_i$$

The activity of a solute in the molality description is given by

$$a_i^{(\mathrm{m})} = \frac{\gamma_i^{(\mathrm{m})} m_i}{m^\circ}$$

The Debye–Hückel theory provides an accurate limiting law for the activity coefficients of electrolyte solutes. A semi-empirical equation, the Davies equation, can provide usable estimates of electrolyte activity coefficients at larger concentrations.

Two-component pressure–composition and temperature–composition phase diagrams give information about phases present at equilibrium. For a three-component system, a composition–composition diagram at constant temperature and pressure is plotted in an equilateral triangle.

The four principal colligative properties are freezing point depression, boiling point elevation, vapor pressure lowering, and osmotic pressure. In each case, the magnitude of the effect in a dilute solution is determined by the concentration of the solute but is independent of its identity.

ADDITIONAL PROBLEMS

6.70 **a.** The vapor pressure of pure water at 25°C is equal to 23.756 torr if the total pressure on the liquid is just that due to the vapor. Calculate the vapor pressure of water at 25°C if enough oxygen gas is added to the vapor to give a total pressure of 1.000 atm. Neglect any oxygen dissolved in the water.

b. Calculate the mole fraction of dissolved oxygen in the water under the conditions of part a. The Henry's law constant is in Example 6.9. Calculate the effect of this dissolved oxygen on the vapor pressure.

c. Repeat parts a and b with 100.00 atm total pressure instead of 1.000 atm.

6.71 The molar enthalpy change of fusion of ethylene glycol is 11.23 kJ mol^{-1}. Its density is 1.1088 g cm^{-3}. Find the freezing temperature of a solution made from 0.500 L of water and 9.500 L of ethylene glycol. State any assumptions.

6.72 Assuming complete dissociation, and assuming that the water activity coefficient equals unity, calculate the osmotic pressure at 25.00°C of a solution of 2.500 g of KCl in 1.000 kg of water. The density of the solution is equal to 1.002 g cm^{-3}.

6.73 **a.** Calculate the osmotic pressure at 20.00°C of a solution of 5.000 g of sucrose in 95.00 g of water, using Eq. (6.7-23). The density of the solution is equal to 1.0194 g cm^{-3}. Calculate the height of a column of the solution sufficient to equilibrate an osmometer like that of Figure 6.26.

b. Repeat the calculation using the version of Eq. (6.7-22) with the natural logarithm in it.

6.74 **a.** Find the osmotic pressure at 25.0°C of a solution containing 1.000 g of sucrose and 99.000 g of water. The density of this solution is 1.0021 g cm^{-3}. Sucrose is $C_{12}H_{22}O_{11}$, with a molar mass of 342.3 g mol^{-1}.

b. Find the height of a column of this solution needed to provide the hydrostatic pressure equal to the osmotic pressure.

6.75 The freezing temperature of CH_2OHCH_2OH, ethylene glycol (the main ingredient of automobile antifreeze), is −11.5°C. Its density is 1.1088 g cm^{-3}, and its enthalpy change of fusion is 11.23 kJ mol^{-1}. Its molar mass is 62.058 g mol^{-1}. Assume that water is insoluble in solid ethylene glycol and find the freezing temperature of a solution containing 10.00 mol of ethylene glycol and 0.250 mol of water.

6.76 A solution is made from 10.00 g of a certain protein and enough water to make 1.000 L at 298.15 K. The osmotic pressure is found to be 1.33 torr. What is the molar mass of the protein?

6.77 Find the osmotic pressure at 298.15 K and the freezing point depression of a solution of horse hemoglobin ($M = 68\ \text{kg mol}^{-1}$) if 1.000 L of solution contains 40.00 g of hemoglobin and 968.00 g of water.

6.78 A solution is made from 5.000 g of glucose and 95.000 g of water. At 20.0°C the density of this solution is 1.0175 g cm^{-3}.

a. Find the freezing temperature of this solution at 1.000 atm.

b. Find the vapor pressure of this solution at 100.0°C.

c. Find the boiling temperature of this solution at 1.000 atm.

d. Find the osmotic pressure of this solution at a temperature of 20.0°C.

6.79 Identify each statement as true or false (if a statement is true only under some special circumstance, count it as false):

a. For small enough concentration of a solute, its activity according to convention I and its activity according to convention II are nearly equal.

b. For small enough concentration of a solute, its activity coefficient according to convention I and its activity coefficient according to convention II are nearly equal.

c. For small enough concentration of a solute, its activity coefficient according to convention I and its molality activity coefficient are nearly equal.

d. For small enough concentration of a solute, its activity coefficient according to convention II and its molality activity coefficient are nearly equal.

e. In a dilute solution, the mole fraction and the activity of a solute are equal.

f. In a dilute solution, the mole fraction and the activity of the solvent are equal.

g. In an ideal solution, the mole fraction of every component is equal to its activity.

h. In an ideal solution, the mole fraction and the activity coefficient of every component are equal.

i. If two substances form an ideal solution, they are miscible in all proportions.

j. The mole fraction of naphthalene in a saturated solution is the same in all solvents with which naphthalene forms ideal solutions.

6.80 The *lever rule* can be used to determine the relative amounts of material in the two coexisting phases represented by the ends of a tie line in a two-component phase diagram, as in Figure 6.27. This rule is

$$L^{(\alpha)}n^{(\alpha)} = L^{(\beta)}n^{(\beta)}$$

where $n^{(\alpha)}$ is the total amount of both substances in phase α and $n^{(\beta)}$ is the total amount of both substances in phase β. The distances $L_1^{(\beta)}$ and $L_1^{(\alpha)}$ are labeled on the diagram. The mole fraction x_1 is the overall mole fraction,

$$x_1 = \frac{n_1^{(\alpha)} + n_1^{(\beta)}}{n_1^{(\alpha)} + n_1^{(\beta)} + n_2^{(\alpha)} + n_2^{(\beta)}}$$

Derive the lever rule.

6.81 The freezing temperature of CH_2OHCH_2OH, (ethylene glycol, the main ingredient of automobile antifreeze), is $-11.5°C$. Its density is $1.1088\ g\ cm^{-3}$, and its enthalpy change of fusion is $11.23\ kJ\ mol^{-1}$.

a. Find the freezing point depression constant for solutions with ethylene glycol as the solvent.

b. Find the freezing temperature of a solution of 10.00 g of water in 1.000 kg of ethylene glycol.

c. Find the freezing temperature of a solution of 10.00 g of ethylene glycol in 1.000 kg of water.

d. Assuming an ideal liquid solution, draw the water–ethylene glycol temperature–composition phase diagram, using Eq. (6.7-7) to calculate the curves. Assume that the enthalpy changes of fusion are constant. Calculate at least three points on each curve leading to the eutectic. What is the temperature of the eutectic point?

e. A common practice is to mix equal parts of water and antifreeze by volume. Find the freezing temperature of this mixture, using your graph from part d. What proportions by volume would give the lowest freezing temperature?

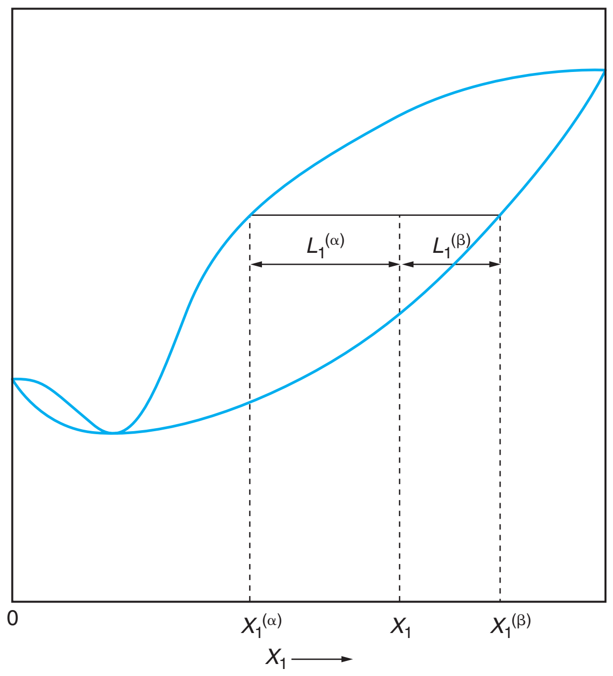

Figure 6.27 Phase Diagram Illustrating the Lever Rule. The lever rule is similar to the formula for levers, $F_1L_1 = F_2L_2$, where the F's stand for forces and the L's stand for the lengths of the lever arms.

6.82 Assume that the partial vapor pressure (assume ideal vapor) of substance 2 in a two-component solution is given adequately at a constant temperature by

$$P_2 = ax_2 + bx_2^2 + cx_2^3$$

where a, b, and c are constants at constant temperature.

a. What is the expression for the Henry's law constant k_2?

b. What conditions must be obeyed by the constants a, b, and c, if Raoult's law is obeyed near $x_1 = 1$?

c. What is the expression for P_2^*?

d. What is the expression for P_2^* if Raoult's law is obeyed near $x_1 = 1$?

e. Using convention I, what is the expression for γ_2 at $x_2 = 0.500$?

f. Using convention II, what is the expression for γ_2 at $x_2 = 0.500$?

6.83 The enthalpy change of fusion of phenol is $28.67\ cal\ g^{-1}$. Find the freezing depression of a mixture of 0.09500 mol of p-toluidine and 0.95 mol of phenol.

7

Chemical Equilibrium

PRINCIPAL FACTS AND IDEAS

1. The principles of thermodynamics determine the state of chemical equilibrium for any reaction.
2. The equilibrium constant expression of elementary chemistry is equal to a constant at constant temperature when it is expressed in terms of activities.
3. The principle of Le Châtelier can predict how a chemical system at equilibrium responds to changes in temperature, pressure, or amounts of substances.
4. The coupling of biochemical reactions can be understood through thermodynamics and the use of postulated mechanisms.

7.1 Gibbs Energy Changes and the Equilibrium Constant

In a general chemistry course a quotient of concentrations and/or partial pressures is set equal to an equilibrium constant. We now use thermodynamics to derive an equilibrium constant expression in terms of activities that will apply to all cases. Equation (2.7-7) is a generic chemical equation that can stand for any chemical reaction:

$$0 = \sum_{i=1}^{c} v_i \mathscr{F}_i \tag{7.1-1}$$

where the chemical formula of substance number i is abbreviated by $\mathscr{F}_i$ and its stoichiometric coefficient is denoted by v_i. The stoichiometric coefficients of products are positive, and those of reactants are negative. The arrow or double arrow that we ordinarily use is replaced by an equals sign, and all substances' formulas are on the right side of the equation. For example, the equation for the gas-phase decomposition of N_2O_4 is written as

$$N_2O_4(g) \rightleftharpoons 2NO_2(g) \tag{7.1-2a}$$

or

$$0 = 2NO_2(g) - N_2O_4(g) \tag{7.1-2b}$$

so that

$$\nu(NO_2) = 2$$
$$\nu(N_2O_4) = -1$$

The inconvenience of writing chemical equations in this unfamiliar way is outweighed by the resulting ability to write compact thermodynamic equations that apply to any chemical reaction.

Consider a one-phase closed system maintained at constant pressure and temperature in which a single chemical reaction can occur. We assume that the system is in a metastable state as equilibrium is approached so that the Gibbs energy and other thermodynamic variables of the system have well-defined values. From Chapter 4, we know that the Gibbs energy of the system must decrease until it reaches a stable minimum value at equilibrium.

The Gibbs energy of the system is a function of $T, P, n_1, n_2, \ldots, n_c$, where c is the number of substances in the system. If an infinitesimal amount of reaction takes place at constant T and P, it changes the amounts of the substances and the change in the Gibbs energy is given by Eq. (4.5-3):

$$dG = \sum_{i=1}^{c} \mu_i dn_i \quad \text{(constant } T \text{ and } P\text{)} \tag{7.1-3}$$

Since the system is closed the n's can change only by the progress of the reaction. To express dG in terms of the amount of reaction that takes place, we define the *extent of* *reaction* ξ by

$$n_i = n_i(\text{initial}) + \nu_i\xi \quad (\text{definition of } \xi) \tag{7.1-4}$$

Equation (7.1-4) gives the same value of ξ for any choice of the substance i. The extent of reaction has the dimensions of moles. If ξ changes in value from 0 to 1 mol, we say that 1 mol of reaction has occurred. If 1 mol of reaction occurs, ν_i moles of i have appeared if i is a product, and $|\nu_i|$ moles of i have disappeared if i is a reactant. Think of a stoichiometric coefficient as representing moles of substance per mole of reaction, so that the stoichiometric coefficients are dimensionless.

For an infinitesimal extent of reaction, $d\xi$,

$$dn_i = \nu_i d\xi \tag{7.1-5}$$

Equation (7.1-3) now becomes, for constant T and P,

$$dG = \sum_{i=1}^{c} \mu_i \nu_i d\xi = \left[\sum_{i=1}^{c} \nu_i \mu_i\right] d\xi \tag{7.1-6}$$

where we have factored the common factor $d\xi$ out of the sum. For our reacting system G is a function of T, P, and ξ so that

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \sum_{i=1}^{c} \nu_i \mu_i \tag{7.1-7}$$

The quantity $(\partial G/\partial\xi)_{T,P}$ is the *rate of change of Gibbs energy per mole of reaction*.

A spontaneous process at constant T and P corresponds to $dG < 0$. If the forward reaction is spontaneous, $d\xi > 0$ and

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} < 0 \quad \begin{array}{l}\text{(forward reaction}\\ \text{spontaneous)}\end{array} \tag{7.1-8}$$

If the reverse reaction is spontaneous, $d\xi < 0$ and

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} > 0 \quad \begin{array}{l}\text{(reverse reaction}\\ \text{spontaneous)}\end{array} \tag{7.1-9}$$

If the equilibrium state has been attained, there is no tendency for the reaction to proceed, and $dG = 0$, so that

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \sum_{i=1}^{c} \nu_i \mu_i = 0 \quad (\text{equilibrium}) \tag{7.1-10}$$

The situation is as represented in Figure 7.1, with a smooth minimum in G at the equilibrium value of ξ. A system in any nonequilibrium state will spontaneously react to approach the equilibrium state at the minimum in the curve representing G as a function of ξ, beginning from either side of the minimum.

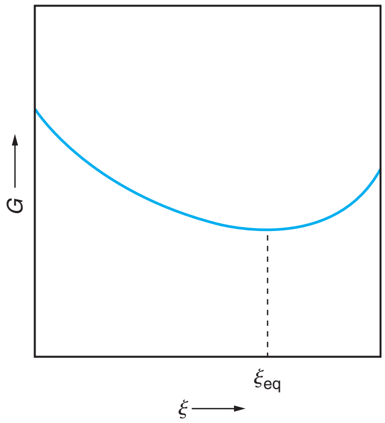

Figure 7.1 The Gibbs Energy of a Reacting System as a Function of the Progress Variable.

In Chapter 6 we expressed the chemical potential of a general substance i in terms of its activity a_i:

$$\mu_i = \mu_i^\circ + RT\ln(a_i) \tag{7.1-11}$$

where μ_i° is the chemical potential of substance i in whatever standard state applies. The rate of change of the Gibbs energy per mole of reaction is now expressed in terms of activities:

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \sum_{i=1}^{c} v_i\mu_i^\circ + RT\sum_{i=1}^{c} v_i\ln(a_i) \tag{7.1-12}$$

If it is possible to maintain all of the reactants and products in their standard states, all activities are equal to unity. The second sum in the right-hand side of Eq. (7.1-12) vanishes and the change in G for 1 mol of reaction is

$$\begin{aligned}\Delta G^\circ &= \int_0^1 \left[\left(\frac{\partial G}{\partial \xi}\right)_{T,P}\bigg|_{\text{standard state}}\right] d\xi \\ &= \int_0^1 \left(\sum_{i=1}^{c} v_i\mu_i^\circ\right) d\xi = \left(\sum_{i=1}^{c} v_i\mu_i^\circ\right)\int_0^1 d\xi\end{aligned}$$

so that for 1 mol of reaction

$$\Delta G^\circ = \sum_{i=1}^{c} v_i\mu_i^\circ \quad \text{(standard-state reaction)} \tag{7.1-13}$$

The quantity ΔG° is the *standard-state Gibbs energy change for 1 mol of reaction*. It applies to a reaction in which all reactants and products are in their standard states. If the standard-state Gibbs energy change is negative, the forward reaction would be spontaneous under standard conditions, and if it is positive, the reverse reaction would be spontaneous under standard conditions.

The *Gibbs energy change of formation* is similar to the enthalpy change of formation defined in Chapter 2. It is the Gibbs energy change to produce 1 mol of the substance in question from the appropriate elements in their most stable forms.[1] If substance number i and the elements are in their standard states, the Gibbs energy change of formation of substance i is denoted by $\Delta_f G^\circ(i)$. The Gibbs energy change for the standard-state reaction can be calculated from standard-state Gibbs energy changes of formation in the same way as ΔH° was calculated in Chapter 2:

$$\Delta G^\circ = \sum_{i=1}^{c} v_i\Delta_f G^\circ(i) \tag{7.1-14}$$

---

[1] An exception to the practice of taking the most stable form of the element in defining the formation reaction is in the case of phosphorus, for which the less reactive white phosphorus is taken instead of the more stable but more reactive red phosphorus.

Values of standard-state Gibbs energy changes of formation for a number of substances are included in Table A.8 of Appendix A, and larger tables are available. This table also includes values of the function $-(G^\circ_{\mathrm{m}} - H_{\mathrm{m},298^\circ})/T$, which can also be used to calculate ΔG° for a reaction, as is done in Example 7.1. This function generally varies more slowly with temperature than does $\Delta_{\mathrm{f}}G^\circ$. If a value of ΔG° is needed for a temperature that is not included in the table, interpolation of this function usually gives better accuracy than does interpolation in a table of $\Delta_{\mathrm{f}}G^\circ$ values.

The Gibbs energy change of a constant-temperature reaction can also be calculated from

$$\Delta G = \Delta H - T\Delta S \tag{7.1-15}$$

where the enthalpy change is calculated from enthalpy changes of formation, using Eq. (2.7-12), and the entropy change for a reaction is calculated from third-law ("absolute") entropies, using Eq. (3.5-7).

EXAMPLE 7.1

a. Using tabulated Gibbs energy changes of formation, find the standard-state Gibbs energy change at 298.15 K for the reaction $2\,\mathrm{CO(g)} + \mathrm{O_2(g)} \rightleftharpoons 2\,\mathrm{CO_2(g)}$.

b. Calculate ΔG° for this reaction at 298.15 K from ΔH° and ΔS°.

c. Calculate ΔG° for the same reaction using values of $-(G^\circ_{\mathrm{m}} - H^\circ_{\mathrm{m},298})/T$ and values of $\Delta_{\mathrm{f}}H^\circ$.

Solution

a. From values in Table A.8 of Appendix A,

$$\begin{aligned}\Delta G^\circ &= 2\Delta_{\mathrm{f}}G^\circ(\mathrm{CO_2}) + (-2)\Delta_{\mathrm{f}}G^\circ(\mathrm{CO}) + (-1)\Delta_{\mathrm{f}}G^\circ(\mathrm{O_2})\\ &= 2(-394.389\,\mathrm{kJ\,mol^{-1}}) - 2(-137.163\,\mathrm{kJ\,mol^{-1}}) + 0\\ &= -514.452\,\mathrm{kJ\ mol^{-1}}\end{aligned}$$

b. From values in Table A.8 of Appendix A,

$$\begin{aligned}\Delta H^\circ &= 2\Delta_{\mathrm{f}}H^\circ(\mathrm{CO_2}) + (-2)\Delta_{\mathrm{f}}H^\circ(\mathrm{CO}) + (-1)\Delta_{\mathrm{f}}H^\circ(\mathrm{O_2})\\ &= 2(-393.522\,\mathrm{kJ\,mol^{-1}}) - 2(-110.527\,\mathrm{kJ\,mol^{-1}}) - 0\\ &= -565.990\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= 2S^\circ(\mathrm{CO_2}) + (-2)S^\circ(\mathrm{CO}) - 1S^\circ(\mathrm{O_2})\\ &= 2(213.795\,\mathrm{J\,K^{-1}\,mol^{-1}}) - 2(197.653\,\mathrm{J\,K^{-1}\,mol^{-1}})\\ &\quad + (-1)(205.147\,\mathrm{J\,K^{-1}\,mol^{-1}})\\ &= -172.863\,\mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ\\ &= -565.990\,\mathrm{kJ\,mol^{-1}} - (298.15\,\mathrm{K})(-0.172863\,\mathrm{kJ\,K^{-1}\,mol^{-1}})\\ &= -514.451\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

c.

$$T\Delta\left(\frac{-\left(G_{\mathrm{m}}^{\circ}-H_{\mathrm{m},298^{\circ}}^{\circ}\right)}{T}\right) = (298.15\ \mathrm{K})2(213.795\ \mathrm{J\,K^{-1}\,mol^{-1}})$$

$$-\,2\left(197.653\ \mathrm{J\,K^{-1}\,mol^{-1}}\right)$$

$$-\,205.147\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

$$= (298.15\ \mathrm{K})(-0.172863\ \mathrm{kJ\,K^{-1}\,mol^{-1}})$$

$$= -51.539\ \mathrm{kJ\,mol^{-1}}$$

$$\Delta G^{\circ} = \Delta H_{298}^{\circ} - T\Delta\left(\frac{-\left(G_{\mathrm{m}}^{\circ}-H_{\mathrm{m},298^{\circ}}^{\circ}\right)}{T}\right)$$

$$= -565.990\ \mathrm{kJ\,mol^{-1}} + 51.539\ \mathrm{kJ\,mol^{-1}}$$

$$= -514.451\ \mathrm{kJ\,mol^{-1}}$$

Exercise 7.1

a. Using Gibbs energy changes of formation from Table A.8, calculate ΔG° at 298.15 K for the reaction

$$\mathrm{PCl_5(g)} \rightleftharpoons \mathrm{PCl_3(g)} + \mathrm{Cl_2(g)}$$

b. Calculate ΔH° and ΔS° at 298.15 K for the same reaction.

c. Calculate ΔG° at 298.15 K for the same reaction using Eq. (7.1-15). Compare with the answer of part a.

d. Calculate ΔG° at 298.15 K for the same reaction using values of $-(G_{\mathrm{m}}^{\circ} - H_{\mathrm{m},298}^{\circ})/T$ and the value of ΔH°.

The Gibbs Energy Change at Fixed Composition

Using the identity that a sum of logarithms is equal to the logarithm of a product, we write Eq. (7.1-12) in the form

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta G^{\circ} + RT\ln(Q) \qquad (7.1\text{-}16)$$

where

$$Q = a_1^{v_1} a_2^{v_2} \cdots a_c^{v_c} = \prod_{i=1}^{c} a_i^{v_i} \qquad (7.1\text{-}17)$$

The notation Π denotes a product of factors, just as Σ denotes a sum of terms. The quantity Q is called the *activity quotient*. It is called a quotient because the factors for reactants have negative exponents.

Exercise 7.2

Carry out the steps to obtain Eqs. (7.1-16) and (7.1-17).

If it is possible to keep the activity of every substance fixed during a chemical reaction, the value of Q is fixed and the change in Gibbs energy for 1 mol of reaction can be written

$$\begin{aligned}\Delta G(\text{fixed composition}) &= \left(\frac{\partial G}{\partial \xi}\right)_{T,P}\Bigg|_{\text{fixed comp}} \\ &= \int_0^1 \Delta G^\circ + RT\ln(Q)d\xi \\ &= \Delta G^\circ + RT\ln(Q)\int_0^1 d\xi\end{aligned}$$

$$\Delta G(\text{fixed composition}) = \Delta G^\circ + RT\ln(Q) \tag{7.1-18}$$

EXAMPLE 7.2

Calculate the value of ΔG(fixed composition) at 298.15 K for the reaction of Exercise 7.1 if the partial pressure of PCl_5 is maintained equal to 0.0100 bar, the partial pressure of PCl_3 is maintained equal to 0.00600 bar, and the partial pressure of Cl_2 is maintained equal to 0.00300 bar. Assume that the gases are ideal.

Solution

$$Q = \frac{a(PCl_3)\,a(Cl_2)}{a(PCl_5)} = \frac{(0.00600)(0.00300)}{(0.0100)} = 0.00180$$

$$\begin{aligned}\left(\frac{\partial G}{\partial \xi}\right)_{T,P} &= 20.661\ \text{kJ mol}^{-1} + (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})\ln(0.00180) \\ &= 20.661\ \text{kJ mol}^{-1} + (-15667\ \text{J mol}^{-1}) \\ &= 4994\ \text{J mol}^{-1} = 4.994\ \text{kJ mol}^{-1}\end{aligned}$$

Exercise 7.3

Repeat the calculation of the previous example if the partial pressure of PCl_5 is maintained equal to 0.00600 bar, the partial pressure of PCl_3 is maintained equal to 0.0100 bar, and the partial pressure of Cl_2 is maintained equal to 0.00300 bar.

At equilibrium, $(\partial G/\partial \xi)_{T,P} = 0$, and Eq. (7.1-16) becomes

$$0 = \Delta G^\circ + RT\ln(Q_{\text{eq}}) \tag{7.1-19}$$

The standard-state Gibbs energy change ΔG° depends only on temperature since the standard-state chemical potentials depend only on temperature. The value of Q_{eq} is therefore equal to a constant at constant temperature. It is the *equilibrium constant*, denoted by K and given by the relation

$$\boxed{K = Q_{\mathrm{eq}} = \prod_{i=1}^{c} a_{i,\mathrm{eq}}^{\nu_i} = e^{-\Delta G^\circ/RT}} \tag{7.1-20}$$

where $a_{i,\mathrm{eq}}$ denotes the equilibrium value of a_i. Since we have derived expressions for the activity of any kind of a substance in Chapter 6, Eq. (7.1-20) is valid for any kind of a reacting system. If activity coefficients are assumed equal to unity and if concentrations or partial pressures are used for activities, Eq. (7.1-20) becomes the familiar equilibrium constant expression of a general chemistry course.

PROBLEMS

Section 7.1: Gibbs Energy Changes and the Equilibrium Constant

7.1 A hypothetical gaseous isomerization reaction

$$\mathrm{A} \rightleftharpoons \mathrm{B}$$

has $\Delta G^\circ = -5.000\,\mathrm{kJ\,mol^{-1}}$ at 298.15 K. Construct an accurate graph of $G - \mu_A^*$ as a function of the extent of reaction ξ for the case that the initial amount of A is 1.000 mol and that of B is 0. Assume that the gases are ideal. The total pressure is kept fixed at 1.000 bar and the temperature is kept fixed at 298.15 K. Locate the minimum in G on the graph and calculate the equilibrium constant from the value of ξ at the minimum.

7.2 Consider a hypothetical gas-phase reaction

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C}$$

for which $\Delta G^\circ = -10.00\,\mathrm{kJ\,mol}$ at 298.15 K. Assume that the gases are ideal.

a. Find the value of $\left(\frac{\partial G}{\partial \xi}\right)_{T,P}$ if $P_{\mathrm{A}} = 1.00\,\mathrm{bar}$, $P_{\mathrm{B}} = 0.500\,\mathrm{bar}$, and $P_{\mathrm{C}} = 0.250\,\mathrm{bar}$.

b. Find the value of the equilibrium constant.

c. If the initial partial pressures are those in part a, find the equilibrium values of the partial pressures.

7.3 A hypothetical gaseous isomerization reaction $\mathrm{A} \rightleftharpoons \mathrm{B}$ has $\Delta G^\circ = -5.000\,\mathrm{kJ\,mol^{-1}}$ at 298.15 K. Consider the case that the initial amount of A is 1.000 mol and that of B is 0. Evaluate for $\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = 0.10\,\mathrm{mol}$, 0.20 mol, 0.40 mol, 0.60 mol, 0.80 mol, and 0.90 mol. Construct an accurate graph of this quantity. Assume that the gases are ideal.

7.2 Reactions Involving Gases and Pure Solids or Liquids

For this class of chemical reactions we will assume that all gases are ideal and that all liquids and solids have constant volumes. We first consider reactions involving only gases. For an ideal gas,

$$a_i = P_i/P^\circ \text{ (ideal gas)} \tag{7.2-1}$$

and Eq. (7.1-20) for the equilibrium constant is

$$K=\prod_{i=1}^{c}\left(\frac{P_{i,\mathrm{eq}}}{P^\circ}\right)^{\nu_i}\quad\text{(ideal gas reaction)}\tag{7.2-2}$$

EXAMPLE 7.3

Consider the reaction:

$$0=2\,\mathrm{NO_2(g)}-\mathrm{N_2O_4(g)}$$

a. Calculate the value of ΔG° at 298.15 K.

b. Calculate the value of K at 298.15 K.

c. Calculate the equilibrium pressure of a system that initially consists of 1.000 mol of N_2O_4 and that is confined in a fixed volume of 24.46 L at 298.15 K. Assume ideal gases.

Solution

a. From the Gibbs energy changes of formation,

$$\begin{aligned}\Delta G^\circ &= 2\Delta_\mathrm{f}G^\circ(\mathrm{NO_2})-\Delta_\mathrm{f}G^\circ(\mathrm{N_2O_4})\\ &=(2)(51.258\,\mathrm{kJ\,mol^{-1}})-(97.787\,\mathrm{kJ\,mol^{-1}})\\ &=4.729\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

b. The equilibrium constant is

$$\begin{aligned}K&=\frac{\left(P_\mathrm{eq}(\mathrm{NO_2})/P\right)^2}{P_\mathrm{eq}(\mathrm{N_2O_4})/P^\circ}\\ &=\exp\left(\frac{-4729\,\mathrm{J\,mol^{-1}}}{\left(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}\right)(298.15\,\mathrm{K})}\right)\\ &=0.148\end{aligned}$$

c. Let α be the degree of dissociation (the fraction of the initial N_2O_4 that dissociates at equilibrium).

$$\begin{aligned}P_\mathrm{eq}(\mathrm{NO_2})&=\frac{n(\mathrm{NO_2})\,\mathrm{RT}}{V}=\frac{(1.000\,\mathrm{mol})(2\alpha)\,RT}{V}\\ P_\mathrm{eq}(\mathrm{N_2O_4})&=\frac{n(\mathrm{N_2O_4})\,RT}{V}=\frac{(1.000\,\mathrm{mol})(1-\alpha)\,RT}{V}\end{aligned}$$

We now can write

$$\begin{aligned}K=0.148&=\frac{(2\alpha)^2}{1-\alpha}\,\frac{(1.000\,\mathrm{mol})\,RT}{P^\circ V}\\ &=\frac{(2\alpha)^2}{1-\alpha}\,\frac{(1.000\,\mathrm{mol})(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\,(298.15\,\mathrm{K})}{(100{,}000\,\mathrm{Pa})(0.02446\,\mathrm{m^3})}\\ &=\frac{4\alpha^2(1.0135)}{1-\alpha}\end{aligned}$$

which is the same as

$$4.054\alpha^2 + 0.148\alpha - 0.148 = 0$$

Use of the quadratic formula gives

$$\alpha = \frac{-0.148 \pm \sqrt{(0.148)^2 + (4)(4.054)(0.148)}}{2(4.054)}$$
$$= 0.174$$

We have disregarded the negative root to the quadratic equation, since a negative value of α is not physically possible if no NO_2 is initially present. The total amount of gas is $(1.000\,\text{mol})(1 - \alpha + 2\alpha) = 1.174\,\text{mol}$, so the equilibrium total pressure is

$$P_{\text{eq}} = \frac{(1.174\,\text{mol})\left(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}\right)(298.15\,\text{K})}{0.02446\,\text{m}^3}$$
$$= 1.190 \times 10^5\,\text{Pa} = 1.174\,\text{atm}$$

It is always the case that when a quadratic equation is solved in a chemistry problem, only one of the two roots corresponds to a physically possible situation.

We now consider reactions involving pure liquids and solids as well as gases. If the pressure of the system does not differ very much from P°, then Eq. (6.3-14) gives for the activity of a pure liquid or solid

$$a_i \approx 1 \text{ (pure liquid or solid near } P^\circ) \tag{7.2-3}$$

The activities of pure liquids or solids can be omitted from an activity quotient unless the pressure is very large.

EXAMPLE 7.4

a. Write the equilibrium constant quotient for the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$.
b. Find the value of the equilibrium constant at 298.15 K and $P_{\text{eq}}(CO_2)$ at 298.15 K.

Solution

a. Since the activities of the solids are nearly equal to unity,

$$K = \frac{a_{\text{eq}}(CaO)a_{\text{eq}}(CO_2)}{a_{\text{eq}}(CaCO_3)} \approx a_{\text{eq}}(CO_2) \approx \frac{P_{\text{eq}}(CO_2)}{P^\circ}$$

b. From the Gibbs energy changes of formation

$$\Delta G^\circ = (1)(-603.501\,\text{kJ mol}^{-1}) - 394.389\,\text{kJ mol}^{-1}$$
$$+ (-1)(-1128.79\,\text{kJ mol}^{-1})$$
$$= 130.90\,\text{kJ mol}^{-1}$$

$$K = \exp\left[-\frac{130900\,\text{J mol}^{-1}}{\left(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}\right)(298.15\,\text{K})}\right]$$
$$= 1.17 \times 10^{-23}$$

$$P_{\text{eq}}(\text{CO}_2) = (P^\circ)\left(1.17 \times 10^{-23}\right)$$
$$= 1.17 \times 10^{-23}\,\text{bar} = 1.15 \times 10^{-23}\,\text{atm}$$

This equilibrium constant is strongly temperature-dependent and becomes much larger at higher temperatures. At high temperatures this reaction is used to make CaO(s) ("quicklime") commercially from limestone.

Reactions that appear to proceed to completion are not fundamentally different from other reactions. They just have very large equilibrium constants.

EXAMPLE 7.5

a. Write the activity quotient for the combustion of propane at 298.15 K.
b. Find the value of the equilibrium constant for this reaction.

Solution

a. The reaction equation is

$$0 = 3\text{CO}_2(\text{g}) + 4\text{H}_2\text{O(l)} - \text{C}_3\text{H}_8(\text{g}) - 5\text{O}_2(\text{g})$$

$$Q = \frac{(P(\text{CO}_2))/P^\circ)^3(1)^4}{(P(\text{C}_3\text{H}_8)/P^\circ)(P(\text{O}_2))/P^\circ)^5}$$

b.

$$\begin{aligned}\Delta G^\circ &= 3\Delta_f G^\circ(\text{CO}_2) + 4\Delta_f G^\circ(\text{H}_2\text{O}) - 1\Delta_f G^\circ(\text{C}_3\text{H}_8) \\ &\quad + (-5)\Delta_f G^\circ(\text{O}_2) \\ &= (3)(-394.389\,\text{kJ mol}^{-1}) + (4)(-237.141\,\text{kJ mol}^{-1}) \\ &\quad + (-1)(-23.27\,\text{kJ mol}^{-1}) - 5(0) \\ &= -2108.46\,\text{kJ mol}^{-1}\end{aligned}$$

$$K = \exp\left[\frac{2108460\,\text{J mol}^{-1}}{\left(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1}\right)(298.15\,\text{K})}\right]$$
$$= e^{850.5} = 2 \times 10^{369}$$

Exercise 7.4

a. Find the final partial pressure of propane and oxygen if a stoichiometric mixture of propane and oxygen comes to equilibrium at 298.15 K and a total pressure of 760.0 torr.
b. Find the volume containing one molecule of propane at the equilibrium of part a. Comment on the magnitude of your result.

PROBLEMS

Section 7.2: Reactions Involving Gases and Pure Solids or Liquids

7.4 Find the value of the equilibrium constant for the reaction of Problem 7.1 from the $\Delta G°$ value and compare it with the value found graphically in Problem 7.1.

7.5 **a.** Find the value of the equilibrium constant at 298.15 K for the reaction

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

b. 0.2000 mol of SO_2 and 0.1000 mol of O_2 are mixed and maintained at a constant total pressure of 1.000 bar and a constant temperature of 298.15 K. Find the equilibrium partial pressure of each gas.

7.6 A mixture of 1.000 mol of N_2 and 3.000 mol of H_2 was placed in contact with a catalyst and allowed to come to equilibrium at 450°C. It was found that the mole fraction of NH_3 was equal to 0.0402 at a total pressure of 10.00 atm.

a. Find the value of the equilibrium constant at this temperature for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2\ NH_3$$

b. Find the value of $\Delta G°$ for this reaction at 450°C.

c. Calculate the value of $\Delta_f G°(NH_3)$ at this temperature.

7.7 For the reaction

$$H_2(g) + D_2(g) \rightleftharpoons 2HD(g)$$

where D is ^{2}H(deuterium),

a. Find $\Delta H°$ and $\Delta S°$ at 298.5 K.

b. Find $\Delta G°$ and K at 298.15 K.

c. Find the equilibrium partial pressure of each gas at a total pressure of 1.000 bar and a temperature of 298.15 K, starting with an equimolar mixture of H_2 and D_2.

d. Construct a graph of $G - G$(initial) as a function of the progress variable ξ, starting with 0.500 mol of H_2 and 0.500 mol of D_2 and maintaining a temperature of 298.15 K and a total pressure of 1.000 bar.
Data for HD(g) at 298.15 K:
$\Delta_f H° = 0.33\ \text{kJ mol}^{-1}$, $\Delta_f G° = -1.46\ \text{kJ mol}^{-1}$,
$S°_m = 143.69\ \text{J K}^{-1}\ \text{mol}^{-1}$
Data for D_2(g) at 298.15 K:
$\Delta_f H° = 0\ \text{kJ mol}^{-1}$, $\Delta_f G° = 0\ \text{kJ mol}^{-1}$,
$S°_m = 144.85\ \text{J K}^{-1}\ \text{mol}^{-1}$

7.8 Find the standard-state Gibbs energy change at 298.15 K for each of the reactions:

a. $2NO(g) + O_2(g) \rightleftharpoons N_2O_4(g)$

b. $4NO_2(g) + O_2(g) \rightleftharpoons 2N_2O_5(g)$

7.9 Find the standard-state Gibbs energy change at 298.15 K for each of the reactions:

a. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

b. $S(s,\text{rhombic}) + O_2(g) \rightleftharpoons O_2(g)$

c. $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

7.10 Using formation values and third-law entropies, find $\Delta H°$, $\Delta S°$, and $\Delta G°$ for each of the following reactions. Calculate $\Delta H° - T\Delta S°$ and compare it with $\Delta G°$ to check the consistency of the data.

a. $2\ HgO(s) \rightleftharpoons 2Hg(l) + O_2(g)$

b. $CaCO_3(\text{calcite},s) + 2HCl(g) \rightleftharpoons CaCl_2(s) + H_2O(l) + CO_2(g)$

7.11 Using formation values and third-law entropies, find $\Delta H°$, $\Delta S°$, and $\Delta G°$ for each of the following reactions. Calculate $\Delta H° - T\Delta S°$ and compare it with $\Delta G°$ to check the consistency of the data.

a. $2\ Mg(s) + O_2(g) \rightleftharpoons 2MgO(s)$

b. $CaCO_3(\text{calcite},s) \rightleftharpoons CaO(s) + CO_2(g)$

7.12 Find the equilibrium constant at 298.15 K for each of the reactions of Problem 7.10.

7.13 Find the equilibrium constant at 298.15 K for each of the reactions of Problem 7.11.

7.14 **a.** Find the value of the equilibrium constant at 298.15 K for the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

b. Find the total pressure if 0.00100 mol of $PCl_5(g)$ is placed in a vessel with a volume of 20.000 L at 298.15 K and allowed to equilibrate. Assume ideal gas behavior.

7.15 The equilibrium constant for the reaction

$$N_2O_4(g) \rightleftharpoons 2NO_2$$

is equal to 0.148 at 298.15 K. If a system containing these gases is maintained at a constant total pressure of 1.000 bar and a temperature of 298.15 K, find the partial pressure of each gas at equilibrium.

7.16 **a.** Find ΔG° at 298.15 K for the gas-phase reaction

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

b. Find K for the reaction at 298.15 K.

c. If a stoichiometric mixture of SO_2 and O_2 is allowed come to equilibrium at 298.15 K and 1.000 bar, find the partial pressure of SO_2.

7.17 **a.** Find the equilibrium constant at 298.15 K for the reaction

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

b. Find the equilibrium composition of a system originally consisting of 0.250 mol of N_2 and 0.750 mol of H_2, maintained at 298.15 K and 1.000 atm.

7.18 **a.** Find ΔG° and K for each of the following reactions at 298.15 K:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$
$$2NO(g) + O_2(g) \rightleftharpoons 2\,NO_2(g)$$

b. Using the results of part a, find ΔG° and K for the reaction at 298.15 K:

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$$

c. Find ΔG° and K for the reaction at 298.15 K:

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

7.19 Find ΔG° and K at 298.15 K for each of the gas-phase reactions:

a. $N_2O + O \rightleftharpoons 2NO$

b. $H_2 + CO_2 \rightleftharpoons H_2O + CO$

c. $O_2 + O \rightleftharpoons O_3$

7.20 Find ΔG° and K at 298.15 K for each of the gas-phase reactions:

a. $H_2O + \frac{7}{2}H_2S + 3NO_2 \rightleftharpoons 3NH_3 + \frac{7}{2}SO_2$

b. $3O_2 \rightleftharpoons 2O_3$

7.21 Find the total pressure such that at equilibrium at 298.15 K the partial pressure of NO_2 is twice as large as the partial pressure of N_2O_4. Assume that the gases are ideal.

7.3 Chemical Equilibrium in Solutions

The activity of a solute is given in one of several different ways, as described in Chapter 6. In discussing chemical equilibrium, one must specify which description is being used, since activities and standard states are different for different descriptions, and equilibrium constants have different values in different descriptions. We will usually use the molality description for aqueous solutions, but the molarity description and convention II can also be used. In the molality description, the activity of a solute is given in Eq. (6.3-37):

$$a_i = \gamma_i m_i / m^\circ \tag{7.3-1}$$

where m_i is the molality of substance number i, m° is exactly equal to 1 mol kg^{-1}, and γ_i is the activity coefficient of substance i. We will usually omit superscripts on the activity coefficients and rely on the context to tell which description is being used. The activity of the solvent is given by Eq. (6.3-46) for any description:

$$a_1 = \gamma_1 x_1 \tag{7.3-2a}$$

In a dilute solution, both the activity coefficient and the mole fraction of the solvent are nearly equal to unity, so that the activity of the solvent is frequently approximated by unity:

$$a_1 \approx 1 \quad \text{(solvent in a dilute solution)} \tag{7.3-2b}$$

The Gibbs energy change for a standard-state solution reaction can be calculated from tables of the standard-state Gibbs energy changes of formation, using Eq. (7.1-14). Table A.8 of Appendix A includes some values of $\Delta_f G^\circ$ for some solids, liquids, gases, and solutes (using the molality description).

EXAMPLE 7.6

Using tabulated $\Delta_f G^\circ$ values, find ΔG° at 298.15 K for the reaction

$$2\,\mathrm{CO(aq)} + \mathrm{O_2(aq)} \rightleftharpoons 2\,\mathrm{CO_2(aq)}$$

Solution

From values for the molality description in Table A.8 of Appendix A,

$$\begin{aligned}\Delta G^\circ &= 2\Delta_f G^\circ(\mathrm{CO_2}) + (-2)\Delta_f G^\circ(\mathrm{CO}) - \Delta_f G^\circ(\mathrm{O_2})\\ &= 2(-385.98\ \mathrm{kJ\,mol^{-1}}) + (-2)(-119.90\ \mathrm{kJ\,mol^{-1}})\\ &\quad + (-1)(16.4\ \mathrm{kJ\,mol^{-1}})\\ &= -548.56\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

This value compares with $-514.452\ \mathrm{kJ\,mol^{-1}}$ for the gas-phase reaction at the same temperature.

Exercise 7.5

Find the value of ΔG° for the reaction of Example 7.6 using convention II instead of the molality description.

The equilibrium constant for a reaction involving only solutes is given in the molality description by

$$K = Q_{\mathrm{eq}} = \prod_{i=2}^{c}\left(\frac{\gamma_i m_{\mathrm{i,eq}}}{m^\circ}\right)^{v_i} \quad \text{(only solutes in reaction)} \tag{7.3-3}$$

The equilibrium constant for a reaction involving the solvent is given by

$$K = Q_{\mathrm{eq}} = (\gamma_1 x_1)^{v_1}\prod_{i=2}^{c}\left(\frac{\gamma_i m_{i,\mathrm{eq}}}{m^\circ}\right)^{v_\mathrm{P}} \quad \text{(solvent and solutes in reaction)} \tag{7.3-4}$$

In a dilute solution, x_1 and γ_1 are both nearly equal to unity, so that the $(\gamma_1 x_1)^{v_1}$ factor can be omitted to a good approximation.

The value of the equilibrium constant for any reaction can be calculated from the value of ΔG°. Once the equilibrium constant is evaluated, the equilibrium composition can be calculated for any particular case, if information about activity coefficients is available from experimental data or from theoretical estimates. If a solution is dilute and the reactant molecules are uncharged, we can often assume that activity coefficients are nearly equal to unity.

EXAMPLE 7.7

a. Find the value of the equilibrium constant for the reaction of Example 7.6 at 298.15 K.

b. Find the value of $(\partial G/\partial \xi)_{T,P}$ for the case that the molality of carbon monoxide is equal to $0.00010\ \mathrm{mol\,kg^{-1}}$, that of carbon dioxide is equal to $0.00015\ \mathrm{mol\,kg^{-1}}$, and that of oxygen is equal to $0.00020\ \mathrm{mol\,kg^{-1}}$. Assume activity coefficients equal to unity.

c. Find the equilibrium composition for an initial molality of carbon dioxide equal to $0.00015\ \mathrm{mol\,kg^{-1}}$, an initial molality of oxygen equal to $0.00020\ \mathrm{mol\,kg^{-1}}$, and an initial molality of carbon monoxide equal to zero. Assume activity coefficients equal to unity.

Solution

a. From Example 7.6, $\Delta G^\circ = -548.56\ \mathrm{kJ\ mol^{-1}}$ at 298.15 K.

$$K = e^{-\Delta G^\circ/RT} = \exp\left(\frac{548560\ \mathrm{J\,mol^{-1}}}{\left(8.3145\ \mathrm{J\,K^{-1}\ mol^{-1}}\right)(298.15\ \mathrm{K})}\right)$$
$$= 1.27 \times 10^{96}$$

b.

$$\begin{aligned}(\partial G/\partial \xi)_{T,P} &= \Delta G^\circ + RT\ln(Q)\\ &= -548{,}560\ \mathrm{J\,mol^{-1}}\\ &\quad + \left(8.3145\ \mathrm{J\,K^{-1}mol^{-1}}\right)(298.15\ \mathrm{K})\ln\left(\frac{(0.00015)^2}{(0.00010)^2(0.00020)}\right)\\ &= -548560\ \mathrm{J\,mol^{-1}} + 23000\ \mathrm{J\,mol^{-1}}\\ &= -525000\ \mathrm{J\,mol^{-1}} = -525\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

c. Let $m_{\mathrm{eq}}(\mathrm{CO})/m^\circ = 2x$, so that $m_{\mathrm{eq}}(\mathrm{O_2})/m^\circ = 0.00020 + x$ and $m_{\mathrm{eq}}(\mathrm{CO_2})/m^\circ = 0.00015 - 2x$.

$$K = 1.27\times 10^{96} = \frac{\left[m_{\mathrm{eq}}(\mathrm{CO_2})/m^\circ\right]^2}{\left[m_{\mathrm{eq}}(\mathrm{CO})/m^\circ\right]^2 m_{\mathrm{eq}}(\mathrm{O_2})/m^\circ} = \left(\frac{(0.00015-2x)^2}{(2x)^2(0.00020+x)}\right)$$

We neglect $2x$ compared with 0.00015 and neglect x compared with 0.00020, obtaining

$$x^2 \approx \left(\frac{(0.00015)^2}{4\left(1.27\times 10^{96}\right)(0.00020)}\right) = 2.21\times 10^{-101}$$
$$x \approx 4.7\times 10^{-51};\ m(\mathrm{CO}) \approx 9.4\times 10^{-51}\ \mathrm{mol\,kg^{-1}}$$

This value of x indicates that the reaction goes essentially to completion. A very large volume of solution would be required to contain a single CO molecule at equilibrium.

Exercise 7.6

Calculate the volume of solution that contains one CO molecule at equilibrium. Comment on the likelihood that equilibrium will actually be attained.

Reactions with Electrolyte Solutes

Reactions involving electrolyte solutes present some new aspects. Consider the reaction

$$\mathrm{NaOH(aq)} + \mathrm{HCl(aq)} \rightleftharpoons \mathrm{H_2O} + \mathrm{NaCl} \tag{7.3-5}$$

The solutes in this reaction are all *strong electrolytes*, which means that they appear to exist in solution in completely ionized or dissociated form. We can write the reaction equation in ionic form:

$$\mathrm{Na^+} + \mathrm{OH^-} + \mathrm{H^+} + \mathrm{Cl^-} \rightleftharpoons \mathrm{H_2O} + \mathrm{Na^+} + \mathrm{Cl^-} \tag{7.3-6}$$

We can also write the *net ionic equation*, which omits the Na^+ and Cl^- ions that occur on both sides of the reaction equation:

$$\mathrm{OH^-} + \mathrm{H^+} \rightleftharpoons \mathrm{H_2O} \tag{7.3-7}$$

Writing H^+ does not express any particular assumption about hydration of the hydrogen ions. Many aqueous hydrogen ions are apparently covalently bonded to a water molecule, forming H_3O^+ (the *hydronium ion*), but others are apparently bonded to water dimers, producing $H_5O_2^+$.[2] Others can be attached to trimers, etc. The symbol H^+ stands for all of these species taken together.

The standard-state Gibbs energy change for the reaction of Eq. (7.3-7) could be calculated from the Gibbs energy changes of formation of H_2O, NaCl, NaOH, and HCl if the data were available. However, actual tables include data for separate ions instead of neutral electrolytes. We use the net ionic equation

$$\Delta G^\circ = \Delta_f G^\circ(\mathrm{H_2O}) - \Delta_f G^\circ(\mathrm{H^+}) - \Delta_f G^\circ(\mathrm{OH^-}) \tag{7.3-8}$$

Gibbs energy changes of formation for separate ions cannot be determined experimentally because of the near impossibility of adding ions of one charge to a system without also adding ions of the opposite charge. An arbitrary choice has been made that assigns zero value to the Gibbs energy change of formation, enthalpy change of formation, and molar entropy of the hydrogen ion in its standard state in aqueous solution. This convention is equivalent to assigning the entire Gibbs energy change of formation of aqueous HCl to the Cl^- ion or that of aqueous HNO_3 to the NO_3^- ion, and so on. All other table values are made consistent with this convention.

EXAMPLE 7.8

Using values in Table A.8 of Appendix A, calculate ΔH°, ΔG°, and ΔS° for the reaction of Eq. (7.3-7):

$$\begin{aligned}\Delta H^\circ &= \Delta_f H^\circ(\mathrm{H_2O}) + (-1)\Delta_f H^\circ(\mathrm{OH^-}) - \Delta_f H^\circ(\mathrm{H^+}) \\ &= (-285.830\ \mathrm{kJ\ mol^{-1}}) + (-1)(-229.994\ \mathrm{kJ\ mol^{-1}}) + (-1)0 \\ &= -55.836\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

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[2] H.-P. Cheng and J. L. Krause, *J. Chem. Phys.*, **107**, 8461 (1997).

$$\begin{aligned}\Delta G^\circ &= \Delta_f G^\circ(\mathrm{H_2O}) + (-1)\Delta_f G^\circ(\mathrm{OH^-}) - \Delta_f G^\circ(\mathrm{H^+})\\ &= (-237.141\ \mathrm{kJ\,mol^{-1}}) + (-1)(-157.244\ \mathrm{kJ\,mol^{-1}}) + (-1)0\\ &= -79.892\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

$$\begin{aligned}\Delta S^\circ &= S^\circ_\mathrm{m}(\mathrm{H_2O}) + (-1)S^\circ_\mathrm{m}(\mathrm{OH^-}) + (-1)S^\circ_\mathrm{m}(\mathrm{H^+})\\ &= (69.95\ \mathrm{J\,K^{-1}\,mol^{-1}}) + (-1)(-10.75\ \mathrm{J\,K^{-1}\,mol^{-1}}) - 10\\ &= 80.70\ \mathrm{J\,K^{-1}\,mol^{-1}}\end{aligned}$$

There is no need to include the “spectator ions” Na^+ and Cl^- since they occur on both sides of the equation and their contributions cancel.

The previous example involved a reaction of strong electrolytes, which appear to ionize or dissociate completely in aqueous solution. There are only six common strong acids (acids that appear to ionize completely). In addition to HCl, the others are $HClO_4$, HI, HBr, HNO_3, and H_2SO_4. Other acids are *weak acids*, which means that they ionize only partially in aqueous solution. NaOH and other metal hydroxides are strong bases. There are many weak bases, including ammonia (NH_3).

EXAMPLE 7.9

Find the equilibrium molality of hydroxide ions in a solution formed from 0.1000 mol of NH_3 and 1.000 kg of water at 298.15 K.

Solution

The reaction that occurs is

$$\mathrm{NH_3(aq) + H_2O \rightleftharpoons NH_4^+ + OH^-}$$

We omit the label “aq” on the ions since they occur only in the aqueous phase.

$$\begin{aligned}\Delta G^\circ &= \Delta_f G^\circ(\mathrm{NH_4^+}) + \Delta_f G^\circ(\mathrm{OH^-}) - \Delta_f G^\circ(\mathrm{NH_3}) - \Delta_f G^\circ(\mathrm{H_2O})\\ &= (-79.31\ \mathrm{kJ\,mol^{-1}}) + (-157.244\ \mathrm{kJ\,mol^{-1}}) - (-26.50\ \mathrm{kJ\,mol^{-1}})\\ &\quad - (237.141\ \mathrm{kJ\,mol^{-1}})\\ &= -27.087\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

We denote the equilibrium constant of a weak base by K_b.

$$\begin{aligned}K_\mathrm{b} &= \frac{\gamma(\mathrm{NH_4^+})(m_\mathrm{eq}(\mathrm{NH_4^+})/m^\circ)\gamma(\mathrm{OH^-})(m_\mathrm{eq}(\mathrm{OH^-})/m^\circ)}{\gamma(\mathrm{NH_3})(m_\mathrm{eq}(\mathrm{NH_3})/m^\circ)\gamma(\mathrm{H_2O})x_\mathrm{eq}(\mathrm{H_2O})}\\ &= e^{-\Delta G^\circ/RT} = \exp\left[-\frac{27087\ \mathrm{J\,mol^{-1}}}{\left(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}\right)(298.15\ \mathrm{K})}\right]\\ &= 1.80\times 10^{-5}\end{aligned}$$

Since the solution is dilute we assume that $\gamma(H_2O)x(H_2O) \approx 1$ and that $\gamma(NH_3) \approx 1$. We introduce the mean ionic activity coefficient defined in Eq. (6.4-6):

$$\gamma_{\pm} = \left[\gamma(NH_4^+)\,\gamma(OH^-)\right]^{1/2}$$

We assume that the contribution of OH^- from the ionization of water is negligible and let

$$x = \frac{m_{\mathrm{eq}}(NH_4^+)}{m^\circ} = \frac{m_{\mathrm{eq}}(OH^-)}{m^\circ}$$

so that

$$1.80 \times 10^{-5} = \frac{\gamma_{\pm}^2 x^2}{0.100 - x}$$

We use successive approximations. For our first approximation we assume that $\gamma\pm \approx 1$:

$$x^2 = (1.80 \times 10^{-5})(0.100 - x)$$
$$x^2 + (1.80 \times 10^{-5})x - 1.80 \times 10^{-6} = 0$$

From the quadratic formula

$$\begin{aligned} x &= \frac{-1.80 \times 10^{-5} \pm \sqrt{\left(1.80 \times 10^{-5}\right)^2 + 4\left(1.80 \times 10^{-6}\right)}}{2} \\ &= 0.00133 \end{aligned}$$

We disregard a negative root to the quadratic equation, which is physically impossible. It is always the case in a chemistry problem that one of the solutions to a quadratic equation is unusable. For our next approximation we estimate the mean ionic activity coefficient for this molality using the Davies equation. Since NH_4^+ and OH^- are the only ions present, the first estimate of the ionic strength is 0.00133 mol kg^{-1}

$$\begin{aligned} \log_{10}(\gamma\pm) &= -0.510\left(\frac{\sqrt{0.00133}}{1 + \sqrt{0.00133}} - (0.30)(0.00133)\right) \\ &= -0.01774 \end{aligned}$$

$$\gamma_{\pm} = 10^{-0.01774} = 0.960$$

$$1.80 \times 10^{-5} = \frac{(0.960)^2 x^2}{0.100 - x}$$

Use of the quadratic formula on this equation yields $x = 0.00140$, or $m_{\mathrm{eq}}(NH_4^+) = m_{\mathrm{eq}}(OH^-) = 0.00140$ mol kg^{-1}. A further approximation produces only a small change, so we stop at this approximation. Even for the low ionic strength of 0.00140 mol kg^{-1}, neglect of the activity coefficient has produced an error of about 5%.

The Ionization of Water

Water ionizes according to the chemical equation

$$H_2O \rightleftharpoons H^+ + OH^-$$

EXAMPLE 7.10

Find ΔG° and K at 298.15 K for the ionization of water.

Solution

The Gibbs energy change of this reaction is the negative of that of Example 7.8:

$$\Delta G^\circ = 79.892\ \mathrm{kJ\ mol^{-1}}$$

$$\begin{aligned} K_\mathrm{w} &= e^{-\Delta G^\circ/RT} \\ &= \exp\left(\frac{-79892\ \mathrm{J\ mol^{-1}}}{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})}\right) \\ &= 1.008 \times 10^{-14} \end{aligned}$$

The equilibrium constant for the ionization of water can be used to calculate the equilibrium molalities of hydrogen and hydroxide ions:

$$\begin{aligned} K_\mathrm{w} &= \frac{a_\mathrm{eq}(\mathrm{H^+})a_\mathrm{eq}(\mathrm{OH^-})}{a_\mathrm{eq}(\mathrm{H_2O})} \\ &= \frac{\gamma(\mathrm{H^+})(m_\mathrm{eq}(\mathrm{H^+})/m^\circ)\gamma(\mathrm{OH^-})(m_\mathrm{eq}(\mathrm{OH^-})/m^\circ)}{\gamma(\mathrm{H_2O})x_\mathrm{eq}(\mathrm{H_2O})} \\ &= \frac{\gamma_\pm^2(m_\mathrm{eq}(\mathrm{H^+})/m^\circ)\,m_\mathrm{eq}(\mathrm{OH^-})/m^\circ)}{\gamma(\mathrm{H_2O})\,x_\mathrm{eq}(\mathrm{H_2O})} \\ &= \gamma_\pm^2(m_\mathrm{eq}(\mathrm{H^+})/m^\circ)(m_\mathrm{eq}(\mathrm{OH^-})/m^\circ) \end{aligned} \tag{7.3-9}$$

where we assume that $\gamma(\mathrm{H_2O})x_\mathrm{eq}(\mathrm{H_2O}) = 1$.

Exercise 7.7

Calculate the molalities of hydrogen and hydroxide ions in pure water at 298.15 K. Use the Davies equation to estimate activity coefficients if necessary.

In any aqueous solution, the ionization of water will equilibrate along with any other equilibria.

EXAMPLE 7.11

Find the value of $m_\mathrm{eq}(\mathrm{H^+})$ in the solution of Example 7.9.

Solution

We use the value of $\gamma_\pm$ from Example 7.9.

$$\frac{m_\mathrm{eq}(\mathrm{H^+})}{m^\circ} = \frac{K_\mathrm{w}}{\gamma_\pm^2 m_\mathrm{eq}(\mathrm{OH^-})/m^\circ} = \frac{\left(1.008 \times 10^{-14}\right)}{(0.960)^2(0.00140)}$$
$$= 7.80 \times 10^{-12}$$

It is customary to specify the acidity of a solution in terms of the pH, which has been variously defined. We would like to use the definition

$$\mathrm{pH} = -\log_{10}[a(\mathrm{H}^+)] = -\log_{10}\left(\frac{\gamma(\mathrm{H}^+)m(\mathrm{H}^+)}{m^\circ}\right) \quad \text{(desired definition)} \tag{7.3-10}$$

where $\log_{10}$ denotes the logarithm to the base 10 (the *common logarithm*). The activity coefficient $\gamma(\mathrm{H}^+)$ cannot be measured, but if it can be approximated in some way we can use Eq. (7.3-10) as a working equation.

Exercise 7.8

Find the pH of the solution in Example 7.11.

EXAMPLE 7.12

a. Find the value of the equilibrium constant at 298.15 K for the ionization of acetic acid.

b. Find the percentage of acetic acid molecules that ionize and the pH in a solution prepared from 0.100 mol of acetic acid and 1.000 kg of water and maintained at 298.15 K. Use the Davies equation to estimate activity coefficients. Neglect any H^+ ions contributed by the ionization of water.

Solution

a. Write the ionization equation in the form

$$\mathrm{HA} \rightleftharpoons \mathrm{H}^+ + \mathrm{A}^-$$

$$\begin{aligned}\Delta G^\circ &= 0 + (-369.31\ \mathrm{kJ\ mol^{-1}}) - (-396.46\ \mathrm{kJ\ mol^{-1}})\\ &= 27.15\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

$$\begin{aligned}K &= \exp\left(\frac{-27{,}150\ \mathrm{J\ mol^{-1}}}{(8.3145\ \mathrm{J\ K^{-1}mol^{-1}})(298.15\ \mathrm{K})}\right)\\ &= 1.752\times 10^{-5}\end{aligned}$$

b. Let $x = m(\mathrm{H}^+)/m^\circ = m(\mathrm{A}^-)/m^\circ$. First assume that all activity coefficients equal 1.

$$1.752\times 10^{-5} = \frac{x^2}{(0.100 - x)}$$

$$x^2 + (1.752\times 10^{-5})x - 1.752\times 10^{-6} = 0$$

$$\begin{aligned}x &= \frac{-1.752\times 10^{-5} \pm \sqrt{(1.752\times 10 - 5)2 + 4(1.752\times 10^{-6})}}{2}\\ &= 1.315\times 10^{-3}\end{aligned}$$

This corresponds to an ionic strength of 1.315×10^{-3} mol $\mathrm{kg^{-1}}$. From the Davies equation

$$\begin{aligned}\log_{10}(\gamma\pm) &= -0.510\left(\frac{\sqrt{0.001315}}{1+\sqrt{0.001315}} - (0.30)(0.001315)\right)\\ &= -0.01523\end{aligned}$$

$$\gamma_{\pm} = 10^{-0.01523} = 0.9655$$

Assume that $\gamma(\mathrm{HA}) \approx 1$

$$1.752 \times 10^{-5} = \frac{(0.9655)^2 x^2}{(0.100 - x)}$$

$$\frac{1.752 \times 10^{-5}}{(0.9655)^2} = 1.879 \times 10^{-5} = \frac{x^2}{(0.100 - x)}$$

$$x^2 + (1.879 \times 10^{-5})x - 1.879 \times 10^{-6} = 0$$

$$x = \frac{-1.879 \times 10^{-5} \pm \sqrt{(1.879 \times 10^{-5})^2 + 4(1.879 \times 10^{-6})}}{2}$$

$$= 1.361 \times 10^{-3}$$

This corresponds to 1.361% ionization. We stop the successive approximations at this point, since this approximation has not changed the result by very much. A further approximation would make an even smaller change.

$$\mathrm{pH} = -\log_{10}(0.9655)(1.361 \times 10^{-3}) = 2.88$$

Exercise 7.9

Find the percentage of acetic acid molecules that ionize and the pH in a solution prepared from 1.000 mol of acetic acid and 1.000 kg of water and maintained at 298.15 K. Use the Davies equation to estimate activity coefficients. Neglect any H^+ ions contributed by the ionization of water.

If a weak acid is quite dilute or if an acid has a very small ionization constant the hydrogen ions that come from the water ionization cannot be neglected and we must solve the equations for two equilibria simultaneously.

EXAMPLE 7.13

Find the pH at 298.15 K of a solution made from 1.00×10^{-7} mol of acetic acid and 1.000 kg of water.

Solution

The ionization of acetic acid corresponds to

$$\mathrm{CH_3CO_2H} \rightleftharpoons \mathrm{H^+} + \mathrm{CH_3CO_2^-}$$

which we abbreviate as

$$\mathrm{HA} \rightleftharpoons \mathrm{H^+} + \mathrm{A^-}$$

We must solve two simultaneous equations. At 298.15 K the equilibrium relation for the acetic acid is:

$$K_a = 1.75 \times 10^{-5} = \frac{\gamma\left(\mathrm{H}^+\right)m_{\mathrm{eq}}\left(\mathrm{H}^+\right)/m^\circ\gamma\left(\mathrm{A}^-\right)m_{\mathrm{eq}}\left(\mathrm{A}^-\right)/m^\circ}{\gamma(\mathrm{HA})(m_{\mathrm{eq}}(\mathrm{HA})/m^\circ)} \tag{7.3-11a}$$

The equilibrium relation for water is

$$K_w = 1.0 \times 10^{-14} = \left(\gamma(\mathrm{H}^+)m_{\mathrm{eq}}(\mathrm{H}^+)/m^\circ\right)\left(\gamma(\mathrm{OH}^-)m_{\mathrm{eq}}(\mathrm{OH}^-)/m^\circ\right) \tag{7.3-11b}$$

We assume that $\gamma(\mathrm{HA}) \approx 1$. Since all of the ions are univalent, we assume that all of their activity coefficients are equal and denote them by γ. We let

$$z = \frac{m_{\mathrm{eq}}\left(\mathrm{H}^+\right)}{m^\circ}, \quad y = \frac{m_{\mathrm{eq}}\left(\mathrm{OH}^-\right)}{m^\circ}$$

We express the other molalities in terms of z and y. For each OH^- ion, there is one H^+ ion released from water, and for each A^- ion there is an H^+ ion released from the acid, so that

$$\frac{m_{\mathrm{eq}}\left(\mathrm{A}^-\right)}{m^\circ} = z - y, \quad \frac{m_{\mathrm{eq}}(\mathrm{HA})}{m^\circ} = \frac{m}{m^\circ} - (z - y)$$

where m is the stoichiometric molality. From Eq. (7.3-11b),

$$y = \frac{K_w}{\gamma^2 z}$$

We use this expression to replace y in the acid equilibrium expression and obtain a single equation:

$$K_a = \frac{\gamma^2 z\left[z - K_w/\left(\gamma^2 z\right)\right]}{m/m^\circ - z + K_w/\left(\gamma^2 z\right)} \tag{7.3-12a}$$

When we multiply this equation out, we obtain a cubic equation:

$$\gamma^2 z^3 + Kz^2 - (m/m^\circ)K + K_w z - KK_w/\gamma^2 = 0 \tag{7.3-12b}$$

For our first approximation, we assume that $\gamma = 1$ and solve for z. A numerical approximation to the root of this cubic equation gives $m_{\mathrm{eq}}(\mathrm{H}^+) = 1.61 \times 10^{-7}$ mol kg^{-1}, only 61% higher than in pure water. Use of the Davies equation for this ionic strength gives $\gamma_\pm = 0.999999$ so that no second approximation is necessary. The value of the pH is 6.79. If the hydrogen ions from water are ignored, the result is that $m_{\mathrm{eq}}(\mathrm{H}^+) = 9.9 \times 10^{-8}$ mol kg^{-1}, which is in error by 38% and is smaller than the value of $m(\mathrm{H}^+)$ in pure water.

Another situation that requires the solution of simultaneous equations is the ionization of a polyprotic acid, which means that one molecule of the acid ionizes successively to give more than one hydrogen ion.

Exercise 7.10

Find the pH of a solution made from 1.000 kg of water and 0.100 mol of phosphoric acid, H_3PO_4, for which the three acid dissociation constants are

$$K_1 = 7.52 \times 10^{-3}, \quad K_2 = 6.23 \times 10^{-8}, \quad K_3 = 2.2 \times 10^{-13}$$

Three simultaneous equations must be solved. It is best to seek simplifying approximations, such as neglecting the H^+ ions from the third ionization in discussing the first two ionizations. The validity of such approximations should be checked at the end of the calculation.

The *conjugate base* of a weak acid is a weak base. The acetate ion is the conjugate base of acetic acid. When sodium acetate is added to water, the acetate ions hydrolyze (react with water):

$$A^- + H_2O \rightleftharpoons HA + OH^- \qquad (7.3\text{-}13)$$

where we use the same abbreviations as before: HA for CH_3CO_2H and A^- for $CH_3CO_2^-$. The equilibrium relation for this reaction is

$$K_b = \frac{\gamma(\mathrm{HA})(m_{eq}(\mathrm{HA})/m^\circ)\gamma(\mathrm{OH}^-)(m_{eq}(\mathrm{OH}^-)/m^\circ)}{\gamma(\mathrm{A}^-)(m_{eq}(\mathrm{A}^-)/m^\circ)\gamma(\mathrm{H_2O})x(\mathrm{H_2O})}$$

We assume that $\gamma(H_2O)x(H_2O) = 1$ and that all of the activity coefficients of the ions are equal to γ. We multiply the right-hand side of this equation top and bottom by $\gamma(H^+)(m_{eq}(H^+)/m^\circ)$:

$$\begin{aligned} K_b &= \frac{\gamma(\mathrm{HA})(m_{eq}(\mathrm{HA})/m^\circ)\gamma(\mathrm{OH}^-)(m_{eq}(\mathrm{OH}^-)/m^\circ)}{\gamma(\mathrm{A}^-)(m_{eq}(\mathrm{A}^-)/m^\circ)\gamma(\mathrm{H}^+)(m_{eq}(\mathrm{H}^+)/m^\circ)}\gamma(\mathrm{H}^+)(m_{eq}(\mathrm{H}^+)/m^\circ) \\ &= \frac{K_w}{K_a} = \frac{1.00 \times 10^{-14}}{1.752 \times 10^{-5}} = 5.71 \times 10^{-10} \end{aligned}$$

where K_a is the equilibrium constant for the ionization of acetic acid and K_w is the equilibrium constant for the ionization of water.

EXAMPLE 7.14

Find the pH of a solution made from 0.100 mol of sodium acetate in 1.000 kg of water. Use the Davies equation to estimate activity coefficients. Remember to include the sodium ions when you calculate the ionic strength.

Solution

We have the value of K_b from the previous example. We assume that the activity of water is nearly equal to unity, and we ignore any OH^- ions contributed by water:

$$\begin{aligned} K_b &= 5.71 \times 10^{-10} \\ &= \frac{\gamma(\mathrm{HA})(m(\mathrm{HA})/m^\circ)\gamma(\mathrm{OH}^-)(m(\mathrm{OH}^-)/m^\circ)}{\gamma(\mathrm{A}^-)(m(\mathrm{A}^-)/m^\circ)} \end{aligned}$$

We let $m(\mathrm{HA})/m^\circ = m(\mathrm{H}^-)/m^\circ = x$, and we first assume that activity coefficients are equal to unity:

$$5.71 \times 10^{-10} = \frac{x^2}{0.100 - x}$$

Instead of using the quadratic formula, we solve by successive approximations within our successive approximations for the activity coefficients. For the first approximation we neglect x compared with 0.100:

$$\begin{aligned} x^2 &\approx (0.100)(5.71 \times 10^{-10}) \\ &\approx 5.71 \times 10^{-11} \\ x &\approx \sqrt{5.71 \times 10^{-11}} = 7.55 \times 10^{-6} \end{aligned}$$

For the second approximation we replace x by its first approximate value:

$$\begin{aligned} x^2 &\approx (0.100 - 2.39 \times 10^{-5})(5.71 \times 10^{-10}) \\ &\approx 5.71 \times 10^{-11} \\ x &\approx \sqrt{5.71 \times 10^{-11}} = 7.55 \times 10^{-6} \end{aligned}$$

There is no change in the value of x, so we discontinue successive approximations at this point. We could have predicted this result from the small size of x from the first approximation. We now return to the successive approximation scheme for the activity coefficients. The ionic strength is the same as though the sodium acetate did not react, since every acetate ion that reacts is replace by a hydroxide ion. The ionic strength is $I = 0.100\,\mathrm{mol\,kg^{-1}}$. By the Davies equation:

$$\begin{aligned} \log_{10}(\gamma_{\pm}) &= -0.510\left(\begin{matrix} \dfrac{\sqrt{0.100}}{1+\sqrt{0.100}} \\ -(0.30)(0.100) \end{matrix}\right) \\ &= -0.1072 \\ \gamma_{\pm} &= 10^{-0.1072} = 0.7813 \end{aligned}$$

Assume that this value can be used for both the acetate ion and the hydroxide ion. The two activity coefficients cancel, so our first value for x can be used.

$$m(\mathrm{OH}^{-1})/m^{\circ} = 7.55 \times 10^{-6}$$

We define the pOH in the same way as the pH:

$$\begin{aligned} \mathrm{pOH} &= -\log_{10}(a(\mathrm{OH}^-)) \\ &= -\log_{10}\left[(0.7813)(7.55 \times 10^{-6})\right] = 5.23 \\ \mathrm{pH} + \mathrm{pOH} &= \log_{10}(K_{\mathrm{w}}) = 14.00 \\ \mathrm{pH} &= 14.00 - \mathrm{pOH} = 8.77 \end{aligned}$$

The conjugate acid of a weak base such as NH_3 hydrolyzes in a way analogous to the hydrolysis of the acetate ion.

Exercise 7.11

Find the pH of a solution made from 0.100 mol of NH_4Cl and 1.000 kg of water at 298.15 K

PROBLEMS

Section 7.3: Chemical Equilibrium in Solutions

7.22 Find $\Delta H°$, $\Delta S°$, and $\Delta G°$ at 298.15 K for each of the following reactions, using formation data and absolute entropy data. Compare the value of $\Delta H° - T\Delta S°$ with that of $\Delta G°$ to test the consistency of the data.

a. $2\,\mathrm{Fe}^{2+}(\mathrm{aq}) + \mathrm{Sn}^{4+}(\mathrm{aq}) \rightleftharpoons 2\,\mathrm{Fe}^{3+}(\mathrm{aq}) + \mathrm{Sn}^{2+}(\mathrm{aq})$

b. $\mathrm{Cl}_2(\mathrm{g}) + 2\mathrm{Br}^-(\mathrm{aq}) \rightleftharpoons 2\,\mathrm{Cl}^-(\mathrm{aq}) + \mathrm{Br}_2(\mathrm{l})$

7.23 Find $\Delta H°$, $\Delta S°$, and $\Delta G°$ at 298.15 K for each of the following reactions, using formation data and absolute entropy data. Compare the value of $\Delta H° - T\Delta S°$ with that of $\Delta G°$ to test the consistency of the data.

a. $\mathrm{Cl}_2(\mathrm{g}) + 2\,\mathrm{I}^-(\mathrm{aq}) \rightleftharpoons 2\,\mathrm{Cl}^-(\mathrm{aq}) + \mathrm{I}_2(\mathrm{s})$

b. $2\,\mathrm{Ag}^+(\mathrm{aq}) + \mathrm{Ca}(\mathrm{s}) \rightleftharpoons 2\,\mathrm{Ag}(\mathrm{s}) + \mathrm{Ca}^{2+}(\mathrm{aq})$

7.24 The equilibrium constant for the dissolving of a sparingly soluble electrolyte is called the *solubility product constant*. The solubility product constant of lithium carbonate is represented by

$$K_{\mathrm{sp}} = \left[\gamma(\mathrm{Li}^+)(m_{\mathrm{eq}}(\mathrm{Li}^+)/m°)\right]^2 \gamma(\mathrm{CO}_3^-)(m_{\mathrm{eq}}(\mathrm{CO}_3^-)/m°)$$

where the activity of water is assumed equal to unity. K_{sp} for lithium carbonate is equal to 1.7×10^{-3} at 25°C.

a. Find the solubility in mol kg^{-1} of lithium carbonate in water at this temperature. Use the Davies equation to estimate activity coefficients.

b. Find the solubility in mol kg^{-1} of lithium carbonate in a solution of 0.100 mol of sodium carbonate in 1.000 kg of water at 25°C. Use the Davies equation.

c. Find the solubility in mol kg^{-1} of lithium carbonate in a solution of 0.100 mol of sodium sulfate in 1.000 kg of water at 25°C. Use the Davies equation.

7.25 **a.** Find the solubility product constant at 298.15 K for the reaction

$$\mathrm{AgCl(s)} \rightleftharpoons \mathrm{Ag}^+ + \mathrm{Cl}^-$$

b. Find the molality of Ag^+ produced by equilibrating solid AgCl with pure water at 298.15 K. Use the Davies equation to approximate activity coefficients.

7.26 The solubility product constant of nickel(II) hydroxide is equal to 2.9×10^{-15} at 25°C.

a. Find the solubility in mol kg^{-1} of nickel(II) hydroxide in water at this temperature. Use the Davies equation to estimate activity coefficients.

b. Find the solubility in mol kg^{-1} of nickel(II) hydroxide in a solution of 0.100 mol of sodium carbonate in 1.000 kg of water at 25°C. Use the Davies equation.

c. Find the solubility in mol kg^{-1} of nickel(II) hydroxide in a solution of 0.100 mol of sodium sulfate in 1.000 kg of water at 25°C. Use the Davies equation.

7.27 For each of the following weak acids, find the pH of a solution made from 0.100 mol of the acid and 1.000 kg of water at 298.15 K. Do each calculation twice: once assuming that $\gamma_\pm$ equals unity, and once using the Davies equation to estimate $\gamma_\pm$. In each case, decide whether hydrogen ions from water must be included:

Acid	K_{a}
a. naphthalene sulfonic	2.7×10^{-1}
b. benzoic	6.46×10^{-5}

7.28 For chloroacetic acid, K_{a} is equal to 1.40×10^{-3}. Find the pH of a solution made from 0.100 mol of this acid and 1.000 kg of water at 298.15 K. Do each calculation twice: once assuming that $\gamma_\pm$ equals unity, and once using the Davies equation to estimate $\gamma_\pm$.

7.29 Find the pH at 298.15 K of a solution made from 0.0100 mol of aspartic acid and 1.000 kg of water. Do the calculation twice, once assuming that $\gamma_\pm$ equals unity, and once using the Davies equation to estimate $\gamma_\pm$. For this acid, $K_1 = 1.38 \times 10^{-4}$ and $K_2 = 1.51 \times 10^{-10}$.

7.30 The solubility of $\mathrm{Ag_2SO_4}$ in pure water at 25°C is equal to 0.0222 mol kg^{-1}. Find the value of the solubility product constant. Use the Davies equation to estimate activity coefficients.

7.31 Find the molalities of $\mathrm{H_2CO_3}$ and $\mathrm{HCO_3^-}$ in an aqueous solution at 298.15 K that has been equilibrated with gaseous $\mathrm{CO_2}$ at 0.0400 atm and in which the pH is equal to 7.40.

7.32 For each of the following weak acids, find the pH of a solution made from 0.0100 mol of the acid and 1.000 kg of water at 298.15 K. Do each calculation twice: once assuming that $\gamma_\pm$ equals unity, and once using the Davies equation to estimate $\gamma_\pm$. In part c, decide whether hydrogen ions from water must be included:

Acid	K_{a}
a. periodic	2.3×10^{-2}
b. *o*-phenylbenzoic	3.47×10^{-4}
c. hydrocyanic	4×10^{-10}

7.33 Calculate the pH of a solution from 0.0500 mol of cacodylic acid in 1.000 kg of water at 298.15 K. The acid dissociation constant is equal to 6.4×10^{-7}. Include the hydrogen ions from water and use the Davies equation to estimate activity coefficients.

7.34 The three acid ionization constants of citric acid are $K_1 = 7.20 \times 10^{-4}$, $K_2 = 1.68 \times 10^{-5}$, and $K_3 = 4.11 \times 10^{-7}$.

a. Find the pH at 25°C of a solution made from 0.100 mol of citric acid and 1.000 kg of water.

b. A solution is made from 0.100 mol of citric acid, 1.000 kg of water, and enough solid NaOH to make the pH equal to 6.00. Find the equilibrium molality of citric acid and of each anion of citric acid.

7.35 The acid ionization constant of hydrocyanic acid (HCN) is equal to 4×10^{-10} at 298.15 K.

a. Find the pH of a solution made from 0.100 mol of HCN and 1.000 kg of water at 298.15 K.

b. Find the value of the equilibrium constant for the hydrolysis reaction $CN^- + H_2O \rightleftharpoons HCN + OH^-$.

c. Find the pH of a solution made from 0.100 mol of KCN and 1.000 kg of water at 298.15 K.

7.36 The two acid ionization constant of *ortho*-phthalic acid are $K_1 = 1.3 \times 10^{-3}$ and $K_2 = 3.9 \times 10^{-6}$. Find the pH of a solution made from 0.100 mol of *ortho*-phthalic acid and 1.000 kg of water.

7.37 A solution is made from 0.0100 mol of ammonium benzoate and 1.000 kg of water. It is maintained at 25°C. For benzoic acid $K_a = 6.46 \times 10^{-5}$ at 25°C, and for ammonia is equal to $K_b = 1.774 \times 10^{-5}$ at 25°C. Aguirre-Ode[3] gives an approximate formula (assuming that all activity coefficients equal unity):

$$m_{\mathrm{eq}}(\mathrm{H}^+)/m^\circ = \left(\frac{K_a K_w}{K_b}\right)^{1/2}\left(\frac{K_b + m/m^\circ}{K_a + m/m^\circ}\right)^{1/2}$$

where m is the stoichiometric molality. Find the pH using this formula.

7.4 Equilibria in Solutions of Strong Electrolytes

Hydrochloric acid, HCl, is one of a half-dozen strong acids, which means that its acid ionization constant is too large to measure accurately. We must find a way to handle the activity of unionized species such as HCl in spite of their unmeasurably small concentrations. Since aqueous HCl has an appreciable vapor pressure we assume that aqueous unionized HCl in an aqueous solution of HCl is at equilibrium with gaseous HCl. From the fundamental fact of phase equilibrium

$$\mu(\mathrm{HCl,aq}) = \mu(\mathrm{HCl,g}) \tag{7.4-1}$$

The aqueous unionized HCl is also at equilibrium with H^+ and Cl^- in the solution:

$$\mathrm{HCl(aq)} \rightleftharpoons \mathrm{H}^+ + \mathrm{Cl}^- \tag{7.4-2}$$

The condition for equilibrium of this reaction is

$$\mu(\mathrm{HCl,aq}) = \mu(\mathrm{H}^+) + \mu(\mathrm{Cl}^-) \tag{7.4-3}$$

For the unionized HCl, we use a new molality description, in which m° is replaced by m', a small constant molality. We will not be able to determine the value of m', but will be able to eliminate it from our equations. We write

$$\begin{aligned}\mu(\mathrm{HCl}) &= \mu^\circ(\mathrm{HCl}) + RT\ln[a(\mathrm{HCl})]\\ &= \mu^\circ(\mathrm{HCl}) + RT\ln\big[\gamma(\mathrm{HCl})\big(m(\mathrm{HCl})/m'\big)\big]\end{aligned} \tag{7.4-4}$$

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[3] F. Aguirre-Ode, *J. Chem. Educ.*, **64**, 957 (1987).

where we now omit the label aq on aqueous HCl. At chemical equilibrium,

$$\mu^\circ(\text{HCl}) + RT\ln(a(\text{HCl})) = \mu^\circ(\text{H}^+) + RT\ln\left[\gamma(\text{H}^+)m_{\text{eq}}(\text{H}^+)/m^\circ\right] \\ + \mu^\circ(\text{Cl}^-) + RT\ln\left[\gamma(\text{Cl}^-)m_{\text{eq}}(\text{Cl}^-)/m^\circ\right] \quad (7.4\text{-}5)$$

To eliminate m' from our equations we specify that

$$\mu^\circ(\text{HCl}) = \mu^\circ(\text{H}^+) + \mu^\circ(\text{Cl}^-) = \mu_+^\circ + \mu_-^\circ \quad (7.4\text{-}6)$$

where we abbreviate $\mu^\circ(\text{H}^+)$ by μ_+° and $\mu^\circ(\text{Cl}^-)$ by μ_-°. This equation determines m', even though we do not know its value. Combining Eq. (7.4-6) with Eq. (7.4-5) and taking antilogarithms, we obtain an expression for the activity of the unionized aqueous HCl:

$$\begin{aligned} a(\text{HCl}) &= (\gamma(\text{H}^+)m_{\text{eq}}(\text{H}^+)/m^\circ)(\gamma(\text{Cl}^-)m_{\text{eq}}(\text{Cl}^-)/m^\circ) \\ &= \gamma_+\gamma_-m_+m_-/m^{\circ 2} = \gamma_\pm^2 m_+m_-/m^{\circ 2} \end{aligned} \quad (7.4\text{-}7)$$

where $\gamma_\pm$ is the mean ionic activity coefficient defined in Eq. (6.4-6) and where we have abbreviated $m_{\text{eq}}(\text{H}^+)$ by m_+ and $m_{\text{eq}}(\text{Cl}^-)$ by m_-. Equation (7.4-7) expresses $a(\text{HCl})$ in terms of measurable quantities.

Equation (7.4-6) is the same as requiring that

$$\Delta G^\circ = 0 \quad (7.4\text{-}8)$$

for the ionization reaction of Eq. (7.4-2), which means that the equilibrium constant for the reaction is given by

$$K = \frac{(\gamma_+m_+/m^\circ)(\gamma_-m_-/m^\circ)}{\gamma(\text{HCl})m_{\text{eq}}(\text{HCl})/m'} = 1 \quad (7.4\text{-}9)$$

Equation (7.4-9) does *not* mean that the molality of the unionized HCl is roughly equal to the product of the molalities of the ions, because m' is not equal to m°.

We can now relate the partial vapor pressure of gaseous HCl to the molality of the solution with which it is at equilibrium. If the vapor is assumed to be an ideal gas mixture,

$$\mu(\text{HCl,g}) = \mu^\circ(\text{HCl,g}) + RT\ln\frac{P(\text{HCl})}{P^\circ} \quad (7.4\text{-}10)$$

From Eqs. (7.4-1) and (7.4-5),

$$\mu^\circ(\text{HCl,g}) + RT\ln(P(\text{HCl})/P^\circ) = \mu_+^\circ + \mu_-^\circ + RT\ln(\gamma_+m_+\gamma_-m_-/m^{\circ 2}) \quad (7.4\text{-}11)$$

Equation (7.4-11) is equivalent to

$$P(\text{HCl}) = k_\pm^{(m)}\gamma_+\gamma_-m^2 = k_\pm^{(m)}\gamma_\pm^2 m^2 \quad (7.4\text{-}12)$$

where m is the *stoichiometric molality* of HCl (the molality of HCl that would occur if no ionization occurred) and where

$$k_\pm^{(m)} = (P^\circ/m^{\circ 2})\exp\left[\frac{\mu_+^\circ + \mu_-^\circ - \mu^\circ(\text{HCl,g})}{RT}\right] \quad (7.4\text{-}13)$$

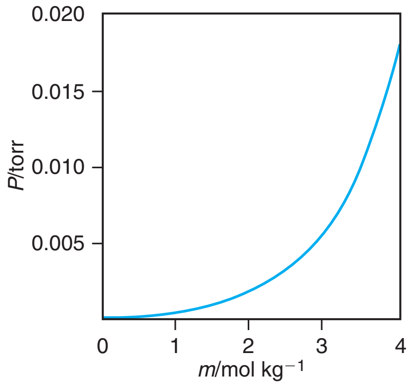

Figure 7.2 The Partial Vapor Pressure of HCl as a Function of Molality.

This equation represents a new version of *Henry's law*. If the activity coefficients are equal to unity, the partial vapor pressure of HCl is proportional to the square of the molality, not proportional to the molality as in Henry's law. Figure 7.2 shows the partial vapor pressure of HCl as a function of molality in an aqueous solution at 298.15 K. Table A.12 gives the values of the partial pressure for larger molalities for the same temperature. The table represents experimental data, and the graph represents values calculated from values of the activity coefficient determined by other techniques.

EXAMPLE 7.15

The partial vapor pressure of a 5.00 mol kg^{-1} aqueous solution of HCl at 298.15 K is equal to 6.97×10^{-5} atm.[a] The mean ionic activity coefficient is equal to 2.38. Find the value of $k_{\pm}^{(m)}$ and of $\mu_{+}^{\circ} + \mu_{-}^{\circ} - \mu^{\circ}(\text{HCl,g})$.

Solution

$$k_{\pm}^{(m)} = \frac{P(\text{HCl})}{\gamma_{\pm}^{2} m^{2}} = \frac{6.97 \times 10^{-5}\ \text{atm}}{(2.38)^{2}\left(5.00\ \text{mol kg}^{-1}\right)^{2}}$$

$$= 4.92 \times 10^{-7}\ \text{atm kg}^{2}\ \text{mol}^{-2}$$

$$\mu_{+}^{\circ} + \mu_{-}^{\circ} - \mu^{\circ}(\text{HCl,g}) = RT \ln\left(\frac{k_{\pm}^{(m)} m^{\circ 2}}{P^{\circ}}\right)$$

$$= (8.3145\ \text{J K}^{-1}\text{mol}^{-1})(298.15\ \text{K})$$

$$\times \ln\left(\frac{\left(4.92 \times 10^{-7}\ \text{atm kg}^{2}\ \text{mol}^{-2}\right)\left(1\ \text{mol kg}^{-1}\right)^{2}}{0.98692\ \text{atm}}\right)$$

$$= -3.60 \times 10^{4}\ \text{J mol}^{-1} = -36.0\ \text{kJ mol}^{-1}$$

where we have used the fact that $P^{\circ} = 0.98692$ atm.

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[a] S. J. Bates and H. D. Kirschman, *J. Am. Chem. Soc.*, **41**, 1991 (1919).

Equations (7.4-5) through (7.4-8) are valid for a nonvolatile strong electrolyte such as NaCl, CaCl_2, or KOH, as well as for a volatile strong electrolyte such as HCl. For CaCl_2

$$a(\text{CaCl}_2) = (\gamma_{\pm} m_{\pm}/m^{\circ})^{3} = (\gamma_{\pm} \nu_{\pm} m/m^{\circ})^{3} \qquad (7.4\text{-}14)$$

where m is the stoichiometric molality, $\gamma_{\pm}$ is defined in Eq. (6.4-6), and $m_{\pm}$ is defined in Eq. (6.4-7). If the formula of an electrolyte is represented by $\text{M}_{\nu_+}\text{X}_{\nu_-}$ and if there is no other source of either ion,

$$a(\text{M}_{\nu_+}\text{X}_{\nu_-}) = (\gamma_{\pm} m_{\pm}/m^{\circ})^{\nu} = (\gamma_{\pm} \nu_{\pm} m/m^{\circ})^{\nu} \qquad (7.4\text{-}15)$$

where ν is the total number of ions in the formula.

Some of the deviation from ideality of electrolyte solutes is due to ion pairing, which means that two ions temporarily remain together as a unit. The ion pair equilibrates with the separated ions. For example

$$\mathrm{Na^+ + Cl^- \rightleftharpoons Na^+Cl^-}$$

The ion pair $\mathrm{Na^+Cl^-}$ is *not* a molecule. A chemical bond is not formed between the ions, which are held together by electrostatic attraction. Each ion retains at least part of its attached water molecules (*hydration sphere*) and one or more water molecules can lie between the ions. Equilibrium constants have been determined for the formation of some ion pairs. Multiply charged ions have a greater tendency to form ion pairs than do singly charged ions. For example,

$$\mathrm{Mg^{2+} + Cl^- \rightleftharpoons Mg^{2+}Cl^-}$$

has a relatively large equilibrium constant. We will not discuss these equilibria, but will regard them as one of the reasons that the activity coefficients deviate from unity.

Exercise 7.12

Write expressions for $\gamma_\pm$ and $m_\pm$ for $\mathrm{Mg_3(PO_4)_2}$ in terms of the stoichiometric molality and the activity coefficients of the ions. Neglect hydrolysis (a poor approximation).

PROBLEMS

Section 7.4: Equilibria in Solutions of Strong Electrolytes

7.38 Find the partial vapor pressure of HCl over a 0.85 mol kg^{-1} aqueous HCl solution at 298.15 K. Use the Davies equation to estimate $\gamma_\pm$.

7.39 Write the expressions for $\gamma_\pm$ and $m_\pm$ for each of the following solutes (assume strong electrolytes):

a. $\mathrm{Na_2SO_4}$

b. $\mathrm{AlCl_3}$

c. $\mathrm{MgSO_4}$

d. $\mathrm{Mg(NO_3)_2}$

7.40 Evaluate $m_\pm$ for each of the solutes in the previous problem if the stoichiometric molality is 0.100 mol kg^{-1}. Use the Davies equation to estimate $\gamma_\pm$ for each of the solutes in the previous problem if the stoichiometric molality is 0.100 mol kg^{-1}.

7.5 Buffer Solutions

A solution that resists changes in pH is called a *buffer solution*. A typical buffer solution contains both a weak acid and its conjugate base, which is a weak base. If acid is added to the solution, the weak base can react with part of it, and if base is added, the weak acid can react with part of it, minimizing the effect of the addition. Consider a solution produced by adding n_a moles of a weak acid (abbreviated by HA) and n_s moles of its salt to 1.000 kg of water (the anion of the salt is the conjugate base, abbreviated by $\mathrm{A^-}$). The acid will ionize slightly, and the anion will hydrolyze slightly. These effects will nearly cancel, and we can write to a good approximation

$$m_\mathrm{eq}(\mathrm{HA}) = \frac{n_\mathrm{a}}{1.000\,\mathrm{kg}} \tag{7.5-1}$$

and

$$m_{\mathrm{eq}}(\mathrm{A}^-) = \frac{n_\mathrm{s}}{1.000\,\mathrm{kg}} \tag{7.5-2}$$

Assuming that γ_{HA} equals unity, we obtain

$$\begin{aligned} K_\mathrm{a} &= \frac{\gamma(\mathrm{H}^+)(m_{\mathrm{eq}}(\mathrm{H}^+)/m^\circ)\gamma(\mathrm{A}^-)(m_{\mathrm{eq}}(\mathrm{A}^-)/m^\circ)}{m_{\mathrm{eq}}(\mathrm{HA})/m^\circ} \\ &= \frac{a(\mathrm{H}^+)\gamma(\mathrm{A}^-)m_{\mathrm{eq}}(\mathrm{A}^-)}{m_{\mathrm{eq}}(\mathrm{HA})} \\ &= \frac{a(\mathrm{H}^+)\gamma(\mathrm{A}^-)n_\mathrm{s}}{n_\mathrm{a}} \end{aligned} \tag{7.5-3}$$

If $\gamma(\mathrm{A}^-)$ is also assumed to equal unity, this equation can be written in the form known as the *Henderson–Hasselbalch equation*:

$$\boxed{\mathrm{pH} = pK_\mathrm{a} + \log_{10}\left(\frac{m_\mathrm{s}}{m_\mathrm{a}}\right) = pK_\mathrm{a} + \log_{10}\left(\frac{n_\mathrm{s}}{n_\mathrm{a}}\right)} \tag{7.5-4}$$

where pK_a is defined by

$$\boxed{pK_\mathrm{a} = -\log_{10}(K_\mathrm{a}) \quad (\text{definition of } pK_\mathrm{a})} \tag{7.5-5}$$

and where m_s and m_a are the stoichiometric molalities of the salt and the acid. If greater accuracy is desired than this equation provides, one can use Eq. (7.5-3) with experimental or theoretical values of $\gamma(\mathrm{A}^-)$.

EXAMPLE 7.16

a. Using the Henderson–Hasselbalch equation, calculate the pH of a solution made from 0.400 mol of acetic acid and 0.600 mol of sodium acetate in 1.000 kg of water.

b. Repeat the calculation of part a using Eq. (7.5-3) and the Davies equation.

Solution

a. Using the value $K_\mathrm{a} = 1.75 \times 10^{-5}$,

$$\mathrm{pH} = 4.757 + \log_{10}\left(\frac{0.600\,\mathrm{mol}}{0.400\,\mathrm{mol}}\right) = 4.932$$

b. Let m_a be the molality of acid that would occur if the acid did not ionize and m_s be the molality of the anion that would occur if the salt did not hydrolyze. We assume that the salt dissociates completely, that $\gamma(\mathrm{H}^+)$, $\gamma(\mathrm{A}^-)$, and $\gamma(\mathrm{OH}^-)$ are equal and can be approximated by the Davies equation, and that $\gamma(\mathrm{HA}) = 1$. The ionization of the acid is represented by

$$\mathrm{HA} \rightleftharpoons \mathrm{H}^+ + \mathrm{A}^-$$

We let $m_{\mathrm{eq}}(\mathrm{OH}^-)/m^\circ = y$ and $m_{\mathrm{eq}}(\mathrm{H}^+)/m^\circ = x$.

$$K_{\mathrm{a}} = \frac{\gamma^2 x\left(m_{\mathrm{s}}/m^\circ + x - y\right)}{m_{\mathrm{a}}/m^\circ - x + y}$$

When y is replaced by $K_{\mathrm{w}}/\gamma^2 x$, we obtain the equation

$$\gamma^2 x^3 + (\gamma^2 m_{\mathrm{s}}/m^\circ + K)x^2 - (K_{\mathrm{w}} + K m_{\mathrm{a}}/m^\circ)x - K_{\mathrm{a}} K_{\mathrm{w}}/\gamma^2 = 0 \qquad (7.5\text{-}6)$$

The ionic strength of the solution is equal to $m_{\mathrm{s}} + x$, so that the activity coefficient γ can be estimated by setting $I = m_{\mathrm{s}}$ in the Davies equation. The cubic equation is solved numerically and the result is that $x = 2.13 \times 10^{-5}$, $\gamma = 0.740$, $a(\mathrm{H}^+) = 1.576 \times 10^{-5}$, and pH $= 4.802$. The pH value differs from that in part a by 0.130. If the activity coefficient is included but x and y are neglected compared with m_{s} and m_{a} the resulting pH is 4.800. The most significant source of error in the Henderson–Hasselbalch equation is the neglect of the activity coefficient, not the neglect of ionization and hydrolysis.

Exercise 7.13

a. Verify Eq. (7.5-6).

b. Substitute the numerical result of part b of Example 7.16 into the equilibrium expression, Eq. (7.5-3), to verify its correctness.

c. Carry out the solution of Example 7.16 including the activity coefficient but neglecting x and y compared with m_{a} and m_{s}.

Biological Buffering

The principal buffering system in mammalian blood is that of carbonic acid (H_2CO_3). We have the following equilibria:

$$\mathrm{CO_2(g)} \rightleftharpoons \mathrm{CO_2(aq)} \qquad (7.5\text{-}7a)$$

$$\mathrm{CO_2(aq)} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_2CO_3(aq)} \qquad (7.5\text{-}7b)$$

$$\mathrm{H_2CO_3(aq)} \rightleftharpoons \mathrm{H^+} + \mathrm{HCO_3^-} \qquad (7.5\text{-}7c)$$

$$\mathrm{HCO_3^-} \rightleftharpoons \mathrm{H^+} + \mathrm{CO_3^{2-}} \qquad (7.5\text{-}7d)$$

EXAMPLE 7.17

The Henry's law constant for CO_2 in water at 25°C is equal to 1.24×10^6 torr. The equilibrium constant for reaction (7.5-7b) is equal to 2.58×10^{-3}, that for reaction (7.5-7c) is equal to 1.70×10^{-4}, and that for reaction in Eq. (7.5-7d) is equal to 4.69×10^{-11}. It is not possible by chemical analysis to distinguish CO_2(aq) from H_2CO_3, but it has been determined that the molality of CO_2(aq) is larger than that of H_2CO_3(aq). Find the value of the first ionization constant of carbonic acid, using the combined molalities of CO_2(aq) and H_2CO_3(aq) in the equilibrium expression instead of the molality of H_2CO_3(aq). Explain why reaction in Eq. (7.5-7c) can act as an effective buffering reaction near the normal pH of blood, around pH 7.4.

Solution

From the equilibrium of Eq. (7.5-7b)

$$a(\mathrm{CO_2(aq)}) = \frac{a(\mathrm{H_2CO_3})}{2.58 \times 10^{-3}} = (389)a(\mathrm{H_2CO_3})$$

$$a(\mathrm{H_2CO_3}) + a(\mathrm{CO_2(aq)}) = (389)a(\mathrm{H_2CO_3})$$

From the equilibrium of Eq. (7.5-7c)

$$a(\mathrm{H^+})a(\mathrm{HCO3^-}) = (1.70 \times 10^{-4})a(\mathrm{H_2CO_3})$$

$$a(\mathrm{H^+})\,a(\mathrm{HCO3^-}) = \frac{1.70 \times 10^{-4}}{389}(a(\mathrm{H_2CO_3}) + a(\mathrm{CO_2(aq)}))$$

$$\begin{aligned} K(\text{effective}) &= \frac{a(\mathrm{H^+})\,a(\mathrm{HCO3^-})}{a(\mathrm{H_2CO_3}) + a(\mathrm{CO_2(aq)})} \\ &= \frac{1.70 \times 10^{-4}}{389} = 4.37 \times 10^{-7} \end{aligned}$$

This equilibrium constant is near 10^{-7}, so that this equilibrium can provide buffering near pH = 7.

Exercise 7.14

a. Find the pH of a solution produced by equilibrating water with gaseous carbon dioxide at 760 torr at 25°C. Assume all activity coefficients are equal to unity.

b. Repeat the calculation of part b, using the Davies equation to estimate activity coefficients.

The pH of human blood can be raised by removing dissolved carbon dioxide from the blood through hyperventilation (rapid breathing). The reaction of Eq. (7.5-7b) is catalyzed by an enzyme, carbonic anhydrase, so that equilibrium is established rapidly. If the molality of dissolved carbon dioxide is lowered below its normal value, the reaction of Eqs. (7.5-7b) and (7.5-7c) shift to the left, raising the pH of the blood and producing a feeling of "light-headedness." A person who has hyperventilated is often told to breathe into and out of a paper bag. Since exhaled air is about 4% carbon dioxide, this practice increases the level of carbon dioxide in the blood and alleviates the symptoms. The body also attempts to correct the situation by increasing the excretion of the bicarbonate ion in urine.

PROBLEMS

Section 7.5: Buffer Solutions

7.41 Find the pH of a buffer solution made from 0.300 mol of acetic acid, 0.500 mol of sodium acetate, and 1.000 kg of water. The acid ionization constant of acetic acid is equal to 1.75×10^{-5}.

a. Use the Henderson–Hasselbalch equation.

- **b.** Neglect the ionization of the acid and the hydrolysis of the salt but use the Davies equation to estimate activity coefficients.

7.42 Consider an acetic acid/acetate buffer solution made from 0.040 mol of acetic acid and 0.060 mol of sodium acetate in 1.000 kg of water and maintained at 298.15 K.

- **a.** Find the pH of the buffer, using the Henderson–Hasselbalch equation.
- **b.** Find the pH of the buffer using the Davies equation to estimate activity coefficients.
- **c.** Find the change in pH if 0.010 mol of solid sodium hydroxide is added.
- **d.** Find the change in pH if 0.010 mol of solid sodium hydroxide is added to a solution of hydrochloric acid and sodium chloride in 1.000 kg of water if the solution has the same pH and ionic strength as the buffer solution in part a.

7.43 How much solid NaOH must be added to 0.100 mol of cacodylic acid in 1.000 kg of water at 298.15 K to make a buffer solution with pH equal to 7.00? The acid dissociation constant is equal to 6.4×10^{-7}.

- **a.** Use the Henderson–Hasselbalch equation.
- **b.** Use Eq. (7.5-3) and the Davies equation.

7.44 The two acid ionization constants of *ortho*-phthalic acid are $K_1 = 1.3 \times 10^{-3}$ and $K_2 = 3.9 \times 10^{-6}$. Find the pH of a solution made from 0.100 mol of *ortho*-phthalic acid, 0.100 mol of potassium hydrogen phthalate, 0.100 mol of dipotassium phthalate, and 1.000 kg of water.

7.45 **a.** Find the value of the equilibrium constant at 298.15 K for the reaction

$$\mathrm{NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-}$$

- **b.** 0.1000 mol of NH_3 and 0.1500 mol of NH_4Cl are dissolved in 1.000 kg of H_2O at a constant temperature of 298.15 K. Write an equation analogous to the Henderson–Hasselbalch equation that applies to this case. Find the equilibrium molality of OH^-, the pOH (defined analogously to the pH), and the pH.
- **c.** Use the Davies equation to estimate activity coefficients and find the pOH. Neglect the ionization of NH_3 and the hydrolysis of NH_4^+.

7.6 The Temperature Dependence of Chemical Equilibrium. The Principle of Le Châtelier

We can calculate ΔG only for a process that begins and ends at the same temperature. However, we can obtain the temperature dependence of ΔG for such processes considered at different temperatures. By differentiation of Eq. (7.1-13) we obtain

$$\frac{d\Delta G^\circ}{dT} = \sum_{i=1}^{c} v_i \left(\frac{\partial \mu_i^\circ}{\partial T}\right)_{P,n} = -\sum_{i=1}^{c} v_i \overline{S}_i^\circ = -\Delta S^\circ \tag{7.6-1}$$

We can also write

$$\frac{d(\Delta G^\circ/T)}{dT} = -\frac{\Delta S^\circ}{T} - \frac{\Delta G^\circ}{T^2} = -\frac{\Delta H^\circ}{T^2} \tag{7.6-2}$$

Exercise 7.15

Show that

$$\frac{d(\Delta G^\circ/T)}{d(1/T)} = \Delta H^\circ \tag{7.6-3}$$

Using Eq. (7.1-20) we can write

$$\frac{d\ln(K)}{dT} = \frac{\Delta H^\circ}{RT^2} \tag{7.6-4}$$

or

$$\frac{d\ln(K)}{d(1/T)} = -\frac{\Delta H^\circ}{R} \tag{7.6-5}$$

Exercise 7.16

Verify Eqs. (7.6-4) and (7.6-5).

If the value of ΔH° is known as a function of temperature, Eq. (7.6-4) can be integrated to obtain the value of K at one temperature from the value at another temperature:

$$\ln\left(\frac{K(T_2)}{K(T_1)}\right) = \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ}{T^2}dT \tag{7.6-6}$$

which is equivalent to

$$\frac{\Delta G^\circ(T_2)}{T_2} - \frac{\Delta G^\circ(T_1)}{T_1} = -\int_{T_1}^{T_2} \frac{\Delta H^\circ}{T^2}dT \tag{7.6-7}$$

where $\Delta G^\circ(T_2)$ is the value of ΔG° at temperature T_2, and $\Delta G^\circ(T_1)$ is the value of ΔG° at temperature T_1. If ΔH° is temperature-independent, Eq. (7.6-6) becomes an equation known as the *van't Hoff equation*.

$$\ln\left(\frac{K(T_2)}{K(T_1)}\right) = -\frac{\Delta H^\circ}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \tag{7.6-8}$$

and Eq. (7.6-7) becomes the *Gibbs–Helmholtz equation*:

$$\frac{\Delta G^\circ(T_2)}{T_2} - \frac{\Delta G^\circ(T_1)}{T_1} = \Delta H^\circ\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \tag{7.6-9}$$

Exercise 7.17

Carry out the integrations to obtain Eqs. (7.6-8) and (7.6-9).

EXAMPLE 7.18

Assuming that ΔH° is temperature-independent, calculate the value of K and ΔG° at 100°C for the reaction

$$0 = 2\,\mathrm{NO_2(g)} - \mathrm{N_2O_4(g)}$$

Solution

$$\begin{aligned}\Delta H^\circ &= 2\Delta_f H^\circ(\mathrm{NO_2}) - \Delta_f H^\circ(\mathrm{N_2O_4}) = 2(33.095\,\mathrm{kJ\,mol^{-1}}) + (-1)(9.179\,\mathrm{kJ\,mol^{-1}})\\ &= 57.011\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

$$\begin{aligned}\ln\left(\frac{K(373.15\,\mathrm{K})}{K(298.15\,\mathrm{K})}\right) &= -\frac{57011\,\mathrm{J\,mol^{-1}}}{8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}}\left[\frac{1}{373.15\,\mathrm{K}} - \frac{1}{298.15\,\mathrm{K}}\right]\\ &= 4.622\end{aligned}$$

Using the value of $K(298.15\,\mathrm{K})$ from Example 7.3,

$$\begin{aligned}K(373.15\,\mathrm{K}) &= K(298.15\,\mathrm{K})\,e^{4.622}\\ &= (0.148)(101.7) = 14.92\\ \Delta G^\circ(373.15\,\mathrm{K}) &= -RT\ln(K(373.15\,\mathrm{K}))\\ &= -(8.3145\,\mathrm{J\,K^{-1}mol^{-1}})(373.15\,\mathrm{K})\ln(14.92)\\ &= -8390\,\mathrm{J\,mol^{-1}} = -8.39\,\mathrm{kJ\,mol^{-1}}\end{aligned}$$

Exercise 7.18

Find the value of K for the reaction of Example 7.4 at 1000 K.

If the assumption of constant ΔH° is not sufficiently accurate, the next simplest assumption is that the heat capacities are constant, so that

$$\Delta H^\circ(T) = \Delta H^\circ(T_1) + \Delta C_\mathrm{P}(T - T_1) \tag{7.6-10}$$

When Eq. (7.6-10) is substituted into Eq. (7.6-4) and an integration is carried out from T_1 to T_2, the result is

$$\ln\left(\frac{K(T_2)}{K(T_1)}\right) = -\frac{\Delta H^\circ(T_1)}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] + \frac{\Delta C_\mathrm{P}}{R}\left[\ln\left(\frac{T_2}{T_1}\right) + \frac{T_1}{T_2} - 1\right] \tag{7.6-11}$$

Exercise 7.19

a. Verify Eq. (7.6-11).

b. Using heat-capacity data from Table A.8 of Appendix A and assuming the heat capacities to be temperature-independent, evaluate K and ΔG° for the reaction of Example 7.18 at 100°C. Calculate the percent difference between your value for K and that in Example 7.18.

The Principle of Le Châtelier

This principle is named for Henri Louis Le Châtelier, 1850–1936, a French chemist.

The behavior of a system at chemical equilibrium when subjected to a change in temperature illustrates the *principle of Le Châtelier*. This principle states: *If possible,* *a system will respond to a stress placed upon it by reacting in the direction that lessens the effect of that stress on intensive properties of the system.*[4]

The transfer of heat to a system is an example of an applied stress. From Eq. (7.6-4) we see that the equilibrium constant for an endothermic reaction ($\Delta H > 0$) has a positive temperature derivative. The stress causes the reaction to shift toward the right, producing more products and absorbing part of the heat put into the system. For a given amount of heat, the temperature of the system rises by a smaller amount than it would if the reaction were somehow prevented from shifting its reaction equilibrium. The heat added to the system is the stress, and the moderation of the temperature rise is the lessening of the effect of the stress referred to in the statement of the principle. For an exothermic reaction ($\Delta H < 0$) transfer of heat to the system will cause the equilibrium to shift toward the left, again causing the temperature of the system to rise by a smaller amount than if the reaction were frozen.

The principle of Le Châtelier applies to other cases, including the shift in the equilibrium of a gas-phase reaction produced by changing the volume of a system at constant temperature. Let us write an equilibrium expression for a gaseous reaction in terms of the mole fractions. The mole fraction of substance i is given for an ideal gas mixture by Dalton's law:

$$x_i = \frac{P_i}{P_{\text{tot}}} \tag{7.6-12}$$

where P_{tot} is the total pressure. Equation (7.2-2) for the equilibrium constant of a gaseous reaction becomes

$$\begin{aligned} K &= \prod_{i=1}^{c}\left(x_i\frac{P_{\text{tot}}}{P^\circ}\right)^{\nu_i} = \left(\frac{P_{\text{tot}}}{P^\circ}\right)^{\Delta\nu}\prod_{i=1}^{c}x_i^{\nu_i} \\ &= \left(\frac{P_{\text{tot}}}{P^\circ}\right)^{\Delta\nu} K_x \end{aligned} \tag{7.6-13}$$

where $\Delta\nu$ is the sum of the stoichiometric coefficients:

$$\Delta\nu = \sum_{i=1}^{c}\nu_i \tag{7.6-14}$$

equal to the net change in the number of moles of gas in the system if 1 mol of reaction occurs. It is positive if the products consist of a greater number of moles of gas than the reactants. The quantity K_{x} is not a true equilibrium constant, since it depends on pressure:

$$K_{\text{x}} = \left(\frac{P_{\text{tot}}}{P^\circ}\right)^{-\Delta\upsilon} K \tag{7.6-15}$$

If the products consist of fewer moles of gas than the reactants and if the volume of the system is decreased (increasing the pressure), K_x will increase and the mole fractions of the products will increase. If the products consist of more moles of gas than the reactants, the mole fractions of the reactants will increase. In either case, a reduction of

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[4] See J. A. Campbell, *J. Chem. Educ.*, **62**, 231 (1985) for an interesting rule for predicting the direction of the shift in a reaction equilibrium produced by a change in temperature if the sign of ΔH° is not known, and also for references to articles discussing the correct statement of the principle of Le Châtelier.

volume (the stress) will increase the pressure by a smaller amount than if the reaction were somehow prevented from shifting.

EXAMPLE 7.19

For the reaction of Example 7.3, calculate the equilibrium degree of dissociation if the volume is reduced to 10.00 L at 298.15 K. Interpret the results in terms of the principle of Le Châtelier.

Solution

Let α equal the degree of dissociation. Assume that the gases are ideal.

$$\begin{aligned} K = 0.148 &= \frac{(2\alpha)^2}{1-\alpha}\frac{(1.000\,\text{mol})RT}{P^\circ V} \\ &= \frac{(2\alpha)^2}{1-\alpha}\frac{(1.000\,\text{mol})(8.3145\,\text{J}\,\text{K}^{-1}\text{mol}^{-1})(298.15\,\text{K})}{(100000\,\text{Pa})(0.01000\,\text{m}^3)} \\ &= \frac{(2\alpha)^2}{1-\alpha}(2.479) = \frac{9.916\alpha^2}{1-\alpha} \end{aligned}$$

$$9.916\alpha^2 + 0.148\alpha - 0.148 = 0$$

$$\alpha = \frac{-0.148 + \sqrt{(0.148)^2 + 4(9.916)(0.148)}}{2(9.916)} = 0.115$$

We have disregarded a negative root to the quadratic equation since α cannot be negative. The decrease in volume causes the reaction to shift to the left, so that fewer moles of gas are present in the smaller volume than in the larger volume of Example 7.3.

The principle of Le Châtelier also applies to the addition of a reactant or a product to an equilibrium system.

EXAMPLE 7.20

For the system of Example 7.3, find the effect of adding an additional 0.500 mol of NO_2.

Solution

Let α be defined by

$$n(\mathrm{N_2O_4}) = (1.000\,\text{mol})(1.000 - \alpha)$$

$$n(\mathrm{NO_2}) = (1.000\,\text{mol})(2.000\alpha + 0.500)$$

$$0.148 = \frac{(2.000\alpha + 0.500)^2}{1.000 - \alpha}(1.000\,\text{mol})\frac{RT}{P^\circ V}$$

$$\begin{aligned} \frac{RT}{P^\circ V} &= \frac{\left(8.3145\,\text{J}\,\text{K}\,\text{mol}^{-1}\right)(298.15\,\text{K})}{(100000\,\text{Pa})\left(0.02446\,\text{m}^3\right)} \\ &= 1.0135\,\text{mol}^{-1} \end{aligned}$$

$$\frac{0.148}{1.0135} = 0.146 = \frac{(2.000\alpha + 0.5000)^2}{1.000 - \alpha}$$

which gives

$$4.0540\alpha^2 + 2.1750\alpha + 0.1054 = 0$$

Use of the quadratic formula gives

$$\alpha = -0.0539$$

where a root to the quadratic equation has been disregarded that gives a physically impossible value of α. Note that α can be negative since additional NO_2 has been added. The final amount of N_2O_4 is equal to 1.0539 mol. The mole fraction of NO_2 has shifted to a value of 0.271 instead of 0.506, in agreement with the principle of Le Châtelier.

Exercise 7.20

Verify the result of the previous example by substituting the value of α. Find the physically unacceptable root and explain why it cannot be correct.

The action of a buffer solution can also be interpreted according to the principle of Le Châtelier.

EXAMPLE 7.21

Assume that 0.00200 mol of solid NaOH is added to the buffer solution of Example 7.16. Calculate the change in the pH of the solution.

Solution

The resulting solution is the same as a solution made with 0.3980 mol of acetic acid and 0.6020 mol of sodium acetate. Neglect the ionization and hydrolysis and use the value of γ from the example. Let $x = m(\mathrm{H}^+)/m^\circ$.

$$K_a = 1.75 \times 10^{-5} = \frac{\gamma^2 x(m_s/m^\circ)}{m_a/m^\circ}$$

$$= \frac{(0.740)^2(0.6020)x}{0.3980} = 0.8283x$$

$$x = \frac{1.75 \times 10^{-5}}{0.8283} = 2.11 \times 10^{-5}$$

$$\mathrm{pH} = -\log_{10}((0.740)(2.11 \times 10^{-5})) = 4.81$$

The pH has changed by only 0.01.

Exercise 7.21

Calculate the change in the pH if 0.00200 mol of solid NaOH is added to a solution of HCl with the same pH as the buffer solution of Example 7.21.

PROBLEMS

Section 7.6: The Temperature Dependence of Chemical Equilibrium. The Principle of Le Châtelier

7.46 Calculate $\Delta G°$ and the equilibrium constant for the reaction

$$\mathrm{CaCO_3(s)} \rightleftharpoons \mathrm{CaO(s)} + \mathrm{CO_2(g)}$$

at 500 K and at 1000 K.

a. Use the value of $\Delta G°$ at 298.15 K and assume that the heat capacities are constant over the temperature range.

b. Find the temperature at which the equilibrium pressure of CO_2 is equal to 1.00 atm (1.01325 bar). Compare your result with the experimental value of 898°C (1171 K).

7.47 **a.** Find the value of the ionization constant of water at 50.0°C.

b. What is the molality of H^+ ions in pure water at 50°C? What is the pH of pure water at 50.0°C?

c. What is the pH at 50.0°C of a solution containing 1.000 mol of NaCl and 1.000 kg of water? What is the molality of H^+ ions? Assume that the Davies equation can be used for the activity coefficients, and assume that $\gamma(\mathrm{OH^-}) = \gamma(\mathrm{H^+}) = \gamma_\pm$.

7.48 Using thermodynamic data at 298.15 K, find the value of the equilibrium constant at 400.0°C for the reaction

$$2\mathrm{SO_2(g)} + \mathrm{O_2(g)} \rightleftharpoons 2\ \mathrm{SO_3(g)}$$

Compare your value with the value at 298.15 K and relate it to the principle of Le Châtelier.

7.49 If a reacting gaseous system is held at constant T and P instead of at constant T and V, under some circumstances addition of one of the reactants or products can shift the equilibrium to produce more of the added substance.

a. Derive an expression for the derivative $\left(\frac{\partial \ln(K_x)}{\partial n_i}\right)$, where n_i is the amount of substance i.

b. Under what circumstances could addition of N_2 to an equilibrium system containing gaseous N_2, H_2, and NH_3 shift the equilibrium to produce more N_2?

7.50 Multiply Eq. (7.6-5) by $d(1/T)$ and carry out an integration to obtain a formula analogous to Eq. (7.6-8). Comment on your result.

7.51 **a.** Find the equilibrium constant for the reaction

$$\mathrm{N_2} + 3\mathrm{H_2} \rightleftharpoons 2\mathrm{NH_3}$$

at 400 K. State any assumptions.

b. Find the equilibrium composition of a system originally consisting of 1.000 mol of N_2 and 3.000 mol of H_2, maintained at 400 K and 1.000 atm. Neglect gas nonideality.

7.52 For the reaction

$$2\mathrm{NOCl(g)} \rightleftharpoons 2\mathrm{NO(g)} + \mathrm{Cl_2(g)}$$

a. Find $\Delta H°$, $\Delta S°$, and $\Delta G°$ at 298.15 K.

b. Find K at 298.15 K and at 373.15 K. State any assumptions.

c. Find the degree of dissociation of 1.000 mol of NOCl placed in a volume of 31.026 L at 373.15 K and allowed to equilibrate. State any assumptions.

7.53 **a.** Find the value of the equilibrium constant at 298.15 K for the reaction

$$\mathrm{H_2(g)} + \mathrm{CO_2(g)} \rightleftharpoons \mathrm{H_2O(g)} + \mathrm{CO(g)}$$

b. Find the value of the equilibrium constant for this reaction at 373.15 K. State any assumptions. Assume that $\Delta H°$ is independent of temperature.

c. Equal amounts (in moles) of H_2 and CO_2 are introduced into a vessel of variable volume and maintained at 373.15 K and a total pressure of 1.000 bar. Find the equilibrium partial pressures of all substances. Assume that all gases are ideal.

d. Tell qualitatively what will occur if the pressure is increased to 5.000 bar. Give the reason for your answer.

7.54 The solubility product constant for MgF_2 is equal to 7.1×10^{-9} at 18°C, and equal to 6.4×10^{-9} at 27°C. Find the value of $\Delta G°$, K_{sp}, $\Delta H°$, and $\Delta S°$ at 25°C.

7.55 **a.** Find $\Delta H°$, $\Delta G°$, and K at 298.15 K for the reaction

$$\mathrm{I_2(g)} \rightleftharpoons 2\mathrm{I(g)}$$

b. Assuming that $\Delta H° =$ constant, find K at 1000 K.

c. Assuming that ΔC_P° = constant, find K at 1000 K.

d. Assuming that ΔH° = constant, find the temperature at which $K = 1.000$.

7.56 The solubility product constant of AgCl is equal to 1.8×10^{-10}. Silver ions form the complex $AgCl_2^-$ with a *formation constant*

$$K_f = \frac{\gamma(AgCl_2^-)m_{eq}(AgCl_2^-)\,m^\circ}{\gamma(Ag^+)m_{eq}(Ag^+)\gamma(Cl^-)^2 m_{eq}(Cl^-)^2}$$
$$= 2.5 \times 10^5$$

a. Find the molality of this complex and the molality of Ag^+ ions in a saturated solution at equilibrium with solid AgCl. Does the presence of the $AgCl_2^-$ complexes affect the molality of Ag^+ to a significant extent? Does it affect the total amount of AgCl that dissolves?

b. Find the molality of this complex and the molality of Ag^+ ions in a solution containing 0.100 mol kg^{-1} of Cl^- and saturated with AgCl. Does the presence of the $AgCl_2^-$ complexes affect the molality of Ag^+ to a significant extent? Does it affect the total amount of AgCl that dissolves?

7.57 Find the value of K at 750 K for the reaction:

$$2SO_2(g) + O_2(g) \rightleftharpoons 2\,SO_3(g)$$

a. Use the van't Hoff equation, Eq. (7.6-8).

b. Use the interpolated values of the $\dfrac{-\left(G_m^\circ - H_{m,298}^\circ\right)}{T}$ function to find ΔG° and find K from that value.

7.58 At 298.15 K the solubility product constant of Ag_2S in water is equal to 8×10^{-58}. The S^{2-} ion hydrolyzes with water:

$$S^{2-} + H_2O \rightleftharpoons HS^- + OH^-$$

The acid ionization constant of HS^- is equal to 1.0×10^{-19}.

a. Find the molality of Ag^+ ions and of S^{2-} ions in a saturated aqueous solution of Ag_2S. Does the presence of the hydrolysis reaction affect the solubility significantly?

b. Find the molality of Ag^+ ions and of S^{2-} ions in a saturated solution of Ag_2S that also contains 0.100 mol of OH^- per kg of water.

7.59 Find the value of K at 750 K for the reaction

$$N_2(g) + 2O_2(g) \rightleftharpoons N_2O_4(g)$$

a. Use the van't Hoff equation, Eq. (7.6-8).

b. Use the interpolated values of the $-(G_m^\circ - H_{m,298}^\circ)/T$ functions to find ΔG° and find K from that value.

7.60 **a.** Find ΔG° and K for each of the following reactions at 1000.0 K:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$
$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

b. Using the results of part a, find ΔG° and K for the reaction at 1000.0 K:

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$$

c. Find ΔG° and K for the reaction at 1000.0 K:

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

7.61 Miller and Murphy[5] give the following values for the distribution coefficient of nicotine between hexane and water at pH 11, where

$$K_d = \frac{[\text{nicotine}]^{(\text{hexane})}}{[\text{nicotine}]^{(\text{water})}}$$

t/°C	5	10	15	20
K_d	0.26	0.41	0.58	0.70

and where the molar concentration of nicotine is denoted by [nicotine] . Find the value of ΔG°, ΔH°, and ΔS° at 15°C for the process of transferring nicotine from water to hexane, using the concentration description.

7.62 Find the value of ΔG° at 750 K for the reaction

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

a. Use interpolated values of $\Delta_f G^\circ$ values.

b. Use the interpolated values of the $-(G_m^\circ - H_{m,298}^\circ)/T$ function.

c. Use the Gibbs–Helmholtz equation.

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[5] D. L. C. Miller and W. R. Murphy, *Ind. Eng. Chem. Res.*, **33**, 3239 (1994).

7.7 Chemical Equilibrium and Biological Systems

An important feature of biochemical reactions of metabolism and respiration is the *coupling* of pairs of reactions, which can result in the driving of a nonspontaneous reaction by the progress of a spontaneous reaction. The hydrolysis of adenosine triphosphate (abbreviated by ATP) to form adenosine diphosphate (abbreviated by ADP) and phosphoric acid (abbreviated by P) is shown in Figure 7.3. This is a spontaneous reaction that drives a number of useful reactions in various organisms.

The hydrolysis reaction equation is abbreviated:

$$\mathrm{ATP} + \mathrm{H_2O} \rightleftharpoons \mathrm{ADP} + \mathrm{P_i} \tag{7.7-1}$$

where $\mathrm{P_i}$ stands for "inorganic phosphate," collectively phosphoric acid and its various anions. Since ATP, ADP, and phosphoric acid are all weak polyprotic acids, they exist as various anions in aqueous solution as well as in the forms shown in Figure 7.3. The abbreviations in Eq. (7.7-1) stand for whatever ionized and unionized forms of ATP, ADP, and phosphoric acid occur.

The anions of ATP and ADP form complexes with positive ions such as $\mathrm{Mg^{2+}}$ or $\mathrm{Ca^{2+}}$. It is customary to define a modified standard-state reaction in which the substances in the reaction equation are at unit activities but the hydrogen ions and any complexing cations are at specified activities not necessarily equal to unity. The symbol $\Delta G^{\circ\prime}$ is used for the Gibbs energy change of such a modified standard-state reaction.

Using the concentration description $\Delta G^{\circ\prime}$ for the reaction of Eq. (7.7-1) is equal to $-29.3\ \mathrm{kJ\ mol^{-1}}$ at 298.15 K if pH = 7.00 and pMg = 4.00. The pMg is defined in the concentration description by analogy with pH:

$$\begin{aligned} \mathrm{pMg} &= -\log_{10} a(\mathrm{Mg^{2+}}) \\ &= -\log_{10} \gamma(\mathrm{Mg^{2+}}) c(\mathrm{Mg^{2+}})/c^{\circ} \end{aligned} \tag{7.7-2}$$

EXAMPLE 7.22

a. Find the equilibrium constant for the reaction of Eq. (7.7-1).

b. Find the equilibrium concentrations of ADP and ATP at pH = 7.00 and pMg = 4.00 if all of the phosphoric acid present comes from the hydrolysis of ATP and if the initial concentration of ATP is $0.0100\ \mathrm{mol\ L^{-1}}$. Approximate all activity coefficients by unity.

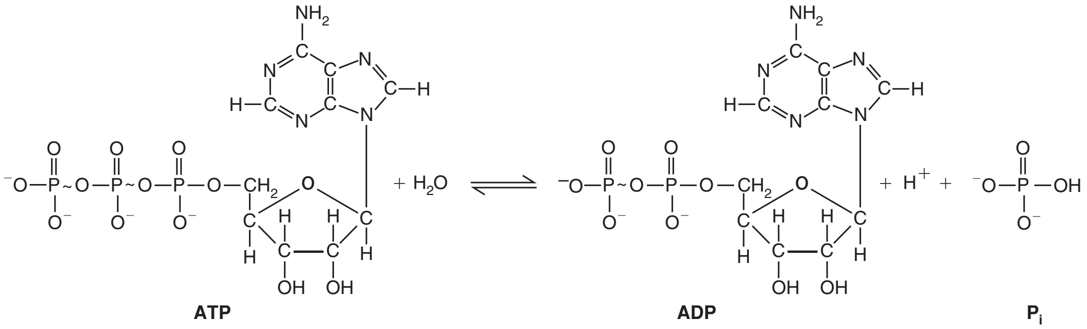


Figure 7.3 The Hydrolysis of Adenosine Triphosphate.

Solution

a.

$$K = \exp\left[\frac{2.93 \times 10^4\,\mathrm{J\,mol^{-1}}}{\left(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}\right)(298.15\,\mathrm{K})}\right]$$

$$= 1.36 \times 10^5$$

b. Let $x = c_{\mathrm{eq}}(\mathrm{ATP})/c^{\circ}$

$$1.36 \times 10^5 = \frac{(0.0100 - x)^2}{x}$$

$$x = \frac{(0.0100 - x)^2}{1.36 \times 10^5} \approx \frac{(0.0100)\,2}{1.36 \times 10^5}$$

$$\approx 7.35 \times 10^{-10}$$

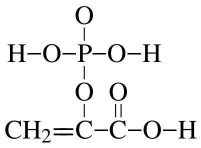
Exercise 7.22

Find the value of $(\partial G/\partial \xi)_{T,P}$ at 298.15 K for the case that $c(\mathrm{ATP}) = 0.0100\,\mathrm{mol\,L^{-1}}$ and $c(\mathrm{ADP}) = c(\mathrm{P_i}) = 0.0200\,\mathrm{mol\,L^{-1}}$ at pH = 7.00 and pMg = 4.00. Approximate all activity coefficients by unity.

The hydrolysis of ATP is "coupled" to various other reactions that would otherwise not be spontaneous. For example, the reaction

$$\mathrm{P_i} + \text{glucose} \rightleftharpoons \text{glucose 6-phosphate} + \mathrm{H_2O} \qquad (7.7\text{-}3)$$

is driven by the reaction of Eq. (7.7-1). We illustrate the coupling of reactions with the regeneration of ATP, which is coupled to the hydrolysis of phosphoenolpyruvic acid (abbreviated PEP).



The hydrolysis of PEP is sufficiently spontaneous to produce ATP from ADP when coupled to this reaction. The sum of the two reactions is equivalent to a spontaneous reaction:

$$\text{(A)} \quad \mathrm{PEP} + \mathrm{H_2O} \rightleftharpoons \mathrm{Py} + \mathrm{P_i} \quad \Delta G^{\circ\prime} = -53.6\,\mathrm{kJ\,mol^{-1}} \qquad (7.7\text{-}4a)$$

$$\text{(B)} \quad \mathrm{ADP} + \mathrm{P_i} \rightleftharpoons \mathrm{ATP} + \mathrm{H_2O} \quad \Delta G^{\circ\prime} = +\,29.3\,\mathrm{kJ\,mol^{-1}} \qquad (7.7\text{-}4b)$$

$$\text{(C)} \quad \mathrm{ADP} + \mathrm{PEP} \rightleftharpoons \mathrm{ATP} + \mathrm{Py} \quad \Delta G^{\circ\prime} = -24.3\,\mathrm{kJ\,mol^{-1}} \qquad (7.7\text{-}4c)$$

where Py stands for pyruvic acid and/or pyruvate ion. The hydrolysis of PEP produces phosphoric acid, which is a reactant in the regeneration of ATP from ADP. We now inquire about the mechanism of the coupling of such reactions. According to the principle of Le Châtelier the phosphoric acid produced in the reaction of Eq. (7.7-4a) would shift the equilibrium of the regeneration reaction in Eq. (7.7-4b), producing more ATP. In the next example we show that the effect of this shift is insignificant. Another mechanism must exist for the coupling to be effective.

EXAMPLE 7.23

Calculate the concentration of ATP produced at 298.15 K by the equilibrium shift because of the principle of Le Châtelier if the initial concentrations of PEP and ADP are equal to 0.0100 mol L^{-1}.

Solution

The equilibrium constant for reaction A is equal to

$$K_A = \exp\left[\frac{5.36 \times 10^4\ \mathrm{J\,mol^{-1}}}{\left(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}\right)(298.15\ \mathrm{K})}\right]$$
$$= 2.46 \times 10^9$$

Since its equilibrium constant is much larger than unity, this reaction proceeds essentially to completion, giving an equilibrium concentration of phosphate that is nearly equal to 0.0100 mol L^{-1}.

The equilibrium constant for reaction B is the reciprocal of that for the reaction of Eq. (7.7-1), or 7.35×10^{-6}. We let $x = c_{\mathrm{eq}}(\mathrm{ATP})/c^\circ$. The equilibrium expression gives

$$x = (8.35 \times 10^{-6})(0.0100 - x)^2 \approx (8.35 \times 10^{-6})(0.0100)^2$$
$$= 7.35 \times 10^{-10}$$

$$c_{\mathrm{eq}}(\mathrm{ATP}) \approx 7.35 \times 10^{-10}\ \mathrm{mol\,L^{-1}}$$

The principle of Le Châtelier is not sufficient to explain the coupling of reactions. There must be a molecular mechanism that makes a single reaction out of two reactions. A proposed mechanism for the coupling of these two reactions involves an enzyme, pyruvate kinase, abbreviated by E.[6] The action of this enzyme is represented by a two-step mechanism:

$$(1)\quad \mathrm{E} + \mathrm{PEP} \rightleftharpoons \mathrm{EP} + \mathrm{Py} \qquad (7.7\text{-}5a)$$

$$(2)\quad \mathrm{EP} + \mathrm{ADP} \rightleftharpoons \mathrm{E} + \mathrm{ATP} \qquad (7.7\text{-}5b)$$

$$\mathrm{ADP} + \mathrm{PEP} \rightleftharpoons \mathrm{ATP} + \mathrm{Py} \qquad (7.7\text{-}5c)$$

An enzyme molecule generally possesses an *active site* into which a reactant molecule can fit. Once in the active site, the reactant molecule is rendered more reactive, possibly

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[6] K. J. Laidler, *Physical Chemistry with Biological Applications*, Benjamin/Cummings, Menlo Park, CA, 1978, p. 246ff.

by being distorted into a conformation resembling a transition state. The important aspect of the proposed mechanism is that the phosphate is not simply released into the solution; it is held in the active site of the enzyme until it reacts with an ADP molecule. Since the first step is not repeated until the second step occurs, the hydrolysis of PEP does not occur without the regeneration of ATP and the two reactions are combined into a single reaction.

EXAMPLE 7.24

Find the equilibrium constant at 298.15 K for the combined reaction:

$$\text{ADP} + \text{PEP} \rightleftharpoons \text{ATP} + \text{Py}$$

Solution

The equilibrium constant for the combined reaction is

$$\begin{aligned} K &= e^{-\Delta G^{\circ\prime}/RT} \\ &= \exp\left(\frac{24300\,\text{J mol}^{-1}}{(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})(298.15\,\text{K})}\right) \\ &= e^{9.803} = 1.81 \times 10^{4} \end{aligned}$$

Exercise 7.23

Find the equilibrium ATP concentration for the initial concentrations of Example 7.23, treating the combined reaction as a single reaction.

EXAMPLE 7.25

The coupling of the spontaneous hydrolysis of ATP to drive other reactions is similar to the coupling that regenerates ATP. Write a possible mechanism for the coupling of the spontaneous hydrolysis of ATP to drive the phosphorylation of glucose, Eq. (7.7-3).

Solution

$$\begin{array}{ll} (1) & \text{E} + \text{ATP} + \text{H}_2\text{O} \rightleftharpoons \text{Ep} + \text{ADP} \\ (2) & \text{Ep} + \text{glucose} \rightleftharpoons \text{glucose 6-phosphate} + \text{E} + \text{H}_2\text{O} \\ \hline & \text{ATP} + \text{glucose} \rightarrow \text{ADP} + \text{glucose 6-phosphate} \end{array}$$

where Ep stands for a phosphorylated enzyme molecule.

Exercise 7.24

For the phosphorylation of glucose, $\Delta G^{\circ\prime} = 19.4\,\text{kJ mol}^{-1}$. Find $\Delta G^{\circ\prime}$ and the equilibrium constant for the combined reaction of the previous example.

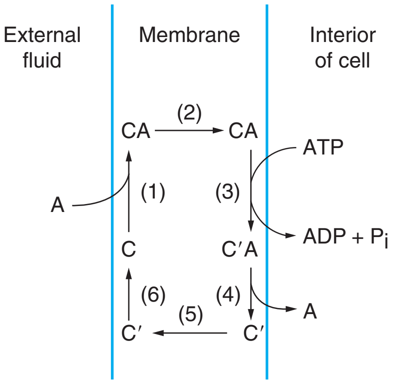

Figure 7.4 A Proposed Mechanism for Active Transport through a Membrane.

Processes other than nonspontaneous chemical reactions are also coupled to the hydrolysis of ATP. Figure 7.4 depicts a proposed mechanism for the *active transport* of a hypothetical substance, A, through a biological membrane from a solution with a low concentration and low chemical potential of A (on the left in the figure) to a region with a high concentration and high chemical potential of A (on the right in the figure).[7] This transport is opposite in direction to the spontaneous transport of A, which is from a higher to a lower value of the chemical potential. The mechanism assumes the existence inside the membrane of a carrier substance that has two forms. The first form of the carrier, denoted by C, has a tendency to form a complex with the substance A, whereas the second form, denoted by C′, has no such tendency.

Step (1) of the mechanism is the passage of A into the membrane and its combination of C at the left surface of the membrane. This process is followed by step (2), the spontaneous transport of the complex CA through the membrane from left to right to a region where the concentration and chemical potential of CA are small. Step (3) is the conversion of C to C′, which is coupled to the hydrolysis of ATP. The transported molecule A is then released in step (4) because C′ has no affinity for A. The conversion of C to C′ keeps the concentration of CA at a small value at the right side of the membrane, which makes step (2) spontaneous. After the molecule A is released from C′, the C′ molecules move spontaneously from right to left in step (5), because they are converted in step (6) back to the form C at the left side of the membrane by an enzyme located there, keeping the concentration of C′ small at the left side of the membrane. The C molecules at the left side of the membrane are now available to complex again with A molecules, and the process can be repeated. The process that causes the overall process to transport A molecules from a lower to a higher chemical potential is step (3), which consumes ATP. Although the chemical potential of A increases as it moves from left to right, the Gibbs energy of the entire system decreases because of the negative Gibbs energy change of hydrolysis of ATP.

PROBLEMS

Section 7.7: Chemical Equilibrium and Biological Systems

7.63 The hydrolysis of ATP to form ADP and phosphate has $\Delta G^{\circ\prime} = -29.3\,\mathrm{kJ\,mol^{-1}}$ and the hydrolysis of glycerol 1-phosphate to form glycerol and phosphate has $\Delta G^{\circ\prime} = -9.6\,\mathrm{kJ\,mol^{-1}}$ at 298.15 K. The reactions are coupled by the enzyme glycerol kinase. If a solution initially contains some of the enzyme and $0.0100\,\mathrm{mol\,L^{-1}}$ ATP and $0.012\,\mathrm{mol\,L^{-1}}$ glycerol at 298.15 K, find the final concentrations of ATP, ADP, glycerol, and glycerol 1-phosphate.

7.64 Creatine phosphate is another substance in addition to phosphoenolpyruvate that can regenerate ATP. If the temperature equals 25°C, if pH = 7.00, and if pMg = 4.00, the value of $\Delta G^{\circ\prime}$ for its hydrolysis is equal to $-43.1\,\mathrm{kJ\,mol^{-1}}$. Assuming that a mechanism exists to couple the reactions, find the value of the equilibrium constant for the combined reaction to regenerate ATP.

7.65 Just as the active transport of a substance through a membrane can be driven by the hydrolysis of ATP, the regeneration of ATP can also be driven by a spontaneous transport of hydrogen ions through a membrane.[8] Assuming the existence of a suitable mechanism, calculate the minimum difference in pH on the two sides of the membrane that would be required to drive this regeneration at 298.15 K.

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[7] *Ibid.*, p. 487ff.

[8] E. D. P. DeRobertis and E. M. F. DeRobertis, Jr., *Cell and Molecular Biology*, Saunders College, Philadelphia, 1980, p. 267ff.

Summary of the Chapter

For a chemical reaction at equilibrium at constant temperature and pressure,

$$0 = \left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \sum_{i=1}^{c} v_i \mu_i$$

which leads to K, the equilibrium constant:

$$K = \prod_{i=1}^{c} a_{i,eq}^{v_i}$$

where $a_{i,\mathrm{eq}}$ is the equilibrium value of the activity of substance i. The equilibrium constant is related to the standard-state Gibbs energy change of the reaction:

$$K = e^{-\Delta G^\circ / RT}$$

The equilibrium constant for a reaction involving ideal gases is

$$K = \prod_{i=1}^{\mathrm{c}} \left(\frac{P_{i,\mathrm{eq}}}{P^\circ}\right)^{v_i} \qquad \text{(gaseous reaction)}$$

The equilibrium constant for a reaction in solution is

$$K = (\gamma_1 x_1)^{v_1} \prod_{i=2}^{c} (\gamma_i m_{i,\mathrm{eq}}/m^\circ)^{v_i} \qquad \text{(solution reaction)}$$

where the solvent is designated as substance number 1. For dilute solution, the $(\gamma_1 x_1)^{v_1}$ factor is approximately equal to unity and can be omitted from the equilibrium expression. The Gibbs–Helmholtz equation for the temperature dependence of an equilibrium constant is

$$\left(\frac{\partial \ln(K)}{\partial T}\right)_P = \frac{\Delta H^\circ}{RT^2}$$

The principle of Le Châtelier asserts that in general a system will react to lessen the effect of a stress on an intensive variable, if it can do so. This effect was illustrated by considering the shift in equilibrium by changing the temperature or the pressure on a system and by adding a reactant or product to the system. The application of the thermodynamics of chemical equilibrium to biological processes was illustrated through a discussion of the coupling of chemical reactions and active transport.

ADDITIONAL PROBLEMS

7.66 The *Haber process* produces gaseous ammonia directly from hydrogen gas and nitrogen gas. This process is named for Fritz Haber, 1868–1934, a German chemist who received the 1919 Nobel Prize in chemistry for developing a catalyst and a set of conditions that made this process commercially feasible. The catalyst used is a mixture of iron oxide and potassium aluminate. The reaction is $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$.

a. Find the value of $\Delta G°$ for this reaction at 298.15 K.

b. Find the value of K for this reaction at 298.15 K.

c. Find the value of K_x for this reaction at 298.15 K and 1.000 bar.

d. Find the value of $\Delta H°$ for this reaction at 298.15 K.

e. Using the principle of Le Châtelier, specify the conditions of temperature and pressure (high or low temperature, high or low pressure) that would increase the yield of ammonia from the process.

f. The process is actually carried out at high pressure (around 500 bar) and fairly high temperature (around 500°C). Comment on this practice. Why might this temperature be used instead of a lower temperature?

g. Calculate the value of K at 500°C, using values of $\Delta G°$ and $\Delta H°$ at 298.15 K and assuming that $\Delta H°$ is constant.

h. Calculate the value of K at 500°C, using values of $-(G_\mathrm{m}^\circ - H_{\mathrm{m},298}^\circ)/T$ from Table A.8 of Appendix A and interpolating. Compare with your result from part g.

i. If equilibrium is attained at a total pressure of 1.000 bar at 298.15 K, calculate the partial pressure of each substance if a stoichiometric mixture of hydrogen and nitrogen is introduced into the system at the start of the reaction.

j. Find the value of K_x at 298.15 K and 1.000 bar. Find the value of K_x at 298.15 K and 500 bar.

k. Find the value of K_x at 500°C and 1.000 bar. Find the value of K_x at 500°C and 500 bar.

l. If equilibrium is attained at a total pressure of 500 bar at 298.15 K, calculate the partial pressure of each substance if a stoichiometric mixture of hydrogen and nitrogen is introduced into the system at the start of the reaction

m. If equilibrium is attained at a total pressure of 500 bar at 500°C, calculate the partial pressure of each substance if a stoichiometric mixture of hydrogen and nitrogen is introduced into the system at the start of the reaction.

7.67 Identify the following statements as either true or false. If a statement requires some special circumstance to make it true, label it as false.

a. Equilibrium constants are true constants.

b. Equilibrium constants depend on temperature, but do not depend on pressure.

c. Equilibrium constants for reactions involving only gases depend on temperature, but do not depend on pressure.

d. Dilution of a solution of a weak acid at constant temperature increases the degree of ionization of the acid.

e. Dilution of a solution of a weak acid can lower the pH of the solution.

f. According to the principle of Le Châtelier, changing the pressure on the system always causes a gas-phase reaction to shift its equilibrium composition.

g. According to the principle of Le Châtelier, changing the temperature always causes the equilibrium composition of a system to shift.

7.68 The following reaction is known as the “water–gas reaction”:

$$\mathrm{H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)}$$

The reaction has been used industrially as a source of carbon monoxide, which is used as a reducing agent in obtaining metallic iron from its ore. The system is allowed to approach equilibrium, using an iron catalyst.

a. Find the value of $\Delta G°$ and of K for this reaction at 298.15 K and at 1000 K.

b. Find the value of $\Delta H°$ for this reaction at 298.15 K and at 1000 K.

c. What experimental conditions will favor the maximum yield of carbon monoxide?

d. Find the value of $\Delta G°$ and of K at 1259 K, interpolating between values of $-(G_\mathrm{m}^\circ - H_{\mathrm{m},298}^\circ)/T$ in Table A.8 of Appendix A. Compare your value of K with the accepted value of 1.60.

e. Find the value of $\Delta G°$ and of K for this reaction at 1259 K, using the values at 1000 K and assuming that $\Delta H°$ is constant between 1000 K and 1259 K. Compare your result with the result of part (d).

7.69 For a sparingly soluble 1-1 electrolyte, the molality at saturation is given by $m_\mathrm{sat}/m° = \sqrt{K_\mathrm{sp}}$ where K_sp is the solubility product constant, if it can be assumed that activity coefficients are equal to unity. Derive a modified version of this equation, assuming the Debye–Hückel expression for activity coefficients.

7.70 All or nearly all of the processes in a living organism seem to be driven by coupling with the hydrolysis of ATP. The body of a 70-kg person contains about 50 g of ATP.[9] The molar mass of ATP is 0.551 kg mol^{-1}. Find the amount of 50.0 g of ATP in moles. Assume that the person ingests food equivalent to 2500 kcal per day and that 40% of this energy is available to regenerate ATP and that the regeneration requires 35 kJ mol^{-1}. Estimate the number of times that ATP is regenerated in one day.

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[9] R. H. Garrett and C. M Grisham, *Biochemistry*, 3rd ed., Thomson-Brooks/Cole, Belmont, CA, 2004, p. 73.

8

The Thermodynamics of Electrochemical Systems

PRINCIPAL FACTS AND IDEAS

1. Thermodynamic relations can be used to obtain information about electrochemical systems.
2. The effects of the electric potential must be included in the chemical potentials of substances with charged particles.
3. In an electrochemical cell, a flow of current is accompanied by the progress of a chemical reaction.
4. In an electrochemical cell, the chemical reaction that occurs is physically divided into two half-reactions, which take place at different electrodes.
5. Electrochemical data can be used to obtain thermodynamic information about chemical reactions.

8.1 The Chemical Potential and the Electric Potential

Our discussion of the chemical potential in the preceding three chapters is incomplete in the case of charged particles in an electric field. If a stationary particle with electric charge Q has an *electrostatic force* $\mathbf{F}$ exerted on it, this corresponds to an electric field $\mathscr{E}$ such that

$$\mathbf{F} = Q\mathscr{E} \tag{8.1-1}$$

The electric field is a vector that is equal to the electrostatic force per unit charge. If Q is positive the electric field and the force are in the same direction and if Q is negative the field and the force are in opposite directions. Since a velocity-independent force can be derived from a potential energy, the electric field can be derived from the *electric potential* φ, which is a potential energy per unit charge. The electric field and the electric potential are related by the equation

$$\mathscr{E} = -\nabla\varphi \tag{8.1-2}$$

The symbol ∇ stands for the *gradient operator*, which is a vector derivative operator that is defined in Eq. (B-43) of Appendix B. The gradient operator is sometimes called *del*. The x component of $\mathscr{E}$ is given by

$$\mathscr{E}_x = -\frac{\partial\varphi}{\partial x} \tag{8.1-3}$$

The volt is named for Alessandro Guiseppi Antonio Anastasio Volta, 1745–1827, the Italian chemist who invented the first practical electrochemical cell around 1799. He was made a count by Napoleon in 1801.

and the other components are similar. The SI unit of the electric potential is the *volt* (V), equivalent to newtons per coulomb. The SI unit of the electric field is volts per meter ($\mathrm{V\,m^{-1}}$). The electrostatic contribution to the potential energy of a particle of charge Q is

$$\mathscr{V}_{\text{electrostatic}} = Q\varphi \tag{8.1-4}$$

A constant can be added to the electric potential without any physical effect, as is the case with any potential energy. The electric potential is generally due to the presence of electric charges. It is customary to assign the value of the electric potential to vanish at a location that is infinitely distant from all charges. Electric potentials relative to this zero are called *absolute potentials*.

The electrostatic potential energy is part of the thermodynamic energy U and is included in the Gibbs energy and in the chemical potential. The chemical potential of a charged species is given by

$$\mu_i = \mu_{i,\text{chem}} + N_{\text{Av}}\mathscr{e}z_i\varphi \tag{8.1-5}$$

Faraday's constant is named for Michael Faraday, 1791–1867, a great English physicist and chemist who discovered the laws of electrolysis, who was the first to isolate metallic sodium and potassium, and who invented the first electric generator.

where N_{Av} is Avogadro's constant, $\mathscr{e}$ is the charge on a proton, and z_i is the valence of the ion (the number of proton charges on the ion). The valence is positive for a cation and negative for an anion. The charge on a mole of protons is denoted by F and called *Faraday's constant*.

$$F = N_{\text{Av}}\mathscr{e} = 96485\ \mathrm{C\,mol^{-1}} \tag{8.1-6}$$

Equation (8.1-5) can be written

$$\mu_i = \mu_{i,\text{chem}} + z_i F\varphi \tag{8.1-7}$$

We call $\mu_{i,\text{chem}}$ the *chemical part of the chemical potential*. It is assumed to be independent of the electric potential and depends only on temperature, pressure, and the composition of the system. The chemical potential including the electric potential term is the true chemical potential that obeys the fundamental fact of phase equilibrium. Some electrochemists use the term *electrochemical potential* for the chemical potential in Eq. (8.1-7) and refer to the chemical part of the chemical potential as the "chemical potential." We will use the term "chemical potential" for the true chemical potential and the term "chemical part of the chemical potential" for $\mu_{i,\text{chem}}$.

The chemical potential of a single charged species cannot be measured, since charged particles cannot easily be added to a system without adding ions of the opposite charge at the same time. Consider an electrolyte solute with the formula $M_{\nu_+}X_{\nu_-}$ and with ion valences z_+ and z_-. The cation is represented by M^{z+} and the anion is represented by X^{z-}. We use a subscript + to indicate the cation, a subscript − to indicate the anion, and a subscript *i* to denote the neutral compound. We use the analogue of Eq. (7.4-3) to write the chemical potential of the neutral electrolyte solute:

$$\mu_i = \nu_+\mu_+ + \nu_-\mu_- = \nu_+\mu_{+,\text{chem}} + \nu_-\mu_{-,\text{chem}} + (\nu_+ z_+ + \nu_- z_-)F\varphi \tag{8.1-8}$$

For example, Eq. (8.1-8) for Na_2SO_4 is

$$\begin{aligned}\mu(Na_2SO_4) &= 2\mu_{\text{chem}}(Na^+) + \mu_{\text{chem}}(SO_4^{2-}) + (2)(+1) + (1)(-2)F\varphi\\ &= 2\mu_{\text{chem}}(Na^+) + \mu_{\text{chem}}(SO_4^{2-})\end{aligned}$$

Electrical neutrality implies that $\nu_+ z_+ + \nu_- z_- = 0$ for any neutral electrolyte, so the term proportional to φ in Eq. (8.1-8) cancels, as it does for any neutral electrolyte solute.

$$\mu_i = \nu_+\mu_{+,\text{chem}} + \nu_-\mu_{-,\text{chem}} = \mu_{i,\text{chem}} \tag{8.1-9}$$

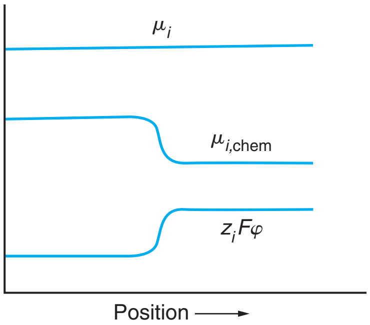

Figure 8.1 The Equilibrium Chemical Potential, The Chemical Part of the Chemical Potential, and the Electric Potential at the Interface between two Metallic Phases (Schematic).

Exercise 8.1

a. Show that the electrochemical potential of aqueous $CaCl_2$ has no dependence on the electric potential.

b. Show that the electrochemical potential of aqueous Na_3PO_4 has no dependence on the electric potential.

Electrons have a chemical potential like any other species:

$$\mu(e^-) = \mu_{\text{chem}}(e^-) - F\varphi \tag{8.1-10}$$

A conducting phase such as a metal contains mobile electrons. If two conducting phases are placed in contact and allowed to come to equilibrium, the chemical potential of the electron will have the same value in both phases. The chemical part of the electron's chemical potential can have different values in the two materials if the electric potential φ has different values, as depicted in Figure 8.1.

PROBLEMS

Section 8.1: The Chemical Potential and the Electric Potential

8.1 Assume that the electric field in a region near a phase boundary in an electrochemical cell is equal to $1.0 \times 10^7\ \mathrm{V\,m^{-1}}$. Find the magnitude of the concentration gradient (derivative of the concentration with respect to position) of a univalent ion that is necessary to make the total chemical potential uniform if the concentration of the ion is $0.100\ \mathrm{mol\,L^{-1}}$ and the temperature is 298.15 K.

8.2 Assume that the concentration of Cd^{2+} ions varies from a value of $0.0100\ \mathrm{mol\,L^{-1}}$ near a cadmium electrode to a value of $0.100\ \mathrm{mol\,L^{-1}}$ at a distance of 8.0 nm from the first position. Find the electric potential difference between these two positions.

8.3 Assume that the equilibrium concentration of Ag^+ ions near an electrode varies from a value of $0.0010\ \mathrm{mol\,L^{-1}}$ at the electrode to a value of $0.100\ \mathrm{mol\,L^{-1}}$ at a distance of 5.0 nm from the electrode.

a. Find the difference in electric potential between a location at the electrode and at a distance of 5.0 nm from the electrode.

b. Find the electric field in this region.

8.2 Electrochemical Cells

An *electric current* is the passage of charged particles. A current in a metal is the passage of electrons, and a current in an electrolyte solution is the passage of ions. An electrochemical cell is a device in which the passage of an electric current is accompanied by the progress of an oxidation-reduction reaction in the cell. In an *electrolytic cell* a current is passed through the cell by an external voltage, causing an otherwise nonspontaneous chemical reaction to proceed. In a *galvanic cell* the progress of a spontaneous chemical reaction causes an electric current to flow.

Galvanic cells are named for Luigi Galvani, 1737–1798, an Italian anatomist who showed that electricity caused frog muscles to contract and that dissimilar metals in contact with the muscle tissue could produce an electric current. They are also called voltaic cells after Alessandro Volta.

An *equilibrium electrochemical cell* is at the state between an electrolytic cell and a galvanic cell. The tendency of a spontaneous reaction to push a current through the eternal circuit is exactly balanced by an external voltage that is called a *counter electromotive force* or *counter e.m.f.* so that no current flows. If this counter voltage is increased the cell becomes an electrolytic cell and if it is decreased the cell becomes a galvanic cell.

Electrochemical cells always contain several phases. There are two or more *electrodes* made of materials that conduct electrons (usually metals or graphite). These electrodes can be connected to an external circuit at *terminals*. There must be at least one electrolyte solution in contact with each electrode. Under certain conditions solvated electrons can occur at low concentrations in solutions,[1] but we will consider uncombined electrons to be insoluble in electrolyte solutions and to occur only in the electrodes. The materials of the electrodes are insoluble in the solutions, and the components of the solutions are insoluble in the electrodes.

Figure 8.2 schematically depicts a particular electrochemical cell. A figure such as this is called a *cell diagram*. This cell belongs to a class called *cells without liquid junction*, which means that both electrodes are in contact with the same solution. If a cell contains two different solutions in contact with each other the interface between the solutions is called a *liquid junction*. The electrode at the left in Figure 8.2 is a *hydrogen electrode*. It has a platinum surface that has been “platinized” (plated with

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[1] L. Kevan and B. Webster, eds., *Electron-Solvent and Anion-Solvent Interactions*, Elsevier, New York, 1976.

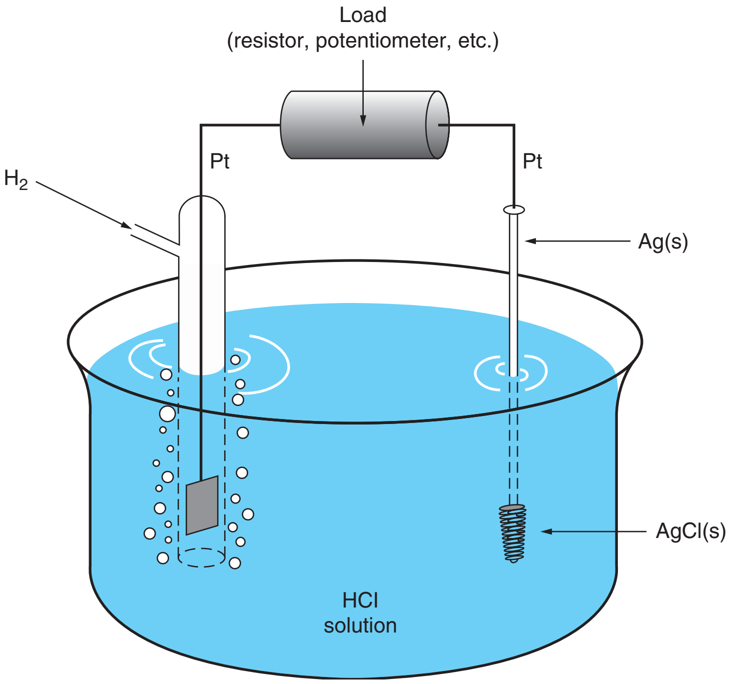

Figure 8.2 An Electrochemical Cell.

porous platinum) to increase its surface area. Hydrogen gas is bubbled through the solution around the electrode and is adsorbed on the platinum, where it can undergo the oxidation process

$$H_2(g) \longrightarrow 2H^+ + 2e^- \qquad (8.2\text{-}1)$$

This process is called a *half-reaction* because it cannot take place unless another process accepts the electrons that are produced. This half-reaction is an oxidation half-reaction. An electrode for which an oxidation half-reaction occurs is called an *anode*.

The electrode at the right in the cell of Figure 8.2 is a silver–silver chloride electrode. It is a piece of silver that is coated with solid silver chloride. The *reduction half-reaction*

$$AgCl(s) + e^- \longrightarrow Ag(s) + Cl^- \qquad (8.2\text{-}2)$$

can occur at this electrode and can accept the electrons produced by the oxidation half-reaction. The electrode for which a reduction half-reaction is written is called a *cathode*. The platinum metal of the hydrogen electrode forms a terminal. We attach a terminal of platinum to the right electrode in order to have two terminals of the same material. In the English language you can remember the names “anode” and “cathode” by noting that “anode” and “oxidation” both begin with vowels, and that “cathode” and “reduction” both begin with consonants.

We multiply the reduction half-reaction equation by 2 and add the two half-reaction equations to obtain the *cell reaction equation*:

$$H_2(g) + 2AgCl(s) + 2e^-(R) \longrightarrow 2H^+ + 2Ag(s) + 2Cl^- + 2e^-(L) \qquad (8.2\text{-}3)$$

Since the electrons are produced at the left electrode and consumed at the right electrode, we have labeled the electrons with (L) and (R). We can rewrite the cell reaction equation using only electrons and uncharged substances:

$$H_2(g) + 2AgCl(s) + 2e^-(R) \longrightarrow 2HCl + 2Ag(s) + 2e^-(L) \tag{8.2-4}$$

There are several conventions that have been adopted to make the description of electrochemical cells systematic. One convention is: *The left electrode in a cell diagram is assigned to be the anode and the right electrode is assigned to be the cathode.* The choice that we make for the right and left electrodes thus dictates the direction in which we write our cell reaction equation. Our example reaction turns out to be spontaneous in the direction it was written, but it can happen that the spontaneous direction of the reaction is opposite to the way we write it. In the English language one way to remember which half-reaction goes with which side of the cell is to note that "reduction" and "right" both begin with the letter "r."

A *cell symbol* communicates the same information as a cell diagram. In this symbol the phases of the cell are listed, beginning with the terminal of the left electrode and proceeding through the cell to the terminal of the right electrode. The symbol for each phase is separated from the next by a vertical line. The cell symbol for our present cell is

$$Pt(s)|H_2(g)|HCl(aq)|AgCl(s)|Ag(s)|Pt(s)$$

The platinum terminals are sometimes omitted from cell symbols. The pressure of a gas and the molality, concentration, or activity of a solute can be included in the cell symbol. If the molality of the HCl is 0.500 mol kg^{-1} and the pressure of the hydrogen gas is 0.990 atm the cell symbol is:

$$Pt(s)|H_2(g,0.990\ \text{atm})|HCl(aq,0.500\ \text{mol kg}^{-1})|AgCl(s)|Ag(s)|Pt(s)$$

A similar specification of composition can be used for an electrode that is a solid solution or an amalgam (solution in mercury).

We first leave our galvanic cell on "open circuit" (with the two terminals not connected to any circuit) and allow the cell to stabilize at constant temperature and pressure. The electric potential will have different values at the two terminals. One way to measure the electric potential difference between two terminals without changing their state is to connect them to a *potentiometer*, which applies an adjustable counter e.m.f. to oppose the electric potential difference of the cell. This counter voltage is adjusted until it is just sufficient to stop the flow of electrons in the external circuit, as indicated by a galvanometer. The cell and the potentiometer are now at equilibrium and the state of the cell is the same as though the cell were on open circuit. The counter voltage can be read from the potentiometer and is equal in magnitude to the potential difference between the electrodes. The value of this potential difference is called the cell's *reversible potential difference* or its *reversible voltage*. To an excellent approximation the cell reaction is now thermodynamically reversible. If the counter voltage is made slightly smaller than its equilibrium value, the cell functions as a galvanic cell and a current flows while the reaction proceeds in the spontaneous direction. If the counter voltage is made slightly larger, the cell becomes an electrolytic cell and the current flows in the opposite direction.

Our system at equilibrium at constant T and P corresponds to a minimum in the Gibbs energy of the system. If an infinitesimal amount of reaction $d\xi$ occurs at equilibrium we can write

$$0 = \left(\frac{\partial G}{\partial \xi}\right) d\xi$$

$$= 2\mu(\mathrm{HCl}) + 2\mu(\mathrm{Ag}) - \mu(\mathrm{H_2}) - 2\mu(\mathrm{AgCl}) + 2\mu(e^-(\mathrm{L})) - 2\mu(e^-(\mathrm{R}))d\xi \tag{8.2-5}$$

which is equivalent to

$$0 = \left(\frac{\partial G_{\mathrm{chem}}}{\partial \xi}\right)_{T,P} d\xi + 2\mu_{\mathrm{chem}}(e^-(\mathrm{L})) - \mu_{\mathrm{chem}}(e^-(\mathrm{R})) + F\varphi(\mathrm{R}) - F\varphi(\mathrm{L})d\xi \tag{8.2-6}$$

where G_{chem} includes the chemical potentials of substances other than electrons. The partial derivative is equal to

$$\left(\frac{\partial G_{\mathrm{chem}}}{\partial \xi}\right)_{T,P} = 2\mu(\mathrm{HCl}) + 2\mu(\mathrm{Ag}) - \mu(\mathrm{H_2}) - 2\mu(\mathrm{AgCl}) \tag{8.2-7}$$

All of these substances are electrically neutral, so only the chemical parts of these chemical potentials are included. The electric potential occurs only in the chemical potential expression of the electrons. If the reaction equation of Eq. (8.2-3) were used, the same equation would result since the electric potential terms of the H^+ and the Cl^- would cancel.

Exercise 8.2

Write the equation for $\left(\frac{\partial G_{\mathrm{chem}}}{\partial \xi}\right)_{T,P}$ based on Eq. (8.2-3) and show that it is identical to Eq. (8.2-6).

Both terminals are made of platinum and are at the same temperature and pressure, so the chemical parts of the chemical potential of the electrons are the same at the two terminals, and we can write from Eq. (8.1-5)

$$0 = \left(\frac{\partial G_{\mathrm{chem}}}{\partial \xi}\right)_{T,P} + 2FE \tag{8.2-8}$$

where E is the *cell voltage*, defined by

$$E = \varphi(\mathrm{R}) - \varphi(\mathrm{L}) \tag{8.2-9}$$

This corresponds to our second convention: *The cell voltage is defined as the electric potential of the right electrode minus that of the left electrode.*

Since electrons are negative, a positive value of E means that the chemical potential of the electron is larger in the left electrode. If a passive circuit (one that does not exert its own voltage) is connected between the terminals, electrons will move spontaneously from the left terminal to the right terminal through this circuit. The cell reaction proceeds spontaneously in the direction in which we wrote it. If E is negative, the reverse of the cell reaction proceeds spontaneously and electrons move spontaneously from right to left in the external circuit.

Equation (6.3-6) relates the chemical potential of each uncharged substance to its activity:

$$\mu_i = \mu_i^\circ + RT\ln(a_i) \quad \text{(uncharged substance)} \tag{8.2-10}$$

We can now write

$$2FE^{\circ} = -\Delta G^{\circ} - RT\ln(Q) \tag{8.2-11}$$

where

$$\Delta G^{\circ} = 2\mu^{\circ}(\mathrm{HCl}) + 2\mu^{\circ}(\mathrm{Ag}) + \mu^{\circ}(\mathrm{H_2}) + 2\mu^{\circ}(\mathrm{AgCl}) \tag{8.2-12}$$

and where Q is the *activity quotient*:

$$Q = a(\mathrm{HCl})^2 a(\mathrm{Ag})^2 a(\mathrm{H_2})^{-1} a(\mathrm{AgCl})^{-2} = \frac{a(\mathrm{HCl})^2 a(\mathrm{Ag})^2}{a(\mathrm{H_2}) a(\mathrm{AgCl})^2} \tag{8.2-13}$$

This quantity is the same as the activity quotient of Chapter 7. If the reaction takes place outside of an electrochemical cell, Q will tend toward its equilibrium value. If the reaction takes place in an electrochemical cell, Q can take on other values at equilibrium. If a passive circuit is connected, the reaction will tend toward the same equilibrium that would occur outside of the cell. If a counter voltage is applied by an external circuit, the equilibrium state will depend on the value of the counter e.m.f., and at equilibrium E will be equal to the counter e.m.f. If all substances are in their standard states, all activities are equal to unity, and Q is equal to unity. In this case we obtain the important equation

$$E^{\circ} = -\frac{\Delta G^{\circ}}{2F} \quad \text{(for the example cell)} \tag{8.2-14a}$$

where E° is the *standard-state cell voltage*. The version of Eq. (8.2-14a) that applies to a general cell is

$$E^{\circ} = -\frac{\Delta G^{\circ}}{nF} \quad \text{(for a general cell)} \tag{8.2-14b}$$

The Nernst equation is named for Walther Hermann Nernst, 1864–1941, the German physical chemist who was mentioned in Chapter 3 for his work on the third law of thermodynamics.

where n is the number of electrons in the cell reaction equation. With this relation, Eq. (8.2-11) becomes the *Nernst equation* for this cell:

$$E = E^{\circ} - \frac{RT}{2F}\ln(Q) \quad \begin{array}{l}\text{(Nernst equation for}\\ \text{the example cell)}\end{array} \tag{8.2-15}$$

Since Ag and AgCl are both pure solids, their activities are nearly equal to unity and can be omitted from the product Q. Treating hydrogen as an ideal gas and using Eq. (6.3-37) for the activity of HCl in terms of molalities,

$$E = E^{\circ} - \frac{RT}{2F}\ln\left[\left(\frac{\gamma(\mathrm{H^+})^2 m(\mathrm{H^+})^2 \gamma(\mathrm{C1^-})^2 m(\mathrm{C1^-})^2}{m^{\circ 4}}\right)\left(\frac{P(\mathrm{H_2})}{P^{\circ}}\right)^{-1}\right] \tag{8.2-16}$$

$$= E^{\circ} - \frac{RT}{2F}\ln\left(\frac{\gamma_{\pm}^4 (m/m^{\circ})^4}{P(\mathrm{H_2})/P^{\circ}}\right) \tag{8.2-17}$$

where we assume that $m(\mathrm{H^+})$ and $m(\mathrm{Cl^-})$ are both equal to m.

EXAMPLE 8.1

Find the potential difference of our cell at 298.15 K if the hydrogen pressure is equal to 744 torr and if $m = 0.500\,\mathrm{mol\,kg^{-1}}$. The value of E° is 0.2223 V, and at this molality the mean ionic activity, coefficient is equal to 0.757.

Solution

$$\begin{aligned} E &= 0.2223\,\mathrm{V} - \left(\frac{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})}{(2)(96485\,\mathrm{C\,mol^{-1}})}\right)\ln\left(\frac{(0.757)^4(0.500)^4}{(744\,\mathrm{torr})/(750\,\mathrm{torr})}\right) \\ &= 0.2223\,\mathrm{V} - (-0.0498\,\mathrm{V}) = 0.2721\,\mathrm{V} \end{aligned}$$

Our discussion of the Nernst equation applies to a particular cell. Consider now a general cell without liquid junction. The chemical reaction equation can be written:

$$0 = \sum_{i=1}^{c} v_i \mathscr{F}_i + n\mathscr{e}^-(\mathrm{R}) - n\mathscr{e}^-(\mathrm{L}) \tag{8.2-18}$$

where n is the number of electrons in the reaction equation. The Nernst equation for a general cell is

$$\boxed{E = E^\circ - \frac{RT}{nF}\ln(Q) \quad \text{(general Nernst equation)}} \tag{8.2-19}$$

where

$$Q = \prod_{i=1}^{c} a_i^{v_i} \tag{8.2-20}$$

The activity quotient Q does not include the activity of the electron.

EXAMPLE 8.2

Write the cell symbol, the cell reaction equation, and the Nernst equation for the cell with the half-reactions

$$\begin{aligned} 2\mathrm{Hg(l)} + 2\mathrm{Cl}^- &\longrightarrow \mathrm{Hg_2Cl_2(s)} + 2\mathscr{e}^- \\ \mathrm{Cl_2(g)} + 2\mathscr{e}^- &\longrightarrow 2\mathrm{Cl}^- \end{aligned}$$

Solution

The cell symbol is

$$\mathrm{Pt|Hg(l)|Hg_2Cl_2(s)|HCl|Cl_2(g)|Pt}$$

The cell reaction equation is

$$2\mathrm{Hg(l)} + \mathrm{Cl_2(g)} + 2\mathrm{Cl}^- \longrightarrow \mathrm{Hg_2Cl_2(s)} + 2\mathrm{Cl}^-$$

If we omit the chloride ion from both sides, this is the same as

$$2\mathrm{Hg(l)} + \mathrm{Cl_2(g)} \longrightarrow \mathrm{Hg_2Cl_2(s)}$$

The Nernst equation is

$$E = E^\circ - \frac{RT}{2F}\ln(Q)$$

where

$$Q = \frac{1}{P(\mathrm{Cl_2})/P^\circ} = \frac{P^\circ}{P(\mathrm{Cl_2})} = \frac{100000\,\mathrm{Pa}}{(0.965\,\mathrm{atm})(101325\,\mathrm{Pa\,atm^{-1}})} = 1.0227$$

Exercise 8.3

Find E for the cell at 298.15 K if $P(\mathrm{Cl_2}) = 0.965$ atm and $a(\mathrm{Cl^-}) = 0.250$. The value of E° is 1.091 V.

If the cell reaction equation is modified by multiplying all of the stoichiometric coefficients by the same constant, say C, the Nernst equation is unchanged, because Q will be raised to the power C, while the n divisor in front of $\ln(Q)$ will be increased by the same factor C, canceling the effect of the exponent C.

Exercise 8.4

Multiply the cell reaction equation in Eq. (8.2-4) by 1/2. Write the Nernst equation for the new reaction equation and show that it is the same as Eq. (8.2-17).

Determination of E° Values

Using the Nernst equation, E° for a cell can be calculated from a measured value of E if the activity coefficients are known. If the activity coefficients are not known we can measure E at different concentrations and carry out an extrapolation to zero concentration, since the activity coefficients approach unity in this limit. Consider the cell of Figure 8.2. We keep the pressure of the hydrogen equal to P°, and measure E at various molalities. We will use the augmented Debye–Hückel formula for $\gamma_\pm$ in Eq. (6.4-30) to guide our extrapolation. For HCl, the ionic strength is equal to the molality m if no other electrolytes are present. If Eq. (6.4-30) is substituted into Eq. (8.2-17) we obtain

$$E = E^\circ + \frac{2RT}{F}\left(\frac{\alpha m^{1/2}}{1 + (m/m^\circ)^{1/2}} + bm - \ln\left(\frac{m}{m^\circ}\right)\right)$$

which can be rewritten

$$E + \frac{2RT}{F}\left(-\frac{\alpha m^{1/2}}{1 + (m/m^\circ)^{1/2}} - \ln\left(\frac{m}{m^\circ}\right)\right) = E^\circ - \frac{2RT}{F}bm \tag{8.2-21}$$

The left-hand side of Eq. (8.2-21) contains only measurable quantities and known constants. If this function is plotted as a function of m the plot should be linear in the region near $m = 0$, and extrapolation to $m = 0$ gives the value of E°. The slope of the tangent line near the axis can be used to obtain a value of the parameter b since the slope is equal to $2RTb/F$.

An alternate extrapolation method can also be used. For small values of m the $(m/m^{\circ})^{1/2}$ term negligible compared to unity and the bm term is negligible compared to the $\alpha m^{1/2}$ term. If these terms are omitted, Eq. (8.2-21) becomes

$$E + \frac{2RT}{F}\ln\left(\frac{m}{m^{\circ}}\right) = E^{\circ} + \frac{2RT}{F}\alpha m^{1/2} \tag{8.2-22}$$

If the left-hand side of this equation is plotted as a function of $m^{1/2}$ the extrapolation to $m = 0$ should be nearly linear for small values of $m^{1/2}$, giving the value of E° from the intercept.

PROBLEMS

Section 8.2: Electrochemical Cells

8.4 **a.** Find the reversible cell voltage for the cell of Figure 8.2 at 298.15 K if the partial pressure of hydrogen is equal to 712 torr and the molality of the HCl solution is $0.100\ \mathrm{mol\ kg^{-1}}$. Assume the hydrogen gas to be ideal and use the Davies equation to estimate the activity coefficient of the HCl.

b. Repeat the calculation of part a using the value of the activity coefficient from Table A.11 of Appendix A.

8.5 Find the reversible voltage of the cell of Figure 8.2 at 298.15 K if the HCl solution has a molality of $1.00\ \mathrm{mol\ kg^{-1}}$ and the pressure of the hydrogen gas is 755 torr. Use the value of the activity coefficient from Table A.11 of Appendix A.

8.6 The cell

$$\mathrm{Cd|CdCl_2(6.62\ m)|Cl_2(1.000\ atm)|Pt}$$

has a cell voltage equal to 1.8111 V at 25°C. The $6.62\ \mathrm{mol\ kg^{-1}}$ solution of $CdCl_2$ is saturated and is at equilibrium with $CdCl_2 \cdot \frac{5}{2}H_2O$ and water vapor at 16.5 torr. The activity coefficient of $CdCl_2$ at this molality is equal to 0.025. The vapor pressure of pure water at this temperature is 23.8 torr. Find E° for the cell and ΔG° for the reaction

$$\mathrm{Cd(s) + Cl_2(g) + \frac{5}{2}H_2O(l) \longrightarrow CdCl_2 \cdot \frac{5}{2}H_2O(s)}$$

8.3 Half-Cell Potentials and Cell Potentials

Figure 8.3 depicts a cell that has a hydrogen electrode on the left side and a *calomel electrode* on the right side. The calomel electrode contains liquid mercury in contact with solid calomel (Hg_2Cl_2). A platinum wire extends from the pool of mercury and acts as a terminal. The solution in this cell is an aqueous solution of HCl, just as in the cell of Figure 8.2. The reduction half-reaction at the calomel electrode is

$$\mathrm{Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2Cl^-} \tag{8.3-1}$$

The oxidation half-reaction of the hydrogen electrode is the same as in Eq. (8.2-1). The cell reaction equation is

$$\mathrm{H_2(g) + Hg_2Cl_2(s) \longrightarrow 2Hg(l) + 2H^+ + 2Cl^-}$$

The standard-state cell voltage is equal to 0.268 V for this cell.

Exercise 8.5

a. Write the Nernst equation for the cell of Figure 8.3.

b. Write an equation analogous to Eq. (8.2-21) that could be used to determine the value of E° for the cell of Figure 8.3.

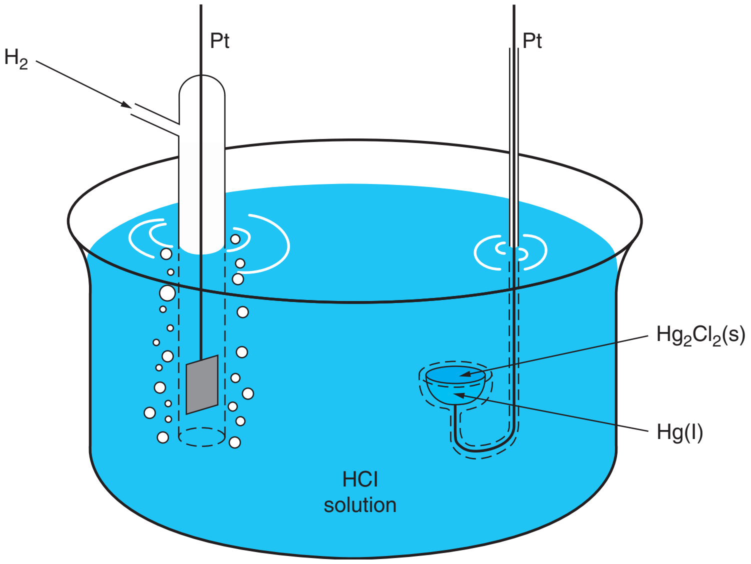

Figure 8.3 An Electrochemical Cell with a Hydrogen Electrode and a Calomel Electrode.

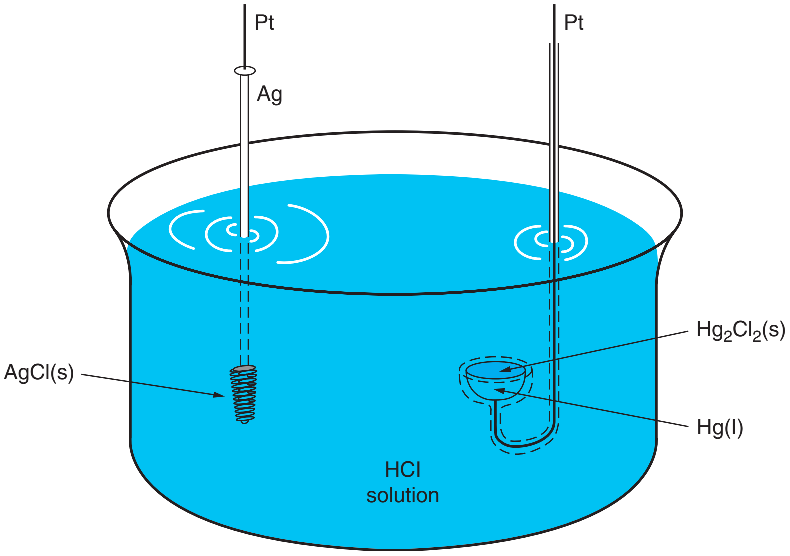

Figure 8.4 An Electrochemical Cell with a Silver–Silver Chloride Anode and a Calomel Cathode.

Now consider the cell shown in Figure 8.4. This cell contains a silver–silver chloride electrode on the left, a calomel electrode on the right, and an aqueous solution of HCl. We construct a double cell as depicted in Figure 8.5. This double cell consists of two complete cells, one of which is the cell of Figure 8.3. The other cell is obtained by interchanging the right and left half-cells of Figure 8.2. It has the cell reaction equation

$$2\mathrm{HCl} + 2\mathrm{Ag(s)} + 2e^{-}(\mathrm{R}) \longrightarrow \mathrm{H_2(g)} + 2\mathrm{AgCl(s)} + 2e^{-}(\mathrm{L}) \qquad (8.3\text{-}2)$$

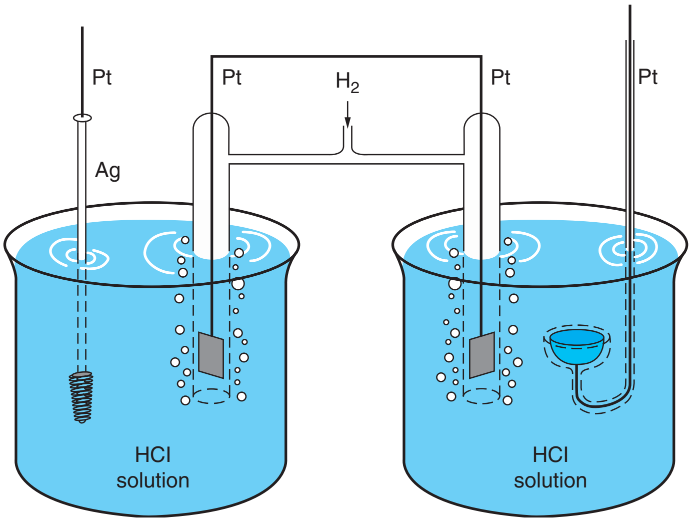

Figure 8.5 A Double Cell Equivalent to the Cell of Figure 8.4.

The standard-state cell potential difference of this cell is −0.2223 V, the negative of that of the cell of Figure 8.2. Hydrogen gas at the same pressure is fed into both hydrogen electrodes and the two HCl solutions are at the same concentration. A wire is connected between the two hydrogen electrodes and maintains them at the same electric potential. We can write

$$\begin{aligned} E(\text{double cell}) &= \varphi(\text{R,right cell}) - \varphi(\text{L, left cell}) \\ &= \varphi(\text{R,right cell}) - \varphi(\text{L, right cell}) + \varphi(\text{R,left cell}) - \varphi(\text{L,left cell}) \end{aligned} \tag{8.3-3}$$

The second equality follows from the fact that the two hydrogen electrodes have the same value of φ.

$$\begin{aligned} E^\circ(\text{double cell}) &= E^\circ(\text{right cell}) + E^\circ(\text{left cell}) \\ &= 0.268\ \text{V} + (-0.2223\ \text{V}) = 0.046\ \text{V} \end{aligned} \tag{8.3-4}$$

The voltage of the single cell in Figure 8.4 is also 0.046 V, because the state of the left electrode of the left cell in Figure 8.5 is the same as the state of the left electrode of the cell in Figure 8.4 and the state of the right electrode of the right cell in Figure 8.5 is the same as the state of the right electrode of the cell in Figure 8.4.

We now adopt the following definition for the standard reduction potential: *The standard-state potential difference of a cell consisting of a hydrogen electrode on the left and any other electrode on the right is called the standard reduction potential of the right electrode or of the right half-cell. It is also sometimes called the standard half-cell potential or standard electrode potential*. This convention assigns the value zero to the standard reduction potential of the hydrogen electrode.

The standard-state potential difference of the cell of Figure 8.4 can now be written

$$E^\circ = E^\circ(\text{right half-cell}) - E^\circ(\text{left half-cell}) \tag{8.3-5}$$

There is now a subtraction instead of an addition because the standard reduction potential of the left cell corresponds to reversing the left cell from its configuration in the double cell. The procedure that led to Eq. (8.3-5) for the cell of Figure 8.4 can be applied to any pair of electrodes that can be combined to make a cell without liquid junction: *To obtain the standard-state potential difference of any cell, take the standard reduction potential of the right half-cell and subtract the standard reduction potential of the left half-cell from it.* This procedure allows us to use a table of standard electrode potentials for half-cells, which is a much shorter table than a table containing entries for all possible cells.

Exercise 8.6

a. Show that from a table of N half-cell potentials, the potential differences for $N(N-1)/2$ cells can be calculated if each half-cell can be combined with every other half-cell to make a cell.

b. Find the number of cells that can be made from 100 electrodes, assuming that each can be paired with any one of the others.

Table A.13 in the appendix gives values for standard reduction potentials for a number of half-cells. Longer versions of such tables are available in handbooks. Unfortunately, some older works use values that are the negative of the standard reduction potentials (they are called *oxidation potentials*). If you are not certain whether an old table gives reduction potentials or oxidation potentials, look for an active metal electrode such as sodium or potassium. If the table contains reduction potentials, the half-cell potential of such a metal electrode will be negative.

There have been a number of theoretical approaches to the determination of *"absolute" electrode potentials* (relative to the electric potential at a location infinitely distant from all charges). All of them require the use of nonthermodynamic theories. One work cites a value of −4.43 V (absolute) for the standard hydrogen electrode.[2] Other workers have come up with values ranging from this value to −4.73 V. We will use only half-cell potentials relative to the standard hydrogen electrode.

EXAMPLE 8.3

Write the cell reaction equation and find the standard-state potential difference of the cell

$$\mathrm{Pt(s)|Cl_2(g)|FeCl_2(aq)|Fe(s)|Pt(s)}$$

Solution

The half-cell reaction equations are

$$\begin{aligned} \text{anode:} &\quad 2\mathrm{Cl}^- \longrightarrow \mathrm{Cl_2(g)} + 2e^- \\ \text{cathode:} &\quad \mathrm{Fe}^{2+} + 2e^- \longrightarrow \mathrm{Fe(s)} \end{aligned}$$

The standard-state potential difference of the cell is

$$E^\circ = -0.409\,\mathrm{V} - (+1.3583\,\mathrm{V}) = -1.767\,\mathrm{V}$$

Since E° is negative the cell reaction would spontaneously proceed in the reverse direction under standard conditions.

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[2] H. Reiss and A. Heller, *J. Phys. Chem.*, **89**, 4207 (1985).

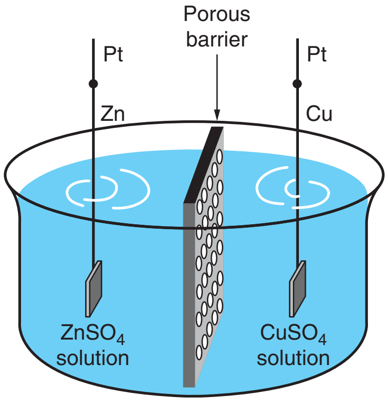

Figure 8.6 The Daniell Cell.

Cells with Liquid Junctions

Some pairs of half-cells cannot be combined to make a cell with a single liquid solution because a single solution in contact with both electrodes would allow undesired chemical reactions at the electrode surfaces or in the solution. Consider the cell with the half-reactions

$$\mathrm{Zn(s)} \longrightarrow \mathrm{Zn^{2+}} + 2e^-$$
$$\mathrm{Cu^{2+}} + 2e^- \longrightarrow \mathrm{Cu(s)}$$

If the Cu^{2+} ions were in the solution that contacts the zinc electrode the oxidation and reduction half-reactions would both take place at the zinc electrode without transferring electrons through an external circuit. Two separate solutions are needed. A cell with two compartments can be constructed, as shown in Figure 8.6. This cell is known as the *Daniell cell*, and these cells were once used commercially. The left compartment contains a zinc electrode and a solution of zinc sulfate, and the right compartment contains a copper electrode and a solution of copper(II) sulfate. The two solutions are separated by a porous barrier that keeps the *liquid junction* between the solutions confined to one location. Ions can diffuse through the liquid filling its pores, but the two solutions cannot mix by flowing together.

A cell with a liquid junction is called a *cell with transference*. In a cell symbol, a liquid junction is sometimes represented by a vertical broken line, but it can be represented by an unbroken vertical line like that representing any other phase boundary. The presence of the liquid junction makes it impossible to bring the cell to equilibrium with a counter voltage. Ions can diffuse through the liquid junction even if the cell is on open circuit or has a counter voltage to stop the flow of current. These irreversible diffusion processes can produce excess positive ions on one side of the liquid junction and excess negative ions on the other side. This makes a contribution to the potential difference of the cell, called the *liquid junction potential*, denoted by E_{LJ}.

EXAMPLE 8.4

a. Write the cell reaction equation and the cell symbol for the Daniell cell.

b. Write the Nernst equation for the Daniell cell.

c. Find the standard-state potential difference of the Daniell cell, neglecting the liquid junction potential. In which direction will the cell reaction proceed spontaneously under standard conditions?

Solution

a. If we omit the electrons the cell reaction equation is

$$\mathrm{Zn(s)} + \mathrm{Cu^{2+}} \longrightarrow \mathrm{Zn^{2+}} + \mathrm{Cu(s)}$$

and the cell symbol is $\mathrm{Zn(s)|Zn^{2+}|Cu^{2+}|Cu(s)}$, where we represent the liquid junction by a vertical line segment, as with any other phase boundary. We have omitted the symbols for the platinum terminals.

b. If the pressure is not greatly different from P°, the activities of the solid electrodes can be approximated by unity, and the Nernst equation is

$$E = E^\circ + E_{\mathrm{LJ}} - \frac{RT}{2F}\ln\left(\frac{a(\mathrm{Zn^{2+}})}{a(\mathrm{Cu^{2+}})}\right)$$

where E_{LJ} represents the liquid junction potential.

c. Neglecting E_{LJ},

$$E^{\circ} = 0.3402\,\mathrm{V} - (-0.7628\,\mathrm{V}) = 1.1030\,\mathrm{V}$$

Since $E > 0$, the reaction would proceed spontaneously as written in the standard-state cell if the terminals were connected to a passive circuit. Electrons would flow spontaneously from left to right in the external circuit.

Exercise 8.7

Find the potential difference of a Daniell cell if the activity of zinc ions is equal to 0.500 and the activity of copper ions is equal to 0.350. Neglect the liquid junction potential.

Since a liquid junction is not an equilibrium or metastable system, it cannot be treated thermodynamically. Nonthermodynamic analyses have been carried out, but we do not discuss these theories.[3] A common device for minimizing the liquid junction potential is a *salt bridge*, shown schematically in Figure 8.7. The salt bridge contains a concentrated electrolyte such as KCl that forms two liquid junctions, one with each cell solution. Since the KCl is more concentrated than the cell solutions, the K^+ and Cl^- ions dominate the liquid junction potential. The K^+ ions and the Cl^- are nearly the same size and have nearly equal tendencies to diffuse into the cell solutions. Their contributions to the liquid junction potential are of opposite signs and nearly cancel, so a fairly small liquid junction potential results. Furthermore, the liquid junction potentials at the two ends of the salt bridge oppose each other. The net liquid junction potential with a salt bridge is generally no larger in magnitude than a few millivolts and can be negligible in some cells. Liquid junction potentials without a salt bridge can range up to 40 millivolts. In a cell symbol a salt bridge is represented by a double vertical line.

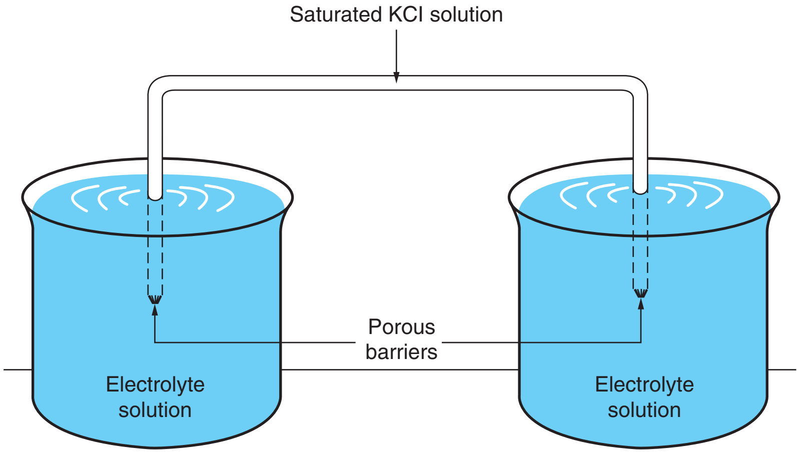

Figure 8.7 A Salt Bridge.

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[3] J. G. Kirkwood and I. Oppenheim, *Chemical Thermodynamics*, McGraw-Hill, New York, 1961, p. 211ff.

The cell symbol for the Daniell cell with a salt bridge would be

$$\mathrm{Zn(s)|Zn^{2+}||Cu^{2+}|Cu(s)}$$

where we have omitted the symbols for the platinum terminals.

Concentration Cells

Figure 8.8 schematically depicts a concentration cell, which contains two solutions of the same electrolyte with different concentrations. The cell symbol of this cell can be written

$$\mathrm{Pt(s)|H_2(g,}\ P_1\mathrm{)|HCl(}m_1\mathrm{)||HCl(}m_2\mathrm{)|H_2(g,}\ P_2\mathrm{)|Pt(s)}$$

where P_1 and P_2 represent two pressures of the hydrogen gas and m_1 and m_2 represent the different molalities of the HCl solutions. A salt bridge is used to minimize the liquid junction potential. If the hydrogen is at the same pressure in both sides of the cell, the cell reaction for this concentration cell is

$$\mathrm{HCl}(m_2) \longrightarrow \mathrm{HCl}(m_1) \tag{8.3-6}$$

The standard states for the half-cells are the same, so $E°$ vanishes, as it does for any concentration cell. If we neglect the liquid junction potential, the Nernst equation for our concentration cell is

$$E = -\frac{RT}{F}\ln\left(\frac{a_1(\mathrm{HCl})}{a_2(\mathrm{HCl})}\right) = -\frac{RT}{F}\ln\left(\frac{[\gamma_{\pm,1}m_1/m°]^2}{[\gamma_{\pm,2}m_2/m°]^2}\right) = -\frac{2RT}{F}\ln\left(\frac{\gamma_{\pm,1}m_1/m°}{\gamma_{\pm,2}m_2/m°}\right) \tag{8.3-7}$$

where the subscripts on $\gamma_{\pm}$ and on m indicate the half-cell to which that value applies. If the activity coefficient of HCl at one molality is known, this equation can be used to determine the activity coefficient at the other molality if the liquid junction potential can be evaluated or eliminated.

In order to eliminate the liquid junction potential, the concentration cell of Figure 8.8 can be replaced by the double cell of Figure 8.9, which contains two reversible cells

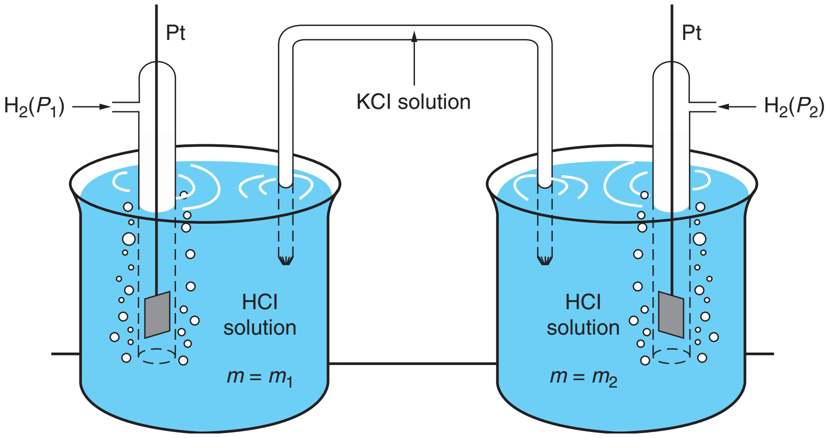

Figure 8.8 A Concentration Cell.

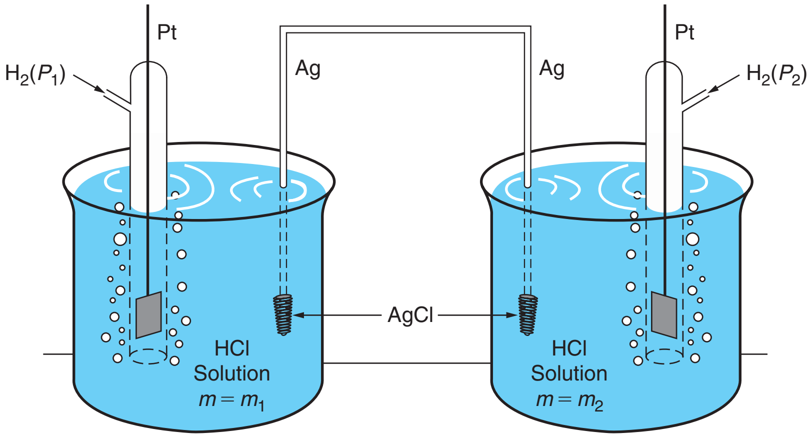

Figure 8.9 A Double Cell Equivalent to a Concentration Cell.

with hydrogen electrodes. Assuming that the pressure of hydrogen is equal to $P°$ in both cells, the Nernst equation for the left-hand cell is

$$E(\text{left cell}) = 0.2223\text{V} - \frac{2RT}{F}\ln(\gamma_{\pm,1}m_1/m°)$$

and that of the right-hand cell is

$$E(\text{right cell}) = -0.2223\text{ V} + \frac{2RT}{F}\ln(\gamma_{\pm,2}m_2/m°)$$

so that the potential difference of the double cell is equal to that of Eq. (8.3-7) without the liquid junction potential. Another possibility is to build just one cell, like half of the double cell, and then to measure its potential difference once when filled with a solution of molality m_1, and once when filled with a solution of molality m_2.

Exercise 8.8

Find the potential difference of the concentration cell of Figure 8.8 if in solution 1 the molality is 0.500 mol kg^{-1} with $\gamma_{\pm,1}$ equal to 0.757, and in solution 2 the molality is 0.200 mol kg^{-1} with $\gamma_{\pm,2}$ equal to 0.767.

The Temperature Dependence of the Cell Voltage

We have already studied the temperature dependence of $\Delta G°$. From Eqs. (7.6-9) and (8.2-14), if $\Delta H°$ can be assumed to be temperature-independent,

$$\boxed{\frac{E°(T_2)}{T_2} - \frac{E°(T_1)}{T_1} = -\frac{\Delta H°}{nF}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]} \tag{8.3-8}$$

EXAMPLE 8.5

Assuming that $\Delta H°$ is constant, find $E°$ at 323.15 K for the Daniell cell. Neglect the liquid junction potential.

Solution

$E° = 1.1030\,\mathrm{V}$ at 298.15 K. We find from enthalpy changes of formation in Table A.8 of Appendix A that $\Delta H° = -218.66\,\mathrm{kJ\,mol^{-1}}$. From Eq. (8.3-8)

$$\begin{aligned}\frac{E°(323.15\,\mathrm{K})}{323.15\,\mathrm{K}} &= \frac{1.1030\,\mathrm{V}}{298.15\,\mathrm{K}} - \frac{-218660\,\mathrm{J\,mol^{-1}}}{(2)(96485\,\mathrm{C\,mol^{-1}})}\left[\frac{1}{323.15\,\mathrm{K}} - \frac{1}{298.15\,\mathrm{K}}\right]\\ &= 3.699\times10^{-3}\,\mathrm{V\,K^{-1}} - 2.94\times10^{-4}\,\mathrm{V\,K^{-1}}\\ &= 3.405\times10^{-3}\,\mathrm{V\,K^{-1}}\\ E°(323.15\,\mathrm{K}) &= (3.405\times10^{-3}\,\mathrm{V\,K^{-1}})(323.15\,\mathrm{K}) = 1.100\,\mathrm{V}\end{aligned}$$

Exercise 8.9

Find $E°$ at 75°C for the cell with a hydrogen electrode on the left, a silver–silver chloride electrode on the right, and a solution of HCl. Assume that $\Delta H°$ is temperature-independent.

PROBLEMS

Section 8.3: Half-Cell Potentials and Cell Potentials

8.7 Find the cell voltage of an electrochemical cell with a Pb/$PbSO_4$ electrode on the left, a PbO_2/$PbSO_4$ electrode on the right, and a solution of H_2SO_4 with a molality of $1.00\,\mathrm{mol\,kg^{-1}}$ at 298.15 K. Assume that the mean ionic activity coefficient of H_2SO_4 at this molality is equal to 0.36.

8.8 **a.** Using the extrapolation of Eq. (8.2-21), find $E°$ for the cell of Figure 8.2. The following are (contrived) data for the cell voltage at 298.15 K with $P(H_2) = P°$:

$m/\mathrm{mol\,kg^{-1}}$:	0.0100	0.0200	0.0300	0.0400	0.0500
E/volt:	0.4643	0.4305	0.4108	0.3970	0.3863
$m/\mathrm{mol\,kg^{-1}}$:	0.0600	0.0700	0.0800	0.0900	0.1000
E/volt:	0.3776	0.3703	0.3639	0.3583	0.3533

b. Using the extrapolation of Eq. (8.2-22), find $E°$ for the cell of Figure 8.2.

8.9 **a.** Write the cell symbol for the cell with the half-reactions

$$\mathrm{Pb^{2+}} + 2e^- \longrightarrow \mathrm{Pb(s)}$$
$$\mathrm{AgCl(s)} + \mathrm{Cl^-} \longrightarrow \mathrm{Ag(s)} + e^-$$

Why is a salt bridge needed? What substance would you not use in the salt bridge?

b. Draw a sketch of the cell of part a.

c. Find the value of E for the cell if the activity of $\mathrm{Pb^{2+}}$ is 0.100 and that of the $\mathrm{Cl^-}$ is 0.200 on the molality scale. State any assumptions.

8.10 Instead of the oxidation half-reaction used in Example 8.1, use the reverse of the half-reaction

$$2\mathrm{H_2O} + 2e^- \longrightarrow \mathrm{H_2} + 2\mathrm{OH^-} \quad E° = -0.8277\,\mathrm{V}$$

to calculate the reversible cell potential. Since the $\mathrm{OH^-}$ ion is not in its standard state, the Nernst equation must be applied.

8.11 In calculating the $E°$ value for a cell from half-reaction $E°$ values, the half-reaction $E°$ values are added or subtracted directly, without multiplying by the number of electrons in the half-reaction equations. This is the proper procedure in the case that the electrons cancel out of the final equation. However, this is not the case in adding equations as in the following case.

Calculate the value of $E°$ for the half-reaction

$$\mathrm{Fe}^{3+} + 3e^- \longrightarrow \mathrm{Fe(s)}$$

from the $E°$ values of the half-reactions

$$\mathrm{Fe}^{2+} + 2e^- \longrightarrow \mathrm{Fe(s)}$$

$$\mathrm{Fe}^{3+} + e^- \longrightarrow \mathrm{Fe}^{2+}$$

Explain why the $E°$ values must be multiplied by the number of electrons in the half-reaction equation before adding. (*Hint*: Think about adding the $\Delta G°$ values.) Comment on the consistency of the data in Table A.13. The measurement of these $E°$ values has apparently been very difficult.

8.12 **a.** Write the cell symbol for an electrochemical cell with a chlorine electrode at the left and a silver–silver chloride electrode at the right and a solution of HCl. The chlorine electrode is similar to a hydrogen electrode, with a platinum electrode surface and a means of bringing Cl_2 gas to the electrode.

b. Find the value of $E°$ for this cell.

c. Find the value of E for this cell if the pressure of the chlorine gas is 755.0 torr and the activity of the Cl^- is 0.100 on the molality scale. In which direction do electrons flow spontaneously if the cell acts as a galvanic cell?

8.13 A cell has a silver electrode at the left, in contact with a solution containing Ag^+ ions, and a silver–silver chloride electrode at the right, in contact with a solution containing Cl^- ions.

a. Write the cell symbol for the cell. Is a salt bridge needed? If a salt bridge is needed, can the usual electrolyte be used? Explain. Propose another electrolyte if one is needed.

b. Write the two half-reaction equations and the cell equation.

c. Find $E°$ for the cell at 298.15 K.

d. Find the cell voltage at 298.15 K if the Ag^+ activity is 0.250 and the Cl^- activity is 0.199. Is the cell reaction spontaneous as written?

8.14 The lead storage battery used in automobiles has an anode made of lead, a cathode containing lead oxide, PbO_2, and an electrolyte solution of sulfuric acid. Solid lead sulfate, $PbSO_4$, is formed.

a. Write the cell reaction of the lead storage battery.

b. Find $E°$ for a six-cell lead storage battery at 25°C.

c. Find E for a six-cell lead storage battery at 25°C if each cell contains aqueous sulfuric acid with 24.4% sulfuric acid by weight and density $1.2023\ \mathrm{g\,cm^{-3}}$. The mean ionic activity coefficient of sulfuric acid under these conditions is equal to 0.150.

d. The voltage regulator in most automobiles is set to charge the battery, which has six cells, at about 13.5 V. Calculate the activity of sulfuric acid necessary to make the reversible voltage equal to 13.5 V. Do you think that the battery could have this reversible voltage?

8.15 Find the reversible cell voltage at 298.15 K of a concentration cell in which both half-cells have calomel electrodes and HCl solutions. In one solution the molality is equal to $2.50\ \mathrm{mol\,kg^{-1}}$ and in the other solution the molality is equal to $0.100\ \mathrm{mol\,kg^{-1}}$. Carry out the calculation once assuming that activity coefficients are equal to unity, and once using activity coefficient values from Figure 6.10.

8.16 Consider the cell with a hydrogen electrode on the left, a silver–silver chloride electrode on the right, and a solution of HCl.

a. Write the cell symbol, the electrode half-reaction equations, the cell reaction equations, and find the value of $E°$ at 298.15 K. Is a salt bridge not needed? Why or why not?

b. When the molality of a solution of HCl is $0.500\ \mathrm{mol\,kg^{-1}}$, the mean ionic activity coefficient, $\gamma_\pm$, is equal to 0.757 at 298.15 K. Find the cell voltage at 298.15 K for a cell with a $0.500\ \mathrm{mol\,kg^{-1}}$ solution of HCl and a partial pressure of H_2 equal to 738 torr.

c. Find the pressure of H_2 gas that would be at equilibrium with the solution of part b at 298.15 K.

8.17 The cell reaction of the lead storage battery is

$$\mathrm{Pb(s)} + \mathrm{PbO_2(s)} + 2\mathrm{H_2SO_4(aq)} \longrightarrow 2\mathrm{PbSO_4(s)} + 2\mathrm{H_2O(l)}$$

a. Find the value of $E°$ at 25°C.

b. Find the value of $\Delta H°$ at 25°C.

c. Find the value of $E°$ at −18°C (approximately 0°F).

8.4 The Determination of Activities and Activity Coefficients of Electrolytes

These activity coefficients can be determined in several ways.

Determination by Vapor Pressure

In the case of a volatile electrolyte such as HCl or HNO_3, the mean ionic activity coefficient can be determined from the partial vapor pressure, using Eq. (7.4-12).

EXAMPLE 8.6

Using information in Example 7.15, find the value of $\gamma_\pm$ for HCl at $10.00\,\mathrm{mol\,kg^{-1}}$ and 298.15 K, in which case the partial vapor pressure of HCl is equal to 4.20 torr.[a]

Solution

$$\gamma_\pm^2 = \frac{P(\mathrm{HCl})}{k_\pm^{(m)} m^2} = \frac{(4.20\,\mathrm{torr})\left(\dfrac{1\,\mathrm{atm}}{760\,\mathrm{torr}}\right)}{(4.92\times 10^{-7}\,\mathrm{atm\,kg^2\,mol^{-2}})(10.00\,\mathrm{mol\,kg^{-1}})^2} = 112$$

$$\gamma_\pm = 10.6$$

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[a] S. J. Bates and H. D. Kirschman, *J. Am. Chem. Soc.*, **41**, 1991 (1919).

Activity Coefficients of Nonvolatile Electrolytes

The activities and activity coefficients of nonvolatile electrolytes can be determined by the isopiestic method, as described in Chapter 6. They can also be determined by electrochemical measurements. As an example consider the cell of Figure 8.2, for which the Nernst equation is

$$E = E^\circ - \frac{RT}{2F}\ln\left(\frac{a(\mathrm{HCl})^2}{P(\mathrm{H_2})/P^\circ}\right) \tag{8.4-1}$$

If the value of E° is known, the activity coefficient of HCl can then be determined from the Nernst equation. Let us maintain $P(H_2)$ equal to P° and measure the voltage at a molality of HCl equal to m. The Nernst equation can be written in the form

$$\ln a(\mathrm{HCl}) = 2\ln\left(\gamma_\pm m/m^\circ\right) = \frac{F(E^\circ - E)}{RT} \tag{8.4-2}$$

EXAMPLE 8.7

In a cell such as that of Figure 8.2, a voltage of 0.3524 V was measured with a solution having a molality of HCl equal to $0.1000\,\mathrm{mol\,kg^{-1}}$ and a hydrogen pressure equal to 1.000 bar. Find the value of the activity and of the mean ionic activity coefficient of HCl, assuming hydrogen to be an ideal gas.

Solution

From Eq. (8.4-2)

$$\ln(\gamma_{\pm} m/m^{\circ}) = \frac{(96{,}485\,\mathrm{C\,mol^{-1}})(0.2223\,\mathrm{V} - 0.3524\,\mathrm{V})}{2(9.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})} = -2.532$$

$$\gamma_{\pm} = \frac{e^{-2.532}}{0.1000} = 0.795$$

For comparison, the Davies equation gives $\gamma_{\pm} = 0.781$.

Determination of the Activity of Hydrogen Ions. pH

Since the activity of a single ion cannot be measured, we cannot correctly use the definition of the pH in terms of the activity of the hydrogen ion that is given in Eq. (7.3-10). We modify the definition by replacing the true activity of hydrogen ions by the closest approximation that we can obtain, denoted by $a'(\mathrm{H}^+)$:

$$\mathrm{pH} = -\log_{10}\left[a'(\mathrm{H}^+)\right] \tag{8.4-3}$$

For a solution of HCl, we can write

$$a(\mathrm{H}^+)a(\mathrm{Cl}^-) = a(\mathrm{HCl}) \tag{8.4-4}$$

If no other ions are present, the molalities of H^+ and Cl^- are equal. If we can assume that $\gamma(\mathrm{H}^+)$ is equal to $\gamma(\mathrm{Cl}^-)$ we have a value of $\gamma(\mathrm{H}^+)m(\mathrm{H}^+)/m^{\circ}$, and thus of the pH for this solution.

Exercise 8.10

Find the pH of the solution in the cell of Example 8.7, assuming that $\gamma(\mathrm{H}^+) = \gamma(\mathrm{Cl}^-)$.

In order to measure the pH of a solution other than an HCl solution the silver–silver chloride electrode in the cell of Figure 8.2 is replaced by a calomel electrode confined in a container that is fitted with a porous plug, as depicted in Figure 8.10. The solution in the container of the calomel electrode is a KCl solution that is saturated with calomel ($\mathrm{Hg_2Cl_2}$). If the concentration of the KCl is $1.0000\,\mathrm{mol\,L^{-1}}$, the electrode is called the *normal calomel electrode*. If the solution is saturated with KCl as well as with calomel, the electrode is called the *saturated calomel electrode*. The half-cell potential of the normal calomel electrode is equal to 0.2802 V and that of the saturated calomel electrode is equal to 0.2415 V. We place a hydrogen electrode and a saturated calomel electrode, including its container, into the solution whose pH we wish to measure, as shown in the figure. A liquid junction is formed inside the porous plug. The solution does not have to be a solution of HCl, since the chloride ions needed to react at the calomel electrode are inside the container of the calomel electrode.

The Nernst equation for the cell of Figure 8.10 is

$$E = 0.2415\,\mathrm{V} + E_{\mathrm{LJ}} - \frac{RT}{F}\ln\left(\frac{a(\mathrm{H}^+)a(\mathrm{Cl}^-)}{(P(\mathrm{H}_2)/P^{\circ})^{1/2}}\right) \tag{8.4-5}$$

where $a(\mathrm{H}^+)$ is measured in one solution and $a(\mathrm{Cl}^-)$ is measured in the solution that is inside the container of the calomel electrode. Since the KCl solution on the calomel

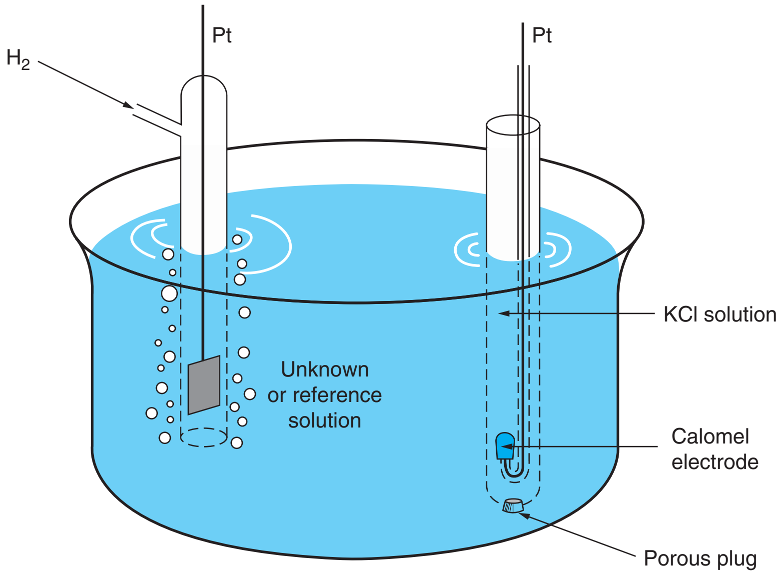

Figure 8.10 A Cell for the Measurement of pH.

electrode side of the liquid junction is much more concentrated than the solution on the other side, the magnitude of the liquid junction potential should not change appreciably when a different solution is placed in the cell.

We do not try to use Eq. (8.4-5) directly since the liquid junction potential is presumably not known. Instead, we first put into the cell a reference solution (solution I) that has a known value of its pH. We measure the voltage of the cell at a known hydrogen pressure, and then remove this solution and put a solution whose pH we wish to determine (solution II) into the cell, and measure the voltage with the same hydrogen pressure as before. We assume that the liquid junction potential has the same value in both cases and that the activity of the chloride ion is the same in both cases, so that

$$E^{(\mathrm{II})} - E^{(\mathrm{I})} = -\frac{RT}{F}\ln\left[a(\mathrm{H}^{+,\mathrm{II}})\right] + \frac{RT}{F}\ln\left[a(\mathrm{H}^{+,\mathrm{I}})\right] \qquad (8.4\text{-}6)$$

where $E^{(\mathrm{I})}$ and $E^{(\mathrm{II})}$ are the two voltages measured. Equation (8.4-6) is the same as

$$\boxed{\mathrm{pH}^{(\mathrm{II})} - \mathrm{pH}^{(\mathrm{I})} = \frac{E}{RT\ln(10)}\left[E^{(\mathrm{II})} - E^{(\mathrm{I})}\right]} \qquad (8.4\text{-}7)$$

We can regard Eq. (8.4-7) as an operational definition of pH. The pH values obtained are probably accurate to two digits after the decimal point.

Exercise 8.11

Show that Eq. (8.4-7) is correct.

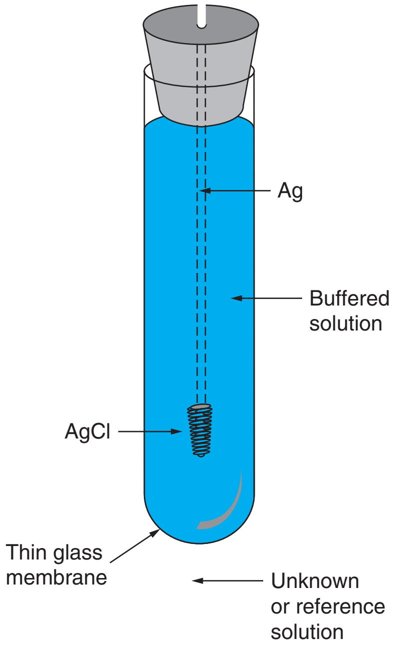

Figure 8.11 A Glass Electrode (Schematic).

Use of the hydrogen electrode can pose a fire hazard. The *glass electrode* has come into common use to replace the hydrogen electrode in pH meters. This electrode is schematically depicted in Figure 8.11. It consists of a silver–silver chloride electrode inside a thin-walled glass bulb filled with a buffered solution of nearly constant pH. To measure the pH of an unknown solution, a glass electrode and a calomel electrode are placed in the solution. The special glass of which the bulb is made allows hydrogen ions to establish chemical equilibrium across the membrane. Since the chemical part of the chemical potential of the hydrogen ions is not the same on the two sides of the membrane, an electrical potential difference is established across the glass membrane when the system equilibrates.

Although the voltage of the cell depends on the exact nature of the glass membrane and on the hydrogen ion activity inside the bulb, the dependence of the voltage on the pH of the unknown solution is the same as in the cell of Figure 8.10, so that Eq. (8.4-7) can be used if a reference solution of known pH is available. A typical pH meter consists of a glass electrode, a reference electrode (usually a calomel electrode), a voltage-measuring device, an analogue or digital display, and a circuit that gives the pH directly without requiring the operator to substitute numbers into Eq. (8.4-7). Since the temperature occurs in Eq. (8.4-7), some pH meters have a control knob with which one can set the temperature, and others automatically adjust for different temperatures.

The first commonly available pH meter was made possible in the 1930s when Arnold Beckman, then a chemistry professor at the California Institute of Technology, invented an amplifier that allowed the cell voltage to be read easily. Professor Beckman left Caltech in 1940 and founded a company that sold the pH meters and the famous Beckman DU spectrophotometer, which used the same amplifier. Beckman became a wealthy man and a great benefactor of Caltech. He died in 2004 at age 104.

Exercise 8.12

Calculate the difference between the cell voltages that occur for a pH reading of 7.00 and one of 12.50 at 298.15 K.

PROBLEMS

Section 8.4: The Determination of Activities and Activity Coefficients of Electrolytes

8.18 In a cell as pictured in Figure 8.2, a solution of HCl with molality 1.000 mol kg^{-1} and a hydrogen pressure of 0.986 atm produces a cell voltage of 0.2332 V at 298.15 K. Find the mean molar activity coefficient of HCl in the solution. Assume the hydrogen gas to be ideal.

8.19 From the data in Problem 8.8, find the value of the mean molar activity coefficient of HCl at 0.0500 mol kg^{-1} and 298.15 K.

8.20 Following are data on the activity of water in a calcium chloride solution at 25°C[4]:

$m(CaCl_2)$/ mol kg^{-1}	$a(H_2O)$	$m(CaCl_2)$/ mol kg^{-1}	$a(H_2O)$
0.1	0.99540	0.6	0.96998
0.2	0.99073	0.7	0.96423
0.3	0.98590	0.8	0.95818
0.4	0.98086	0.9	0.95174
0.5	0.97552	1.0	0.94504

Find the activity coefficient of calcium chloride at 1.000 mol kg^{-1}, using a Gibbs–Duhem integration.

8.21 If a solution of NaOH with a molality of 0.100 mol kg^{-1} is placed in a cell with a standard hydrogen electrode and a normal calomel electrode at 298.15 K, find the cell voltage and the pH of the solution. Neglect the liquid junction potential. State any other assumptions.

8.5 Thermodynamic Information from Electrochemistry

Thermodynamic information about many chemical reactions that occur outside of electrochemical cells can be obtained from electrochemical data. For a general reaction written in the form of Eq. (8.2-18), the analogue of Eq. (8.2-8) is

$$-nFE = \left(\frac{\partial G_{\text{chem}}}{\partial \xi}\right)_{T,P} \qquad (8.5\text{-}1)$$

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[4] Robinson and Stokes, *op. cit.*, p. 478.

where n is the number of electrons in the cell reaction equation. For the standard-state reaction,

$$-nFE^{\circ} = \Delta G^{\circ}_{\text{chem}} \tag{8.5-2}$$

The Gibbs energy change in this equation is the same as for the reaction outside of the cell. The equilibrium constant for the reaction can be calculated using the relations shown in Eq. (7.1-20) and Eq. (8.5-2)

$$K = Q_{\text{eq}} = e^{-\Delta G^{\circ}_{\text{chem}}/RT} = e^{nFE^{\circ}/RT} \tag{8.5-3}$$

EXAMPLE 8.8

a. Find the value of K for the reaction of Eq. (8.2-4) at 298.15 K from the E° value.

b. Find the equilibrium value of the hydrogen pressure when $m(\text{HCl}) = 0.500\ \text{mol kg}^{-1}$ and $\gamma_{\pm}(\text{HCl}) = 0.757$.

Solution

a.

$$K = \exp\left(\frac{2(96485\ \text{C mol}^{-1})(0.2223\ \text{V})}{(9.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})}\right) = e^{17.30} = 3.28 \times 10^{7}$$

b.

$$3.28 \times 10^{7} = \frac{\gamma_{\pm}^{4}(m_{\text{eq}}/m^{\circ})^{4}}{P_{\text{eq}}(\text{H}_2)/P^{\circ}}$$

$$P_{\text{eq}}(\text{H}_2) = P^{\circ}\left(\frac{(0.757)^{4}(0.500)^{4}}{3.28 \times 10^{7}}\right) = (6.26 \times 10^{-10})P^{\circ}$$

$$= 6.26 \times 10^{-10}\ \text{bar} = 4.69 \times 10^{-7}\ \text{torr}$$

Exercise 8.13

Find the value of the equilibrium constant for the reaction of Exercise 8.3 at 298.15 K.

We can write an expression for the entropy change of a reaction outside of an electrochemical cell (we now omit the subscript "chem"):

$$\left(\frac{\partial S}{\partial \xi}\right)_{T,P} = -\left(\frac{\partial}{\partial \xi}\left(\frac{\partial G}{\partial T}\right)_{P}\right)_{T,P} = -\left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial \xi}\right)_{T,P}\right)_{P} = nF\left(\frac{\partial E}{\partial T}\right)_{P} \tag{8.5-4}$$

For the standard-state reaction, this equation becomes

$$\Delta S^{\circ} = -\left(\frac{\partial \Delta G^{\circ}}{\partial T}\right)_{P} = nF\left(\frac{\partial E^{\circ}}{\partial T}\right)_{P} \tag{8.5-5}$$

The rate of enthalpy change per mole of a reaction is given by

$$\left(\frac{\partial H}{\partial \xi}\right)_{T,P} = \left(\frac{\partial G}{\partial \xi}\right)_{T,P} + T\left(\frac{\partial S}{\partial \xi}\right)_{T,P} = -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_{P} \tag{8.5-6}$$

For the standard-state reaction,

$$\Delta H^\circ = -nFE^\circ + nFT\left(\frac{\partial E^\circ}{\partial T}\right)_P \tag{8.5-7}$$

A chemical reaction does not have to be an oxidation-reduction reaction for us to calculate its equilibrium constant. It is only necessary to be able to write the reaction as the sum of an oxidation half-reaction and a reduction half-reaction.

EXAMPLE 8.9

Find the solubility product constant of AgI at 298.15 K from electrochemical data.

Solution

The reaction equation is

$$\mathrm{AgI(s)} \longrightarrow \mathrm{Ag^+} + \mathrm{I^-}$$

This reaction equation can be written as the sum of the oxidation and reduction half-reaction equations:

$$\begin{array}{ll} \mathrm{AgI(s)} + e^- \longrightarrow \mathrm{Ag(s)} + \mathrm{I^-} & E^\circ = -0.1519\ \mathrm{V} \\ \mathrm{Ag(s)} \longrightarrow \mathrm{Ag^+} + e^- & E^\circ = -0.7986\ \mathrm{V} \\ \hline \mathrm{AgI(s)} \longrightarrow \mathrm{Ag^+} + \mathrm{I^-} & E^\circ = -0.9505\ \mathrm{V} \end{array}$$

The solubility product constant is

$$K_{\mathrm{sp}} = \exp\left(\frac{(1)(96485\ \mathrm{C\ mol^{-1}})(-0.9505\ \mathrm{V})}{(9.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})}\right) = e^{-36.99} = 8.6 \times 10^{-17}$$

Many solubility product constants are so small that their values cannot be determined by chemical analysis. Electrochemical data provide the practical means to evaluate them.

Exercise 8.14

a. Using electrochemical data, find the solubility product constant for mercury(I) iodide, Hg_2I_2.

b. Find the volume of a saturated solution of Hg_2I_2 that contains 1.00 mol of Hg_2I_2. Assuming that the ocean has an average depth of 1.00 mile, estimate the area of ocean that contains this volume of water.

PROBLEMS

Section 8.5: Thermodynamic Information from Electrochemistry

8.22 **a.** Using half-cell potentials, find the value of the equilibrium constant for the reaction at 298.15 K:

$$\mathrm{I_2(aq)} + \mathrm{I^-} \rightleftharpoons \mathrm{I_3^-}$$

b. Find the final concentrations if 100 mL of a 0.00100 mol $\mathrm{kg^{-1}}$ solution of I_2 and 100 mL of a 0.00100 mol $\mathrm{kg^{-1}}$ solution of KI are mixed and allowed to equilibrate. Assume that $\gamma(I_2) = 1.00$ and use the Davies equation to estimate the activity coefficients of the ions.

8.23 **a.** Find the solubility product constant for lead(II) chloride at 298.15 K.

b. Find the molality of chloride ions in a saturated aqueous solution of lead(II) chloride at 298.15 K.

c. Find the molality of lead(II) ions in a saturated aqueous solution of lead(II) chloride at 298.15 K if 0.100 mol of sodium chloride has been added per kilogram of water.

8.24 Using electrochemical data, find the value of K_w, the ionization constant of water, at 298.15 K.

8.25 **a.** Find the value of K_{sp} for Ag_2S at 298.15 K.

b. Find the molality of S^{2-} in a saturated solution of Ag_2S in water at 298.15 K.

c. Find the molality of S^{2-} at 298.15 K in a saturated solution of Ag_2S that contains 0.1000 mol kg^{-1} of $AgNO_3$. Use the Davies equation to approximate activity coefficients.

8.26 At 298.15 K the solubility product constant for PbS is quoted as 6.5×10^{-34}. Find the value of $E°$ for the half-reaction at 298.15 K:

$$PbS(s) + 2e^- \longrightarrow Pb(s) + S^{2-}$$

8.27 The solubility product constant of HgS is variously cited as being equal to values between 4×10^{-53} and 2×10^{-49}. Find the largest and smallest value of the standard reduction potential for the following half-reaction that could correspond to these values:

$$HgS(s) + 2e^- \longrightarrow Hg(l) + S^{2-}$$

8.28 **a.** Using half-cell potentials, find the value of the equilibrium constant at 298.15 K for the reaction

$$Hg_2Cl_2(s) + 2Ag^+ \rightleftharpoons Hg_2^{2+} + 2AgCl(s)$$

b. Calculate $\Delta G°$ and the equilibrium constant using Gibbs energies of formation, and compare your value with the value from part a.

c. Calculate the equilibrium values of the molalities of Ag^+ ions and Hg_2^{2+} ions. Remember the solubility product constants.

8.29 **a.** Find the value at 298.15 K of the solubility product constant for $PbSO_4$ in water.

b. Find the molality of SO_4^{2-} ions in a saturated solution of $PbSO_4$ in water at 298.15 K.

c. If 0.200 mol of $NaNO_3$ is added to the saturated solution per kilogram of water, what will be the effect on the solubility of $PbSO_4$? Give a qualitative verbal answer, explaining your reasoning. If there is a change, calculate the new molality of SO_4^{2-} at saturation.

d. If 0.100 mol of solid $Pb(NO_3)_2$ per kilogram of water is added to the original saturated solution (no sodium nitrate present), what will the new molality of SO_4^{2-} be at saturation?

8.30 **a.** Using electrochemical data, find the formation constant at 298.15 K for the complex ion $AuCl_4^-$, which is the equilibrium constant for the reaction

$$Au^{3+} + 4Cl^- \rightleftharpoons AuCl_4^-$$

b. Find $\Delta G°$ for the reaction.

c. If 0.200 mol of $AuCl_4^-$ is added to 1.000 kg of water, find the equilibrium concentration of Cl^- ions.

8.31 Find the solubility product constants at 298.15 K for

a. Hg_2Cl_2

b. Ag_2S

8.32 Find the solubility product constants at 298.15 K for

a. $PbSO_4$

b. AgBr

8.33 **a.** Find the equilibrium constant at 298.15 K for the reaction

$$2Ce^{4+} + 2Cl^- \rightleftharpoons 2Ce^{3+} + Cl_2(g)$$

b. Find the equilibrium composition if a 0.0500 mol kg^{-1} solution of CeF_4 is added to an equal volume of a 0.0500 mol kg^{-1} solution of NaCl at 298.15 K. Assume that the chlorine gas is maintained at pressure $P°$ and use the Davies equation to estimate activity coefficients.

8.34 Find the equilibrium constant at 298.15 K for the reaction

$$I_2(s) + 2Cl^- \rightleftharpoons 2I^- + Cl_2(g)$$

8.35 Find the equilibrium constant at 298.15 K for the reaction

$$AgCl(s) + Br^- \rightleftharpoons AgBr(s) + Cl^-$$

8.36 The solubility product constant of PbS at 298.15 K is quoted as 3.4×10^{-28}. From this value calculate the standard reduction potential at 298.15 K of the half-reaction

$$PbS(s) + 2e^- \longrightarrow Pb(s) + S^{2-}$$

To see how reliable literature values can be, compare your answer with that of Problem 8.26.

Summary of the Chapter

An electrochemical cell can function as an electrolytic cell, in which case an externally imposed voltage produces a chemical reaction, or as a galvanic cell, in which case a spontaneous chemical reaction produces a current in an external circuit. An equilibrium electrochemical cell is at the state between these two conditions.

The chemical potential of a charged species was separated into two contributions:

$$\mu_i = \mu_{i,\text{chem}} + z_i F\varphi$$

where z_i is the valence of the charged species i, F is Faraday's constant, and φ is the electric potential.

The Nernst equation is

$$E = E^\circ - \frac{RT}{nF}\ln(Q)$$

where Q is the activity quotient for the reaction and where E° is the reversible standard state cell voltage.

Standard-state half-cell reduction potentials can be used to obtain the standard-state voltage for any cell that can be made from two half-cells in the table, using the relation

$$E^\circ = E^\circ(\text{R}) - E^\circ(\text{L})$$

where $E^\circ(\text{R})$ and $E^\circ(\text{L})$ are the half-cell potentials for the right and left electrodes in their standard states.

Thermodynamic functions can be determined electrochemically, using the relations

$$\Delta G^\circ_{\text{chem}} = -nFE^\circ$$

$$K = Q_{\text{eq}} = e^{-\Delta G^\circ_{\text{chem}}/RT} = e^{nFE^\circ/RT}$$

where $\Delta G^\circ_{\text{chem}}$ refers to the reaction outside of the cell.

ADDITIONAL PROBLEMS

8.37 A fuel cell is a galvanic cell into which reactants are brought into the cell continuously, so that no recharging or replacement of the cell is necessary. A hydrogen–oxygen fuel cell can have either an acidic or a basic electrolyte solution.

a. Write the half-reaction equations and the cell equation for a hydrogen–oxygen fuel cell with an aqueous KOH electrolyte.

b. Calculate the value of E° for the fuel cell of part a and write its Nernst equation. To what circumstance does the standard state correspond?

c. Write the half-cell reaction equations and the cell reaction for a hydrogen fuel cell with an acidic electrolyte. Find its E°.

d. Find the reversible cell voltage of a hydrogen–oxygen fuel cell at 298.15 K if the hydrogen and oxygen are both at a pressure of 150 torr (roughly the total pressure maintained in a manned space vehicle with a pure oxygen atmosphere) and if the electrolyte solution is an HCl solution at 2.50 mol kg^{-1}.

8.38 **a.** A hydrogen–oxygen fuel cell is operating reversibly at constant $P = P^\circ$ and with unit activity of all substances. Using data from Appendix A, calculate the maximum amount of work that could be done if 2.000 mol of hydrogen gas and 1.000 mol of oxygen gas are consumed at 298.15 K to form liquid water.

b. Using the Carnot efficiency formula, Eq. (3.1-22), find the maximum work that can be done with a heat engine operating reversibly between 1000°C and 100°C if 2.000 mol of hydrogen gas and 1.000 mol of oxygen gas are reacted. Assume that the water is produced as vapor, that the enthalpy change is approximately equal to that at 298.15 K, and that all of the enthalpy change is transferred to the engine. Compare your answer with the result of part a.

c. Calculate the minimum amounts of wasted energy in the form of heat for parts a and b of this problem.

8.39 A fuel cell with an acidic electrolyte using methane as a fuel has the anode half-reaction equation

$$\mathrm{CH_4(g)} + 2\mathrm{H_2O(l)} \longrightarrow \mathrm{CO_2(g)} + 8\mathrm{H^+} + 8e^-$$

a. Write the cathode half-reaction equation and the cell reaction equation for the methane fuel cell. Calculate $\Delta G°$ and $E°$ for the cell reaction.

b. Fuel cells have a thermodynamic advantage over energy delivery systems in which fuel is burned in an internal combustion engine or a turbine in order to drive an electric generator. Calculate the maximum amount of work that can be obtained from the combustion of 100.0 kg of methane in a turbine or other heat-driven engine with an upper temperature of 2000 K and an exhaust temperature of 1200 K.

c. Calculate the maximum energy in kilowatt-hours that can be obtained from the work in part a, assuming that one has an electric generator that is 100% efficient.

d. Calculate the maximum energy in kilowatt-hours that can be obtained from a fuel cell that consumes 100.0 kg of methane. Assume that all products and reactants are in their standard states. Comment on the advisability of using fuel cells for municipal electric power generation. What disadvantages might such use have?

8.40 Find the activity of chloride ion necessary so that chlorine instead of oxygen will be evolved when an infinitesimal current flows at 298.15 K in an electrolysis cell containing an aqueous solution of HCl.

8.41 Identify the following statements as either true or false. If a statement requires some special circumstance to make it true, label it as false.

a. Any electrochemical cell can be used to carry out a chemical reaction reversibly.

b. When an electrochemical cell is changed from a galvanic cell to an electrolytic cell by increasing the counter e.m.f. imposed by the external circuit, the electrode that was the anode now becomes the cathode.

c. A salt bridge minimized a liquid junction potential by creating two liquid junctions whose liquid junction potentials partially cancel.

d. The Nernst equation is an approximate equation whose validity must be verified for each case.

e. Activity coefficients for individual ions cannot be measured directly.

f. Electrochemical data can be used to obtain values of equilibrium constants only for oxidation-reduction reactions.

g. Fuel cells are limited in their efficiency by the Carnot efficiency formula.

8.42 A student at the University of Denver measured the pH of a solution using a hydrogen electrode and a calomel reference electrode at 25°C and a barometric pressure of 630 torr. When she calculated the pH, the result was that pH = 3.00, but she forgot to correct for the fact that the hydrogen gas was not at its standard state. If the barometric pressure was 630 torr, what pH should the student have reported?

2

Dynamics

9

Gas Kinetic Theory: The Molecular Theory of Dilute Gases at Equilibrium

PRINCIPAL FACTS AND IDEAS

1. A model system that represents a dilute gas consists of randomly moving noninteracting point-mass particles that obey classical mechanics.
2. The mathematical analysis of the behavior of this model system includes averages over mechanical states of the molecules, using probability distributions.
3. The probability distribution for molecular velocities is the Maxwell–Boltzmann probability distribution:

$$(\text{probability of a state of velocity } v) \propto e^{-mv^2/2k_\mathrm{B}T}$$

4. The probability distribution for molecular speeds is

$$(\text{probability of a speed } v) \propto v^2 e^{-mv^2/2k_\mathrm{B}T}$$

5. The gas kinetic theory of noninteracting molecules predicts the ideal gas law.
6. The gas kinetic theory of noninteracting molecules predicts the rate of wall collisions and the rate of effusion of a dilute gas.
7. The molecules of real gases and liquids are fairly accurately described by a pair potential function that corresponds to intermolecular attractions at moderate distances and repulsions at short distances.
8. The second model of a dilute gas is the hard-sphere gas, which allows analysis of molecular collisions.
9. The properties of a liquid can be understood qualitatively in terms of intermolecular forces.

9.1

Macroscopic and Microscopic States of Macroscopic Systems

A system of many molecules has both macroscopic and microscopic (molecular) properties. The state of the system involving macroscopic properties is called the *macroscopic state* or *macrostate*. Specification of this state for a system at equilibrium requires only a few variables. The *microscopic state* or *microstate* of a macroscopic system requires information about every atom or molecule in the system, a very large amount of information.

A General Postulate

We now assert that the macroscopic state of a system is determined by its microscopic state. However, if a macroscopic system is at macroscopic equilibrium, its macrostate does not change over a period of time, but the molecules are moving and the microstate changes continually. Many different microscopic states must correspond to the same macrostate, and we have no way of knowing which one is occupied at any instant. We state a general postulate that connects the macrostates and microstates: *The equilibrium value of a macroscopic variable corresponds to an average of the appropriate microscopic variable over all of the microstates that are compatible with the macroscopic state.*

Averages

An *average* is a value that represents the "central tendency" of a set of values. There are several kinds of averages. The *median* of a set is a value such that half of the members of the set are smaller than the median and half are larger. The *mode* is the most commonly occurring value in the set. The *mean* of a set of numbers $w_1, w_2, w_3, w_4, \ldots, w_N$ is denoted by $\langle w \rangle$ and is defined by

$$\langle w \rangle = \frac{1}{N}(w_1 + w_2 + \cdots + w_N) = \frac{1}{N}\sum_{i=1}^{N} w_i \qquad (9.1\text{-}1)$$

We use the standard notation for a sum, a capital Greek sigma (Σ). The index for the first term is indicated below the sigma and the index for the last term is indicated above the sigma. Unless otherwise stated, any average value that we discuss will be a mean value.

Probability Distributions

If some of the values of w are equal to each other we can write Eq. (9.2-1) in a different way. We arrange the N members of our set so that all of the distinct values are at the beginning of the set, with $w_1, w_2, \ldots, w_M$ all different from each other. Every remaining member of the set will be equal to one or another of the first M members. Let N_i be the total number of members of the set equal to w_i. The mean can now be written as a sum over the distinct members of the set

$$\langle w \rangle = \frac{1}{N} \sum_{i=1}^{M} N_i w_i \tag{9.1-2}$$

There are fewer terms in this sum than in the sum of Eq. (9.1-1) unless every N_i equals unity, but the mean value is the same. We define

$$p_i = \frac{N_i}{N} \tag{9.1-3}$$

The quantity p_i is the fraction of the members of the set that are equal to w_i. It is also equal to the probability that a randomly chosen member of the set will be equal to w_i. The set of p_i values is called a *probability distribution*. We can now write

$$\langle w \rangle = \sum_{i=1}^{M} p_i w_i \tag{9.1-4}$$

From the definition of p_i in Eq. (9.1-3) these probabilities are *normalized*, which means that they sum to unity.

$$\sum_{i=1}^{M} p_i = \frac{1}{N} \sum_{i=1}^{M} N_i = \frac{N}{N} = 1 \quad \text{(normalization)} \tag{9.1-5}$$

Exercise 9.1

A quiz was given to a class of 50 students. The scores were as follows:

Score	Number of students
100	5
90	8
80	16
70	17
60	3
50	1

Find the mean score on the quiz without taking a sum of 50 terms.

We can also calculate the mean of a function of our values. If $h(w)$ is some function of w, its mean value is

$$\langle h \rangle = \sum_{i=1}^{M} p_i h(w_i) \tag{9.1-6}$$

Exercise 9.2

For the quiz scores in Exercise 9.1, find the mean of the squares of the scores

$$\left\langle w^2 \right\rangle = \sum_{i=1}^{M} p_i w_i^2$$

and the square root of the mean of the squares, called the *root-mean-square (rms)* value, denoted by w_{rms}.

PROBLEMS

Section 9.1: Macroscopic and Microscopic States of Macroscopic Systems

9.1 A set of people has the following distribution of annual income:

Annual income/$	Number of people
33,000	12
34,000	15
35,000	18
36,000	24
37,000	19
38,000	20
39,000	12
40,000	8
55,000	2
95,000	3

a. Find the probability of each income.

b. The median of a set of numbers is defined such that half of the members of the set are greater than or equal to the median, and half are less than or equal to the median. Find the median income of this set of people.

c. Find the mean income.

d. Find the root-mean-square income.

e. Find the mode.

f. Explain any differences between these average values.

9.2 A group of people has the following distribution of annual income:

Annual income/$	Number of people
32,000	2
34,000	5
36,000	13
38,000	24
40,000	26
42,000	20
44,000	12
50,000	8
65,000	3
95,000	2

a. Find the probability of each income.

b. Find the median income of our set of people.

c. Find the mean income.

d. Find the root-mean-square income.

e. Find the mode.

f. Explain any differences between these average values.

9.2 A Model System to Represent a Dilute Gas

A *dilute gas* is a gas at a low enough pressure that it obeys the ideal gas law to an adequate approximation. We now define a model system to represent a dilute gas of a single monatomic substance:

1. The system consists of a large number, N, of identical particles, each with mass m.
2. The particles are vanishingly small in size. We call them *point-mass particles*.

3. The particles do not exert any forces on each other.
4. The motions of the particles are governed by classical (Newtonian) mechanics.
5. The system is confined in a rectangular box with smooth hard walls.

The study of this model system is called *gas kinetic theory*. It was originated by Bernoulli, who was the first to test the consequences of assuming that a gas was a mechanical system made up of many tiny moving particles. The theory was brought to an advanced state by Joule, Maxwell, and Boltzmann. The fundamentals were worked out independently by Waterston, about 15 years prior to the work of Joule and Maxwell.

Daniel Bernoulli, 1700–1782, was a Swiss mathematician best known for Bernoulli's principle, which states that the pressure decreases as the flow velocity of a fluid increases. The application of this principle allows airplanes to remain in the air.

James Prescott Joule, 1818–1889, was a great English physicist who pioneered in the thermodynamic study of work, heat, and energy while working in a laboratory in his family's brewery.

James Clerk Maxwell, 1831–1879, in addition to his work on gas kinetic theory, also derived the Maxwell relations of thermodynamics and the Maxwell equations of electrodynamics.

Ludwig Boltzmann, 1844–1906, was an Austrian physicist who was one of the inventors of gas kinetic theory. He suffered from depression and apparently killed himself, possibly because his ideas were not widely accepted during his lifetime.

John James Waterston, 1811–1883, was a schoolteacher in India at the time of his independent invention of kinetic theory and was unable to get his work published.

Classical Mechanics

According to classical mechanics, the state of a point-mass particle is specified by its position and its velocity. If the particle moves in three dimensions we can specify its position by the three Cartesian coordinates x, y, and z. These three coordinates are equivalent to a three-dimensional vector, which we denote by $\mathbf{r}$ and call the *position vector*. This vector is a directed line segment that reaches from the origin of coordinates to the location of the particle. We call x, y, and z the *Cartesian components* of the position vector. We will denote a vector by a letter in boldface type, but it can also be denoted by a letter with an arrow above it, as in $\overrightarrow{r}$, by a letter with a wavy underscore, as in $\underset{126}{r}$, or by its three Cartesian components listed inside parentheses, as in $\mathbf{r} = (x, y, z)$. Appendix B contains an elementary survey of vectors.

The *velocity* of a particle is a vector $\mathbf{v}$ with the Cartesian components v_x, v_y, and v_z. These components are the time derivatives of the Cartesian coordinates:

$$v_x = \frac{dx}{dt}, \quad v_y = \frac{dy}{dt}, \quad v_z = \frac{dz}{dt} \tag{9.2-1}$$

These three equations are equivalent to a single vector equation

$$\mathbf{v} = \frac{d\mathbf{r}}{dt} \tag{9.2-2}$$

Newton's Laws of Motion

In classical mechanics, the motion of a particle is governed by Newton's three laws, which we accept as generalizations of experimental fact. *Newton's first law* is called the *law of inertia*: *A stationary particle tends to remain stationary unless acted on by a force, and a moving particle tends to continue moving with unchanged velocity unless acted on by a force.* The first law is a special case of *Newton's second law*, which is called the *law of acceleration*. If a particle moves only in the x direction, Newton's second law is

$$F_x = ma_x = m\frac{dv_x}{dt} = m\frac{d^2x}{dt^2} \tag{9.2-3}$$

In this equation F_x is the force in the x direction acting on an object having mass m, x is its coordinate, v_x is its velocity component in the x direction, and a_x is its acceleration in the x direction. As indicated, the *acceleration* is the time derivative of the velocity and is the second time derivative of the position vector. If a particle moves in three dimensions, Newton's second law is expressed by the vector equation

$$\boxed{\mathbf{F} = m\mathbf{a} = m\frac{d\mathbf{v}}{dt} = m\frac{d^2\mathbf{r}}{dt^2} \quad \text{(Newton's second law)}} \tag{9.2-4}$$

EXAMPLE 9.1

A particle moving on a horizontal dry surface is subject to a frictional force in the direction opposite to its velocity. There is no frictional force if the object is stationary. The magnitude of the frictional force is assumed to be equal to a coefficient of friction times the weight (gravitational force) of the object. Find an expression for the position and velocity of an object of mass 1.000 kg if it moves in the x direction with an initial velocity $v_x(0) = 10.0\,\mathrm{m\,s^{-1}}$ and an initial position of $x = 0$ and if the coefficient of friction is equal to 0.800.

Solution

So long as v_x is nonzero, the frictional force is

$$F_x = -(0.800)(1.000\,\mathrm{kg})\left(9.80\,\mathrm{m\,s^{-2}}\right) = -7.84\,\mathrm{kg\,m\,s^{-2}} = -7.84\,\mathrm{N}$$

Newton's second law gives the *equation of motion*:

$$F_x = m\frac{d^2x}{dt^2} = m\frac{dv_x}{dt}$$

so that

$$\frac{dv_x}{dt} = -\frac{F_x}{m} = -\frac{7.84\,\mathrm{kg\,m\,s^{-2}}}{1.00\,\mathrm{kg}} = -7.84\,\mathrm{m\,s^{-2}}$$

We integrate this equation from $t = 0$ to $t = t'$:

$$\int_0^{t'} \frac{dv_x}{dt}dt = -\left(7.84\,\mathrm{m\,s^{-2}}\right)\int_0^{t'} dt$$

$$v_x(t') - v_x(0) = -(7.84\,\mathrm{m\,s^{-2}})t'$$

$$v_x(t') = 10.0\,\mathrm{m\,s^{-1}} - (7.84\,\mathrm{m\,s^{-2}})t'$$

This solution applies only until v_x vanishes, at which time the force stops and the particle remains stationary. This occurs when

$$t' = \frac{10.0\,\mathrm{m\,s^{-1}}}{7.84\,\mathrm{m\,s^{-2}}} = 1.28\,\mathrm{s}$$

The position is given by another integration:

$$x(t') - x(0) = \int_0^{t'} \frac{dx}{dt}dt = \int_0^{t'} v_x dt = \int_0^{t'} \left[10.0\,\mathrm{m\,s^{-1}}\left(7.84\,\mathrm{m\,s^{-2}}\right)t\right] dt$$

In this equation we have used the expression for the velocity in which t' was replaced by t. The integration yields

$$x(t') = \left(10.0\,\mathrm{m\,s^{-1}}\right)t' - \frac{1}{2}\left(7.84\,\mathrm{m\,s^{-2}}\right)t'^2$$

This solution applies only for values of t' no larger than 1.28 s. The position and velocity are shown in Figure 9.1.

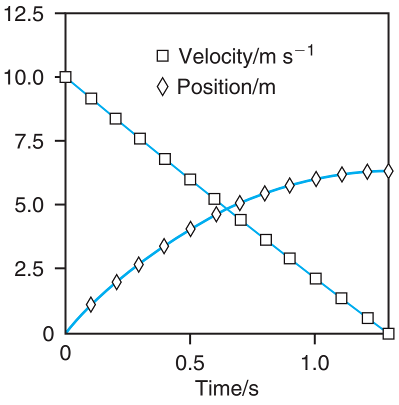

Figure 9.1 Graph for Example 9.1. Position and Velocity as a Function of Time. This figure shows how the velocity decreases linearly to zero and the coordinate attains a constant value.

Exercise 9.3

Assume that a particle of mass m moves in the z direction and is subject to a constant gravitational force given by $F_z = -mg$. If the initial position of the particle is $z(0) = 0$ and its initial velocity is $v_z(0) = 0$, solve its equation of motion, finding v_z and z as functions of time.

Newton's third law is called the *law of action and reaction*. It asserts that if one object exerts a force on a second object, the second object exerts a force on the first that is equal in magnitude and opposite in direction to the first force. If $\mathbf{F}_{21}$ is the force exerted on the second object and if $\mathbf{F}_{12}$ is the force exerted on the first object, then

$$\mathbf{F}_{12} = -\mathbf{F}_{21} \quad \text{(Newton's third law)} \tag{9.2-5}$$

In order to jump into the air from a floor, you push on the floor with your feet, and the floor throws you into the air because of Newton's third law.

Potential Energy

If the force on a particle depends only on its position, the force can be derived from a *potential energy*. For a force in the z direction,

$$F_z = -\frac{\partial \mathscr{V}}{\partial z} \tag{9.2-6}$$

where the potential energy is denoted by $\mathscr{V}$. This derivative is a partial derivative, which means that x and y are treated as constants in the differentiation. Similar equations apply for the x and y directions. If the force on a particle depends only on its position, the total energy of the particle is the sum of its kinetic energy $\mathscr{K}$ and its potential energy $\mathscr{V}$. If the particle moves only in the z direction, $\mathscr{V}$ depends only on z:

$$E = \mathscr{K} + \mathscr{V} = \frac{1}{2}mv_z^2 + \mathscr{V}(z) \tag{9.2-7}$$

The *law of conservation of energy* asserts that the energy of a particle subject only to forces from a potential energy is constant. We say that the energy is *conserved* and that the energy is a *constant of the motion*.

Exercise 9.4

a. Show that the solution to Exercise 9.3 conforms to the conservation of energy. The gravitational potential energy $\mathscr{V}$ corresponding to $F_z = -mg$ is

$$\mathscr{V} = mgz + \text{constant}$$

where the constant can take on any value without any physical effect.

b. Explain why the conservation of kinetic plus potential energy does not apply to the solution of Example 9.1. Because the conservation of total energy is an accepted principle of science, the decrease in kinetic energy in this example must correspond to an increase of some other form of energy. What form is this?

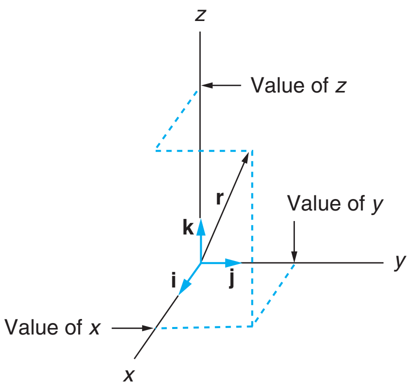

Figure 9.2 A Position Vector r in Three-Dimensional Space. The vector **r** specifies the position of the particle when its tail is at the origin. The unit vectors **i**, **j**, and **k** are also shown.

The Microscopic States of Our Model System

According to classical mechanics, the microstate of our model system is specified by giving the position and velocity of every particle. We number the particles in our model system from 1 to N. The position vector of particle number i can be written as a vector sum of three terms:

$$\mathbf{r}_i = \mathbf{i}x_i + \mathbf{j}y_i + \mathbf{k}z_i \tag{9.2-8}$$

Each term in Eq. (9.2-8) is a product of a scalar quantity (the component) and a unit vector. A *scalar* quantity can be positive, negative, or zero but has no specific direction in space. The unit vector **i** points in the direction of the positive x axis, the unit vector **j** points in the direction of the positive y axis, and the unit vector **k** points in the direction of the positive z axis. Figure 9.2 shows the vector $\mathbf{r}_i$, the Cartesian axes, the unit vectors, and the Cartesian components of the vector.

The product of a positive scalar quantity and a unit vector is a vector with the same direction as the unit vector and length equal to the scalar quantity. If the scalar quantity is negative, the product is a vector that has length equal to the magnitude of the scalar quantity and is in the opposite direction from the unit vector. The *sum of two vectors* can be represented geometrically by moving the second vector without rotating it so that its tail is at the head of the first vector. The sum vector has its tail at the tail of the first vector and its head at the head of the second vector. A third vector is added to the sum of the first two vectors in the same way. Figure 9.3 shows how the three components times their unit vectors add to equal the position vector $\mathbf{r}_i$.

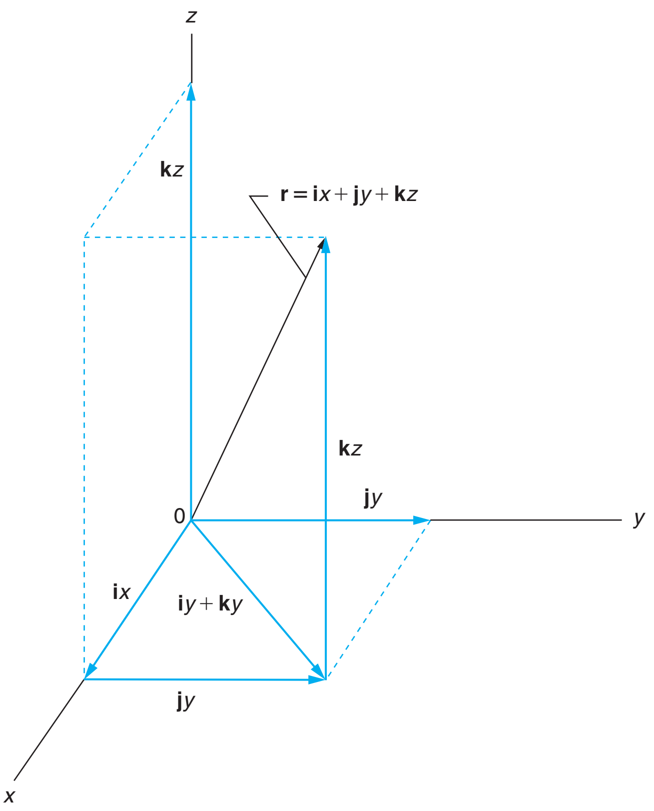

Figure 9.3 The Addition of the Components of a Position Vector.

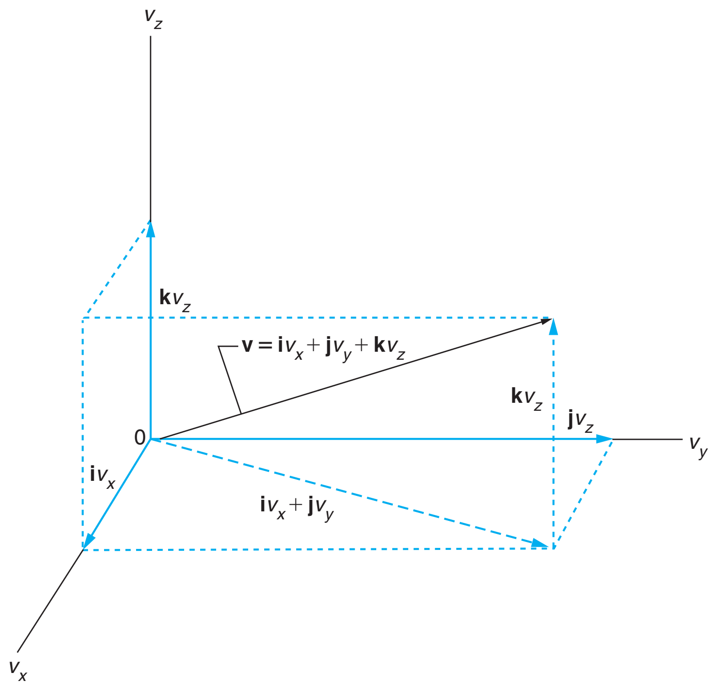

Figure 9.4 A Velocity Vector in Velocity Space.

The velocity of particle number i is specified by the velocity vector $\mathbf{v}_i$:

$$\mathbf{v}_i = \mathbf{i}v_{ix} + \mathbf{j}v_{iy} + \mathbf{k}v_{iz} \tag{9.2-9}$$

The components of the velocity $\mathbf{v}_i$ are the rates of change of x_i, y_i, and z_i:

$$v_{ix} = \frac{dx_i}{dt}, \quad v_{iy} = \frac{dy_i}{dt}, \quad v_{iz} = \frac{dz_i}{dt} \tag{9.2-10}$$

The velocity vector can be represented geometrically as in Figure 9.4. The mathematical space of this figure is called *velocity space*, in which distances on the axes represent velocity components. Cartesian components are shown, and these can be handled in the same way as components in ordinary space.

The direction of the velocity vector is the direction in which the particle is moving. The *speed* is the magnitude of the velocity, given by a three-dimensional version of the theorem of Pythagoras:

$$|\mathbf{v}_i| = v_i = \left(v_{ix}^2 + v_{iy}^2 + v_{iz}^2\right)^{1/2} \tag{9.2-11}$$

We use either of the two notations in Eq. (9.2-11) to denote the magnitude of a vector: the boldface letter within vertical bars or the letter in plain type. The magnitude of a vector is always non-negative (positive or zero).

Exercise 9.5

a. Use the theorem of Pythagoras to verify Eq. (9.2-11). (It must be used twice.)

b. Find the speed of a particle with the velocity components:

$$v_x = 400\,\mathrm{m\,s^{-1}}, \quad v_y = -600\,\mathrm{m\,s^{-1}}, \quad v_z = 750\,\mathrm{m\,s^{-1}}$$

c. The kinetic energy of a particle of mass m is defined by

$$\mathscr{K} = \frac{1}{2}mv^2$$

where v is its speed. If the particle of part b is a neon atom, find its kinetic energy.

There is a vast difference between the amount of information in the specification of the microscopic state and the specification of the macroscopic state of our model gas. Specification of the equilibrium macrostate requires the values of only three variables such as T, V, and n. The microstate of the model system is specified by giving the values of three coordinates and three velocity components for each of the N particles. If the model system contains roughly 1 mol of particles, specification of the microstate requires approximately 4×10^{24} values, which makes it impossible to list them, even if we would determine the values. To apply our postulate, we need a way to average mechanical variables over the microstates without being able to list all of them.

Mean Values of Mechanical Variables

Any variable that depends on the positions and velocities of the particles is determined by the state of the system and is called a *microscopic state function* or a *mechanical state function*. The most important mechanical state function of our model system is the energy, which is the sum of the *kinetic energy* and the *potential energy*:

$$E = \mathscr{K} + \mathscr{V} \tag{9.2-12}$$

The kinetic energy of the system, K, is the sum of kinetic energies of all of the particles,

$$\mathscr{K} = \frac{m}{2}\left(v_1^2 + v_2^2 + v_3^2 + \cdots + v_N^2\right) = \frac{m}{2}\sum_{i=1}^{N} v_i^2 \tag{9.2-13}$$

where we use the fact that all of the particles in our model system have the same mass. The potential energy of the system, $\mathscr{V}$, is a state function of the positions of the particles:

$$\mathscr{V} = \mathscr{V}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_\mathrm{n}) \tag{9.2-14}$$

The component of the force on particle number i in the x direction is

$$F_{ix} = -\frac{\partial \mathscr{V}}{\partial x_i} \tag{9.2-15}$$

with other force components given by analogous equations.

We assume for now that the gravitational forces on the particles of our system can be neglected. The molecules of our model system do not interact with each other and have no forces exerted on them except by the walls of the box confining the system. Their potential energy is constant so long as they remain within the box. We set this potential energy equal to zero (you can always set a constant potential energy equal to zero or to any other constant so long as you do it consistently). In order to represent the confinement of the particles in the box, we assign an infinite value to the potential energy if any particle is outside of the box. Since the total energy of the system must be finite, no particle can escape from the box, and the potential energy remains equal to zero.

Exercise 9.6

Show that any constant can be added to a potential energy without changing the forces.

Since the potential energy equals zero, the energy of the model system is equal to its kinetic energy:

$$E = \mathscr{K} = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \cdots + \varepsilon_N = \kappa_1 + \kappa_2 + \kappa_3 + \cdots + \kappa_N \tag{9.2-16}$$

where ε_i is the energy of particle number i and κ_i is its kinetic energy. The average (mean) molecular energy is given by the sum of the molecular energies divided by the number of molecules:

$$\langle \kappa \rangle = \langle \varepsilon \rangle = \frac{E}{N} = \frac{\mathscr{K}}{N} = \frac{1}{N}\sum_{i=1}^{N} \kappa_i \tag{9.2-17}$$

If N_j is the number of the molecules in a particular state j, then p_j is the fraction of molecules in that state:

$$p_j = \frac{N_j}{N} \tag{9.2-18}$$

The probability that a randomly chosen molecule will be in state j is also equal to p_j. We can write the average molecular energy as a sum over states instead of a sum over molecules:

$$\langle \varepsilon \rangle = \sum_{j=1}^{\infty} p_j \varepsilon_j \tag{9.2-19}$$

where ε_j is the energy of a particle in state j. There are infinitely many states that are possible, as indicated by the limits on the sum. We will omit these limits on sums from now on and understand that the sums are over all possible states.

PROBLEMS

Section 9.2: A Model System to Represent a Dilute Gas

9.3 **a.** Estimate the number of coordinate states that a neon atom might occupy if it is known only that it is contained in a volume of 1.00 L. That is, ignore the different velocities that the atom might have. Assume that the atom obeys classical mechanics and that the precision of measurement of its position is 1.00 nm (1.00×10^{-9} m). That is, if the center of the atom is anywhere in a cubical region 1.00 nm on a side, this counts as one state.

b. Estimate the number of coordinate states occupied by 1.00 mol of neon atoms by the criterion of part a. Assume that the atoms have zero size so that any number of atoms could occupy the same cubical region.

9.4 **a.** The frictional force on a spherical object moving through a fluid is approximately described by the formula

$$\mathbf{F} = -f\mathbf{v}$$

where f is called the *friction coefficient* and where $\mathbf{v}$ is the velocity of the object. Obtain a formula for the velocity and position of an object described by this equation moving in the x direction with initial position $x(0) = x_0$ and initial velocity $v_x(0) = v_0$. Ignore any force due to gravity.

b. Construct a graph of the position of the particle as a function of time for $m = 1.00\,\mathrm{kg}$, $f = 1.00\,\mathrm{kg\,s^{-1}}$, $x_0 = 0$, and $v_0 = 10.0\,\mathrm{m\,s^{-1}}$.

9.5 An object is propelled upward at the surface of the earth with an initial speed of $10.0\,\mathrm{m\,s^{-1}}$. Ignoring air resistance, find the maximum height of the object above its starting point.

9.6 An object with mass 0.100 kg slides down a frictionless surface of some arbitrary shape near the surface of the earth. If it starts with zero speed, find its speed when it is at a location 0.250 m lower in altitude than its initial position, and show that this is independent of the shape of the surface.

9.3

The Velocity Probability Distribution

If a system obeys classical mechanics, averaging over molecular states means averaging over molecular coordinates and momenta. Coordinates and momenta vary continuously, so we must integrate over their possible values instead of summing over discrete energies as in Eq. (9.2-19). Consider a quantity u that can take on any value between u_1 and u_2. We define a *probability distribution* $f(u)$ such that

$$\left(\begin{array}{l}\text{The probability that } u \text{ lies}\\ \text{between } u' \text{ and } u' + du\end{array}\right) = f(u')du \tag{9.3-1}$$

where du is an infinitesimal range of values of u and where u' is some value of u. The probability distribution $f(u)$ is a probability per unit length on the u axis, and we call it a *probability density*. Since $f(u)$ is a probability per unit length on the axis, the probability that u lies between u' and $u' + du$ is represented by an area under the curve representing $f(u)$ as shown schematically in Figure 9.5.

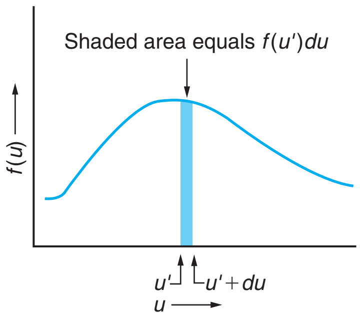

Figure 9.5 An Example Probability Density (Probability Distribution).

The total probability is equal to the integral

$$(\text{total probability}) = \int_{u_1}^{u_2} f(u)du \tag{9.3-2}$$

where u_1 is the smallest possible value of u and u_2 is the largest. This integral is equal to the total area under the curve representing $f(u)$ in Figure 9.5. We commonly multiply the probability density by a constant so that the total probability is equal to 1, which is called *normalization* of the probability distribution.

The *mean value* of u is given by an equation that is analogous to Eq. (9.1-4) and Eq. (9.2-19):

$$\langle u \rangle = \frac{\displaystyle\int_{u_1}^{u_2} u\, f(u)du}{\displaystyle\int_{u_1}^{u_2} f(u)du} \tag{9.3-3a}$$

If the probability density is normalized, the denominator in this equation equals unity:

$$\langle u \rangle = \int_{u_1}^{u_2} u\, f(u)du \quad (f \text{ normalized}) \tag{9.3-3b}$$

If $h(u)$ is a function of u, its mean value is given by

$$\langle h(u)\rangle = \int_{u_1}^{u_2} h(u)f(u)du \tag{9.3-4}$$

EXAMPLE 9.2

If all values of u between u_1 and u_2 are equally probable, then

$$f(u) = \frac{1}{u_2 - u_1}$$

Find the value of $< u^2 >$ if $u_1 = 0$ and $u_2 = 2$.

Solution

$$< u^2 > = \frac{1}{u_2 - u_1}\int_0^2 u^2 du = \frac{1}{2}\frac{1}{3}(2^3 - 0) = \frac{8}{6} = \frac{4}{3} = 1.333\cdots$$

Derivation of the Probability Distribution for Our Model System

We now seek a formula that represents the probability distribution for the molecular states in our model system. Because there are no forces on the molecules inside the box we assert that all positions inside the box are equally probable and focus on the probability distribution for molecular velocities. We begin with a reasonable (but unproved) assumption: *The probability distribution of each velocity component is independent of the other velocity components*. The validity of this assumption must be tested by comparing our results with experiment. Consider a velocity with components v_x, v_y, and v_z. Let the probability that v_x lies between v'_x (a particular value of v_x) and $v'_x + dv_x$ be given by

$$\text{(probability)} = f(v'_x)dv_x \tag{9.3-5}$$

Because the effects of gravity are assumed to be negligible there is no physical difference between any two directions. The probability distributions for v_y and v_z must be given by the same function as that for v_x. Let v'_y, and v'_z be particular values of v_y and v_z. The probability that v_x lies between v'_x and $v'_x + dv_x$, that v_y is in the range between v'_y and $v'_y + dv_y$, and that v_z lies between v'_z and $v'_z + dv_z$ is given by

$$\text{(probability)} = g(v'_x, v'_y, v'_z)dv_x dv_y dv_z = g(\mathbf{v}')d^3\mathbf{v} \tag{9.3-6}$$

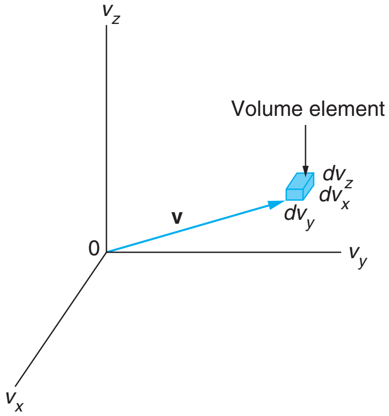

Figure 9.6 A Velocity Vector in Velocity Space, with a Cartesian Volume Element.

where v' is the vector with components v'_x, v'_y, and v'_z and where we abbreviate $dv_x dv_y dv_z$ by the symbol $d^3\mathbf{v}$. The probability distribution (probability density) $g(\mathbf{v})$ is a probability per unit volume in velocity space. The volume element $dv_x dv_y dv_z$ is infinitesimal, but Figure 9.6 shows the velocity space with a finite rectangular region crudely representing $dv_x dv_y dv_z$.

We have assumed that the probability distribution of each velocity component is independent of the other two. The joint probability of three independent events is the product of the probabilities of the three events, so that

$$g(\mathbf{v}) = g(|\mathbf{v}|) = g(v) = f(v_x)\, f(v_y)\, f(v_z) \tag{9.3-7}$$

Since all directions are equivalent, we assert that g will depend only on v, the magnitude of the vector $\mathbf{v}$. We now show that our assumptions determine the mathematical form of the probability distribution f. We first differentiate g with respect to v_x. Using the formula for the speed, Eq. (9.2-11) and the chain rule, Eq. (B-9) of Appendix B, we obtain

$$\begin{aligned}\frac{\partial g}{\partial v_x} &= \frac{dg}{dv}\frac{\partial v}{\partial v_x} = \frac{dg}{dv}\frac{\partial}{\partial v_x}\left[(v_x^2 + v_y^2 + v_z^2)^{1/2}\right] \\ &= \frac{dg}{dv}\frac{1}{2}(v_x^2 + v_y^2 + v_z^2)^{-1/2}(2v_x) = \frac{dg}{dv}\frac{v_x}{v}\end{aligned} \tag{9.3-8}$$

We divide this equation by v_x to obtain

$$\frac{1}{v_x}\frac{\partial g}{\partial v_x} = \frac{1}{v}\frac{dg}{dv} \tag{9.3-9}$$

Since v_x, v_y, and v_z all occur in the expression for the speed v in the same way, the corresponding equation for differentiation by v_y or v_z would be the same except for having v_y or v_z in place of v_x. The right-hand side of each equation would be the same, so that

$$\frac{1}{v_x}\frac{\partial g}{\partial v_x} = \frac{1}{v_y}\frac{\partial g}{\partial v_y} = \frac{1}{v_z}\frac{\partial g}{\partial v_z} = \frac{1}{v}\frac{dg}{dv} \tag{9.3-10}$$

We take the partial derivative of g with respect to v_x:

$$\left(\frac{\partial g}{\partial v_x}\right)_{v_y, v_z} = f(v_y)\, f(v_z)\frac{df(v_x)}{dv_x} \tag{9.3-11}$$

Similar equations for $(\partial g/\partial v_y)$ and $(\partial g/\partial v_z)$ can be written, so that Eq. (9.3-10) becomes

$$\frac{1}{v_x}\, f(v_y)\, f(v_z)\frac{df(v_x)}{dv_x} = \frac{1}{v_y}\, f(v_x)\, f(v_z)\frac{df(v_y)}{dv_y} = \frac{1}{v_z}\, f(v_x)\, f(v_y)\frac{df(v_z)}{dv_z} \tag{9.3-12}$$

Division of this equation by $f(v_x)\, f(v_y)\, f(v_z)$ gives

$$\frac{1}{v_x\, f(v_x)}\frac{df(v_x)}{dv_x} = \frac{1}{v_y\, f(v_y)}\frac{df(v_y)}{dv_y} = \frac{1}{v_z\, f(v_z)}\frac{df(v_z)}{dv_z} \tag{9.3-13}$$

We have *separated the variables* v_x, v_y, and v_z. That is, each term contains only one of the independent variables. Because v_x, v_y, and v_z are independent variables it is possible to keep v_y and v_z constant while allowing v_x to range. The first term must therefore be a constant function of v_x. The second term must be a constant function of v_y, and the third term must be a constant function of v_z. Each term equals the same constant, which we denote by C. Setting the first term equal to C and multiplying by $v_x\, f(v_x)$, we obtain

$$\frac{df}{dv_x} = Cv_x\, f(v_x) \tag{9.3-14}$$

Equation (9.3-14) is a *differential equation*. Solving it means finding a function f that satisfies the equation. It can be solved by a different version of separation of variables, in which we separate a dependent variable from an independent variable. We multiply Eq. (9.3-14) by dv_x and divide it by $f(v_x)$:

$$\frac{1}{f}\frac{df}{dv_x}dv_x = Cv_x dv_x \tag{9.3-15}$$

We recognize $(df/dv_x)dv_x$ as df and write

$$\frac{1}{f}df = Cv_x\ f(v_x) \tag{9.3-16}$$

An indefinite integration of both sides of Eq. (9.3-16) gives

$$\ln(f) = \frac{Cv_x^2}{2} + A \tag{9.3-17}$$

where A is a constant of integration. We take the exponential (antilogarithm) of each side of this equation to obtain

$$f(v_x) = e^A e^{Cv_x^2/2} \tag{9.3-18}$$

We require that f be normalized:

$$\int_{-\infty}^{\infty} f(v_x)dv_x = \int_{-\infty}^{\infty} e^A e^{Cv_x^2/2}dv_x = 1 \tag{9.3-19}$$

Because we are using nonrelativistic classical mechanics, speeds greater than the speed of light are not excluded and we must take infinite limits for the integrations. The constant C must be negative, because otherwise the integrand in Eq. (9.3-19) would grow without bound for large magnitudes of v_x and the integral would diverge (become infinite). We let $b = -C$ so that b is positive. We eliminate the parameter A by the normalization condition

$$1 = e^A \int_{-\infty}^{\infty} e^{-bv_x^2/2}dv_x = e^A\left(\frac{2\pi}{b}\right)^{1/2} \tag{9.3-20}$$

where we have looked up the definite integral in Appendix C. Equation (9.3-18) now becomes

$$f(v_x) = \left(\frac{b}{2\pi}\right)^{1/2} e^{-bv_x^2/2} \tag{9.3-21}$$

The probability distribution for all three components becomes

$$\begin{aligned} g(\mathbf{v}) = f(v_x)\, f(v_y)\, f(v_z) &= \left(\frac{b}{2\pi}\right)^{3/2} e^{-bv_x^2/2}e^{-bv_y^2/2}e^{-bv_z^2/2} \\ &= \left(\frac{b}{2\pi}\right)^{3/2} e^{-b(v_x^2+v_y^2+v_z^2)/2} = \left(\frac{b}{2\pi}\right)^{3/2} e^{-bv^2/2} \end{aligned} \tag{9.3-22}$$

Because $v_x^2 + v_y^2 + v_z^2 = v^2$, the square of the speed, g depends only on the speed, as we anticipated. It can also be written as a function of the kinetic energy of the particle, ε:

$$g(v) = \left(\frac{b}{2\pi}\right)^{3/2} e^{-b\varepsilon/m} \tag{9.3-23}$$

Identification of the Parameter *b*

We need some additional information before we can identify the parameter b. We accept as an experimental fact that the energy of a monatomic dilute gas is given by

$$E(T) - E_0 = \frac{3}{2}n\,RT = \frac{3}{2}Nk_\mathrm{B}T \tag{9.3-24}$$

where k_B is Boltzmann's constant, equal to R/N_Av, where T is the absolute temperature, where n is the amount of gas in moles, and where E_0 is a constant. We show in Chapter 2 that this assertion can be deduced from heat capacity data on monatomic gases. Because a constant can be added to the energy without physical effect, we can choose to set the constant E_0 equal to zero.

Viewed microscopically, the energy of the model gas is N times the mean molecular energy, $\langle\varepsilon\rangle$:

$$E = N\langle\varepsilon\rangle = N\langle\kappa\rangle = N\frac{1}{2}m\left\langle v^2\right\rangle \tag{9.3-25}$$

where $\left\langle v^2\right\rangle$ is the mean of the square of the speed and where we have set the potential energy equal to zero. The mean molecular kinetic energy is

$$\begin{aligned}\langle\kappa\rangle &= \frac{m}{2}\left\langle v_x^2 + v_y^2 + v_z^2\right\rangle \\ &= \frac{m}{2}\left(\left\langle v_x^2\right\rangle + \left\langle v_y^2\right\rangle + \left\langle v_z^2\right\rangle\right)\end{aligned} \tag{9.3-26}$$

Because the x, y, and z velocity component probability distributions are the same function, the three terms in Eq. (9.3-26) will be equal to each other after averaging, and we can write

$$\begin{aligned}\langle\kappa\rangle &= \frac{3m}{2}\left\langle v_x^2\right\rangle \\ &= \left(\frac{3m}{2}\right)\left(\frac{b}{2\pi}\right)^{3/2}\int_{-\infty}^{\infty} v_x^2 e^{-bv_x^2/2}dv_x \int_{-\infty}^{\infty} v_x^2 e^{-bv_y^2/2}dv_y \int_{-\infty}^{\infty} v_x^2 e^{-bv_z^2/2}dv_z \\ &= \left(\frac{3m}{2}\right)\left(\frac{b}{2\pi}\right)^{1/2}\int_{-\infty}^{\infty} v_x^2 e^{-bv_x^2/2}dv_x\end{aligned} \tag{9.3-27}$$

The last two integrals in the first version of this equation cancel two of the factors of $(b/2\pi)^{1/2}$. We look up the remaining integral in Appendix C and obtain

$$\begin{aligned}\langle\varepsilon\rangle &= \left(\frac{3m}{2}\right)\left(\frac{b}{2\pi}\right)^{1/2}\int_{-\infty}^{\infty} v_x^2 e^{-bv_x^2/2}dv_x \\ &= 2\left(\frac{3m}{2}\right)\left(\frac{b}{2\pi}\right)^{1/2}\int_{0}^{\infty} v_x^2 e^{-bv_x^2/2}dv_x \\ &= \left(\frac{3m}{2}\right)\left(\frac{b}{2\pi}\right)^{1/2}\frac{1}{4}\left(\frac{8\pi}{b^3}\right)^{1/2} = \frac{3m}{2b}\end{aligned} \tag{9.3-28}$$

where we have used the fact that this integral from $-\infty$ to ∞ is twice the integral from 0 to ∞, because the integrand is an even function (has the same value for $-v_x$ as for v_x). We now have

$$E = N\frac{3m}{2b} \tag{9.3-29}$$

This must agree with the macroscopic energy of a dilute gas in Eq. (9.3-24), so that

$$N\frac{3m}{2b} = \frac{3}{2}Nk_{\mathrm{B}}T \tag{9.3-30}$$

so that

$$b = m/k_{\mathrm{B}}T \tag{9.3-31}$$

The normalized probability distribution for the x component of the velocity is now

$$f(v_x) = \left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{1/2} e^{-mv_x^2/2k_{\mathrm{B}}T} \tag{9.3-32}$$

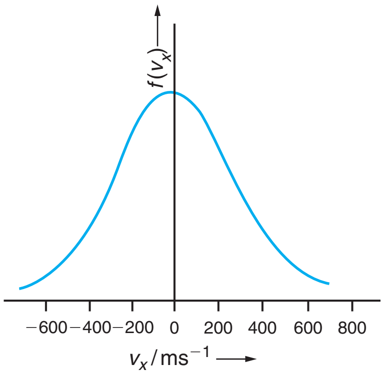

Figure 9.7 The Probability Distribution for a Velocity Component of Oxygen Molecules at 298 K.

We have derived this distribution for particles without rotation or vibration, but we now assert that rotation, vibration, and electronic motion occur independently of translation (the only motion of structureless particles) so that we can use this distribution for the translational motion of any molecules in a dilute gas. The normalized probability distribution is represented in Figure 9.7 for a velocity component of oxygen molecules at 298 K. The most probable value of the velocity component is zero, and most of the oxygen molecules have values of the velocity component between $-400\,\mathrm{m\,s^{-1}}$ and $400\,\mathrm{m\,s^{-1}}$.

The distribution of Eq. (9.3-32) is an example of a *Gaussian distribution*, also called a *normal distribution*. The Gaussian distribution is represented by the formula

$$f(u) = \frac{1}{\sqrt{2\pi}\sigma}e^{-(u-\mu)^2/2\sigma^2} \tag{9.3-33}$$

where μ is the mean value of u and where σ is called the *standard deviation*. If a normal distribution has a standard deviation equal to 1 it is called the *standard normal distribution*. A graph of a Gaussian distribution is shown in Figure 9.8a. This graph is sometimes called a *bell curve*. The shaded area in Figure 9.8b represents the probability that u lies between $\mu - \sigma$ and $\mu + \sigma$.

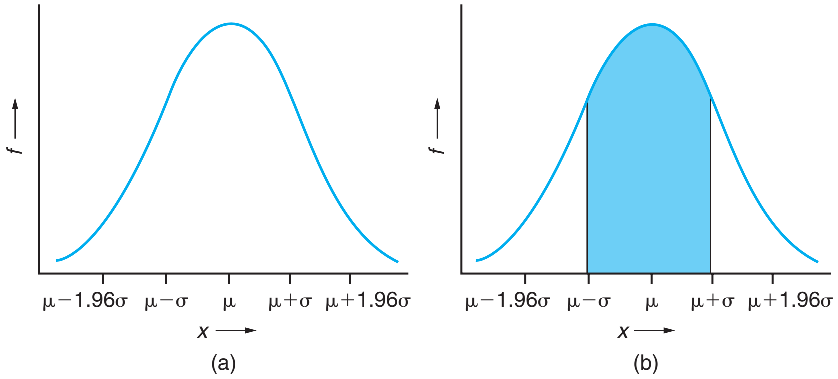

Figure 9.8 The Gaussian (Normal) Probability Distribution. (a) The graph showing the famous "bell-shaped" curve. (b) The probability that the variable deviates no more than one standard deviation from its mean.

The Gaussian curve is named for Johann Carl Friedrich Gauss, 1777–1855, a great German mathematician who made many fundamental contributions to mathematics.

EXAMPLE 9.3

Show that the Gaussian distribution of Eq. (9.3-33) is normalized.

Solution

$$\int_{-\infty}^{\infty} f(u)du = \frac{1}{\sqrt{2\pi}\sigma}\int_{-\infty}^{\infty} e^{-(u-\mu)^2/2\sigma^2}du = \frac{1}{\sqrt{2\pi}\sigma}\int_{-\infty}^{\infty} e^{-w^2/2\sigma^2}dw$$

$$= \frac{1}{\sqrt{2\pi}\sigma}\sqrt{2}\sigma\int_{-\infty}^{\infty} e^{-t^2}dt = \frac{1}{\sqrt{2\pi}\sigma}\sqrt{2}\sigma\sqrt{\pi} = 1$$

where we have looked up the integral in Appendix C.

The standard deviation of an arbitrary probability distribution is defined by

$$\sigma_u = \left(\left\langle u^2\right\rangle - \langle u\rangle^2\right)^{1/2} \quad \text{(definition of } \sigma_u) \tag{9.3-34}$$

The standard deviation is a convenient measure of the width of a probability distribution. For a Gaussian distribution the probability that u lies between $\mu - \sigma$ and $\mu + \sigma$ is equal to 0.683. For most other probability distributions the probability that the independent variable lies within one standard deviation of the mean is approximately equal to two-thirds.

Exercise 9.7

a. Show that $\langle u\rangle = \mu$ for the Gaussian distribution of Eq. (9.3-33).

b. Show that the definition in Eq. (9.3-34) when applied to the Gaussian probability distribution leads to $\sigma_u = \sigma$.

By comparison of Eq. (9.3-32) and Eq. (9.3-33), the standard deviation σ_{v_x} for the probability distribution of v_x is given by

$$\sigma_{v_x} = \sqrt{\frac{k_B T}{m}} = \sqrt{\frac{RT}{M}} \tag{9.3-35}$$

In the second equality M is the molar mass. The value of σ_{v_x} for O_2 molecules at 298 K is equal to 278 m s^{-1}, which is equal to 623 miles per hour.

The standard deviation of a function $h(u)$ is defined by

$$\sigma_h = \left[\left\langle h(u)^2\right\rangle - \langle h(u)\rangle^2\right]^{1/2} \quad \text{(definition)} \tag{9.3-36}$$

EXAMPLE 9.4

Obtain a formula for σ_{κ_x}, the standard deviation of the v_x contribution to the kinetic energy, $\kappa_x = mv_x^2/2$.

Solution

$$< \kappa_x > = \frac{1}{2}k_{\mathrm{B}}T$$

$$\left\langle \kappa_x^2 \right\rangle = \left(\frac{m}{2}\right)^2 \left\langle v_x^4 \right\rangle = \left(\frac{m}{2}\right)^2 \left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{1/2} \int_{-\infty}^{\infty} v_x^4 e^{-mv_x^2/2k_{\mathrm{B}}T} dv_x$$

$$= 2\left(\frac{m}{2}\right)^2 \left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{1/2} \int_{0}^{\infty} v_x^4 e^{-mv_x^2/2k_{\mathrm{B}}T} dv_x$$

$$= 2\left(\frac{m}{2}\right)^2 \left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{1/2} \frac{3}{8}\sqrt{\pi}\left(\frac{2k_{\mathrm{B}}T}{m}\right)^{5/2} = \frac{3}{16}(2k_{\mathrm{B}}T)^2 = \frac{3}{4}k_{\mathrm{B}}^2T^2$$

$$\sigma_{\kappa_x} = \left(\frac{3}{4}k_{\mathrm{B}}^2T^2 - \frac{1}{4}k_{\mathrm{B}}^2T^2\right)^{1/2} = \frac{k_{\mathrm{B}}T}{\sqrt{2}}$$

Exercise 9.8

a. Evaluate σ_{κ_x} for oxygen molecules at 298 K.
b. Express this standard deviation as a fraction of the v_x contribution to the kinetic energy.

The probability that u lies between two values a and b can be obtained by an integration:

$$\left(\begin{array}{l}\text{probability that}\\ a < u < b\end{array}\right) = \int_a^b f(u)du \quad \text{(normalized distribution)} \tag{9.3-37}$$

The Gaussian probability distribution is an integrand function for which no antiderivative has been found, so that a probability integral such as in Eq. (9.3-37) for a Gaussian distribution must be carried out numerically or looked up in a table of values.

EXAMPLE 9.5

Find the probability that v_x lies between 0 and 500 m s^{-1} for neon atoms at 300 K.

Solution

$$(\text{probability}) = \left(\frac{m}{2pk_{\mathrm{B}}T}\right)^{1/2} \int_0^{500\,\mathrm{m/s}} e^{-mv_x^2/2k_{\mathrm{B}}T} dv_x$$

We change variables, letting

$$t = (mv_x^2/2k_{\mathrm{B}}T)^{1/2}; \quad dt = (m/2k_{\mathrm{B}}T)^{1/2}dv_x$$

At the upper limit, we have

$$t = \sqrt{\frac{(3.35 \times 10^{-26}\,\mathrm{kg})(500\,\mathrm{m s^{-1}})^2}{(2)(1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}})(300\,\mathrm{K})}} = 1.0055$$

so that

$$(\text{probability}) = \frac{1}{\sqrt{\pi}} \int_0^{1.0055} e^{-t^2} dt$$

This integral is in the form of the *error function*, defined in Appendix C by[1]

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\,dt \qquad (9.3\text{-}38)$$

Our probability is therefore

$$(\text{probability}) = \frac{1}{2}\operatorname{erf}(1.0055) = 0.4225 = 42.25\%$$

Where the numerical value was obtained from the table of the error function in Appendix C.

We can obtain an approximate probability of a small finite range Δv_x by replacing the infinitesimal interval dv_x in Eq. (9.3-5) by Δv_x:

$$\begin{pmatrix}\text{probability that}\\ v_x \text{ lies in } \Delta v_x\end{pmatrix} \approx f(v_x')\Delta v_x \quad (\text{for small } \Delta v_x) \qquad (9.3\text{-}39)$$

where v_x' is a value of v_x within the range Δv_x.

EXAMPLE 9.6

Find the probability that v_x for an argon atom in a system at 273.15 K is in the range $650.00\,\mathrm{m\,s^{-1}} < v_x < 651.00\,\mathrm{m\,s^{-1}}$.

Solution

From Eq. (9.3-39)

$$\begin{aligned}\text{probability} &\approx \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mv_x^2/2k_BT}\Delta v_x = \left(\frac{M}{2\pi RT}\right)^{1/2} e^{-Mv_x^2/2RT}\Delta v_x\\ &\approx \left(\frac{0.039948\,\mathrm{kg\,mol^{-1}}}{2\pi(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(273.15\,\mathrm{K})}\right)^{1/2}\\ &\quad\times \exp\left(\frac{-(0.039948\,\mathrm{kg\,mol^{-1}})(650\,\mathrm{m\,s^{-1}})^2}{2(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(273.15\,\mathrm{K})}\right)(1.00\,\mathrm{m\,s^{-1}})\\ &\approx 4.05\times 10^{-5}\end{aligned}$$

Exercise 9.9

Find the probability that v_x for an argon atom in a system at 273.15 K is in the range $650\,\mathrm{m\,s^{-1}} < v_x < 652\,\mathrm{m\,s^{-1}}$.

Exercise 9.10

a. What fraction of the molecules has x-components of the velocity between $-\sigma_{v_x}$ and σ_{v_x}?

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[1] M. Abramowitz and I. A. Stegun, eds., *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, U.S. Govt. Printing Office, Washington, DC, 1964, p. 297ff.

b. Find a value v_x' such that there is a 95% probability that a molecule will have a value of v_x between $-v_x'$ and v_x' for N_2 molecules at 298.15 K. Find the ratio of this value to the standard deviation σ_{v_x}.

c. Repeat this calculation for N_2 molecules at 1000.0 K.

The three-dimensional probability distribution $g(v)$ can be written as

$$g(v) = f(v_x)\, f(v_y)\, f(v_z) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-m(v_x^2+v_y^2+v_z^2)/2k_B T}$$

$$\boxed{g(v) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_B T}} \tag{9.3-40}$$

This function is called the *Maxwell probability distribution* or the *Maxwell–Boltzmann probability distribution.* In terms of the molecular kinetic energy,

$$\boxed{g(\mathbf{v}) = \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-\varepsilon/k_B T}} \tag{9.3-41}$$

which is called the *Boltzmann probability distribution*. We do not prove it at this time, but this probability distribution applies to all forms of molecular energy, including potential energy and the vibrational, rotational, and electronic energies. We write

$$\boxed{(\text{probability of a state of energy } \varepsilon) \propto e^{-\varepsilon/k_B T}} \tag{9.3-42}$$

where the symbol $\propto$ means "is proportional to."

There are several important physical facts about the Boltzmann probability distribution:

1. At a finite temperature, molecular states of higher energy are less probable than states of lower energy. States with energy much larger than $k_B T$ are quite improbable compared with states of energy equal to zero.
2. A molecular state of high energy will be more probable at a high temperature than at a low temperature.
3. As the temperature approaches infinity, all states approach equal probability.
4. If the temperature approaches zero, only the state of lowest energy will be populated.

EXAMPLE 9.7

Find the ratio of the probabilities of the two following velocities of neon atoms at 300 K:
first velocity: $v_x = 500\ \text{m s}^{-1}$, $v_y = -400\ \text{m s}^{-1}$, $v_z = 250\ \text{m s}^{-1}$
second velocity: $v_x = 200\ \text{m s}^{-1}$, $v_y = 350\ \text{m s}^{-1}$, $v_z = -275\ \text{m s}^{-1}$

Solution

Neon has several isotopes. We use the average molecular mass,

$$m = \frac{0.020183\ \text{kg mol}^{-1}}{6.022 \times 10^{23}\ \text{mol}^{-1}} = 3.35 \times 10^{-26}\ \text{kg}$$

first velocity,

$$v^2 = \left(500\,\mathrm{m\,s^{-1}}\right)^2 + \left(-400\,\mathrm{m\,s^{-1}}\right)^2 + \left(250\,\mathrm{m\,s^{-1}}\right)^2 = 472500\,\mathrm{m^2\,s^{-2}}$$

$$\frac{\varepsilon}{k_\mathrm{B}T} = \frac{mv^2}{2k_\mathrm{B}T} = \frac{(3.3510^{-26}\,\mathrm{kg})(472,500\,\mathrm{m^2\,s^{-2}})}{(2)(1.3807\times10^{-23}\,\mathrm{J\,K^{-1}})(300\,\mathrm{K})} = 1.91$$

second velocity,

$$\frac{\varepsilon}{k_\mathrm{B}T} = 0.963 \quad \text{(calculation similar to first velocity)}$$

$$\text{probability ratio} = \frac{e^{-1.91}}{e^{-0.963}} = 0.388$$

Exercise 9.11

Find the ratio of the probabilities of the two velocities for argon atoms at 300.0 K:

$$\text{first velocity } v_x = 650\,\mathrm{m\,s^{-1}},\quad v_y = 780\,\mathrm{m\,s^{-1}},\quad v_z = 990\,\mathrm{m\,s^{-1}}$$

$$\text{second velocity } v_x = 300\,\mathrm{m\,s^{-1}},\quad v_y = 290\,\mathrm{m\,s^{-1}},\quad v_z = 430\,\mathrm{m\,s^{-1}}$$

Equation (9.3-40) represents the probability density in the three-dimensional velocity space of Figure 9.4. A point in this velocity space represents the velocity of one molecule. If we have N molecules, we can represent their velocities by a set of N points in the same velocity space. The density (number of points per unit volume) of this swarm of points at the point representing the velocity v' is proportional to the probability density $g(\mathbf{v}')$. Figure 9.9 schematically represents the swarm of points for a system of a few hundred molecules.

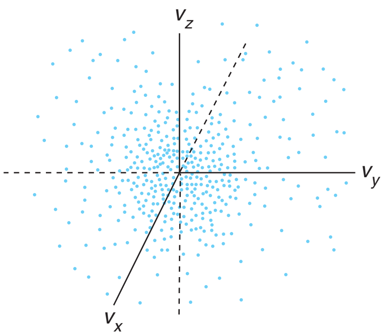

Figure 9.9 Points Representing the Velocity States of Molecules in a System.

PROBLEMS

Section 9.3: The Velocity Probability Distribution

9.7 **a.** Find the probability of drawing the ace of spades from one randomly shuffled deck of 52 cards and drawing the eight of diamonds from another deck of 52 cards.

b. Find the probability of drawing the ace of spades and the eight of diamonds (in that order) from a single deck of 52 cards.

c. Find the probability of drawing the ace of spades and the eight of diamonds (in either order) from a single deck of 52 cards.

9.8 Compute the odds for each possible value of the sum of the two numbers that can show when two dice are thrown.

9.9 Find the mean value and the root-mean-square value of $\sin(x)$ for $0 < x < 2\pi$ radians, assuming a uniform probability distribution.

9.10 **a.** Find the mean value and the root-mean-square value of $\sin^2(x)$ for $0 < x < 2\pi$ radians, assuming a uniform probability distribution.

b. Find the mean value and the root-mean-square value of $\sin^2(x)$ for $0 < x < 4\pi$ radians, assuming a uniform probability distribution. Comment on the relationship between your answers in parts a and b. What can you say about the mean value of $\sin^2(x)$ for $0 < x < \pi$ radians?

9.11 Find the mean value and the sample standard deviation for all possible throws of two dice, assuming that all outcomes are equally probable. The *sample standard deviation* for a sample of N members is different from the standard deviation of an entire population and is given by

$$s_x = \left(\frac{1}{N-1}\sum_{i=1}^{N}(x_i - \langle x\rangle)^2\right)^{1/2} \qquad (9.3\text{-}43)$$

where $\langle x\rangle$ is the mean of the set. If the sample is randomly drawn from a certain population, the sample standard deviation is said to be an unbiased estimate of the population standard deviation.

9.12 Find the mean value and the root-mean-square value of $\sin(x)$ for $-\infty < x < \infty$, assuming the standard normal (Gaussian) probability distribution

$$f(x) = \frac{1}{\sqrt{2\pi}}e^{-x^2/2}$$

9.13 Find the mean value and the root-mean-square value of $\cos(x)$ for $-\infty < x < \infty$, assuming the standard normal probability distribution

$$f(x) = \frac{1}{\sqrt{2\pi}}e^{-x^2/2}$$

9.14 For nitrogen molecules at 300.0 K, estimate the error in the normalization integral of Eq. (9.3-20) that is produced by including velocity components greater than the speed of light. The following asymptotic formula[2] gives values of the error function for large values of z:

$$\operatorname{erf}(z) = 1 - \frac{e^{-z^2}}{\sqrt{\pi}z}\left(1 + \sum_{m=1}^{\infty}(-1)^m\frac{(1)(3)\cdots(2m-1)}{(2z^2)^m}\right)$$

9.15 For N_2 molecules at 298.15 K, calculate the probability that $|v_x|$ exceeds the speed of light, 2.997×10^8 m s^{-1}. See the asymptotic formula in Problem 9.14.

9.16 **a.** Use Eq. (9.3-39) to estimate the probability that an argon atom in a system at 273.15 K has the x component of its velocity between 0 and 20.0 m s^{-1}.

b. Find the correct value of the probability and compare it with your result from part a.

9.17 Find the fraction of the molecules in a gas that have

$$v_x^2 > \frac{k_B T}{m}$$

Show that this fraction is the same for all gases at all temperatures.

9.18 The escape velocity is defined as the minimum upward vertical velocity component required to escape the earth's gravity. At the earth's surface, its value is 1.12×10^4 m s^{-1} $= 2.5 \times 10^4$ miles per hour.

a. Find the fraction of N_2 molecules at 298 K having an upward vertical velocity component exceeding v_{esc}. The asymptotic formula in Problem 9.14 can be used.

b. Find the fraction of helium atoms at 298 K having an upward vertical velocity component exceeding v_{esc}.

9.19 The acceleration due to gravity at the surface of the moon is 1.67 m s^{-2} and its radius is 1.738×10^6 m. The mean daytime temperature at the surface of the moon is roughly 370 K.

a. Find the escape velocity at the surface of the moon.

b. Find the fraction of N_2 molecules at 370 K having an upward vertical velocity component exceeding v_{esc}.

9.4 The Distribution of Molecular Speeds

The speed is the magnitude of the velocity. All velocities that have the same magnitude but different directions correspond to the same speed. In order to obtain a formula for the probability distribution of speeds, we must add up the probabilities of all velocities corresponding to the same speed. To do this conveniently, we change to *spherical polar coordinates* in velocity space. The first coordinate is the speed v. The second coordinate is θ, the angle between the positive v_z axis and the velocity vector. The third coordinate

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[2] M. Abramowitz and I. A. Stegun, *op. cit.*, p. 298 (Note 1).

is ϕ, the angle between the positive v_x axis and the line segment in the v_x–v_y plane that lies directly under the velocity vector.

An infinitesimal volume element in velocity space corresponding to an infinitesimal increment in each velocity component is crudely depicted in Figure 9.10. The volume element is an infinitesimal box with length in the v direction equal to dv. The length of an arc of a circle is the radius of the circle times the measure in radians of the angle subtended by the arc, so the length of the box in the θ direction is equal to $vd\theta$. The length of the line segment in the v_x–v_y plane that lies directly under the velocity vector is $v\sin(\theta)$, so that the length of the box in the ϕ direction is equal to $v\sin(\theta)d\phi$. Since the increments are infinitesimal the volume element is rectangular and its volume is equal to $v^2\sin(\theta)dvd\theta d\phi$. We abbreviate the volume element by the symbol $d^3\mathbf{v}$:

$$d^3\mathbf{v} = v^2\sin(\theta)dvd\theta d\phi \tag{9.4-1}$$

Using the same symbol $d^3\mathbf{v}$ for the volume element in Cartesian coordinates and in spherical polar coordinates enables us to write some equations that apply to either set of coordinates.

The probability that the velocity of a randomly chosen molecule lies in the volume element $v^2\sin(\theta)dvd\theta d\phi$ is

$$\begin{pmatrix}\text{probability that}\\ \mathbf{v}\text{ lies in }d^3\mathbf{v}\end{pmatrix} = g(v)d^3\mathbf{v} = g(v)v^2\sin(\theta)dvd\theta d\phi \tag{9.4-2}$$

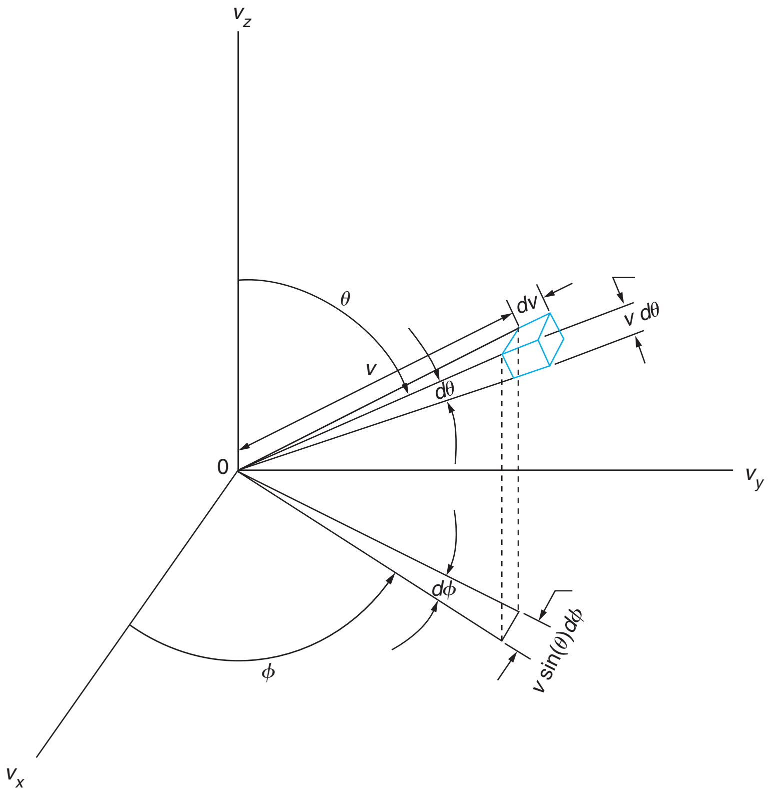

Figure 9.10 Spherical Polar Coordinates in Velocity Space, with a Volume Element.

Consider a spherical shell of radius v and thickness dv as shown in Figure 9.11. This shell contains all of the points in velocity space that represent speeds between v and $v + dv$. To find the probability of speeds in this shell we integrate the probability shown in Eq. (9.4-2) over all values of θ and ϕ for fixed values of v and dv:

$$\begin{aligned}\begin{pmatrix}\text{probability that}\\ v \text{ lies in } dv\end{pmatrix} &= f_v(v)dv = \left(\int_0^{\pi}\int_0^{2\pi} g(v)\,v^2 \sin(\theta)d\phi d\theta\right)dv \\ &= g(v)v^2 dv \int_0^{\pi} \sin(\theta)d\theta \int_0^{2\pi} d\phi \qquad (9.4\text{-}3) \\ &= 4\pi v^2 g(v)dv\end{aligned}$$

The *speed probability distribution* or probability density (probability per unit length on the speed axis) is denoted by f_v:

$$f_v(v) = 4\pi v^2 g(v) = 4\pi v^2\left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_B T} \qquad (9.4\text{-}4)$$

Exercise 9.12

a. Argue that while ϕ ranges from 0 to 2π, θ ranges only from 0 to π to cover all possible angles.
b. Carry out the integrals in Eq. (9.4-3) that lead to the factor 4π in Eq. (9.4-3).

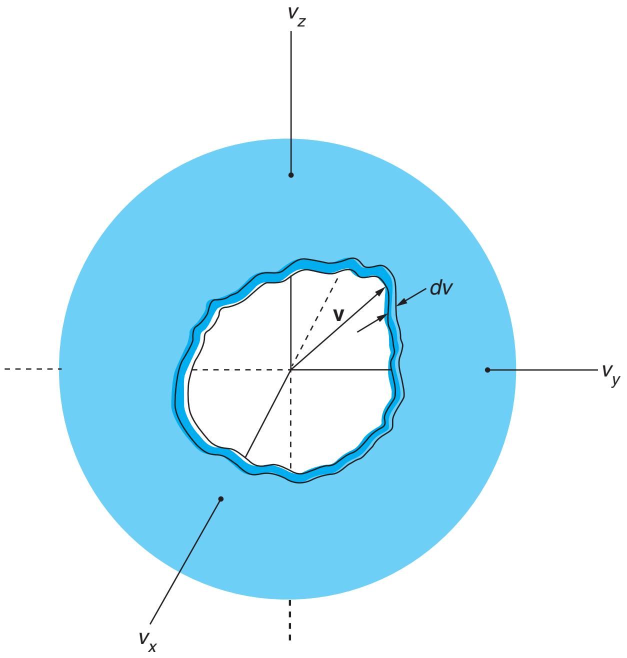

Figure 9.11 A Spherical Shell of Thickness *dv* in Velocity Space.

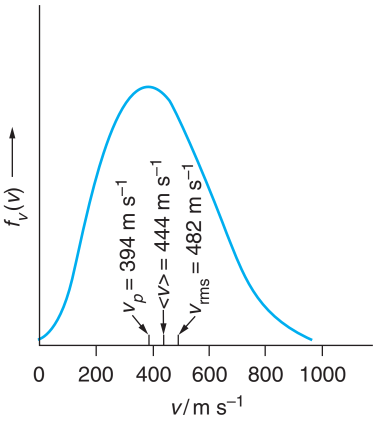

Figure 9.12 The Probability Distribution of Molecular Speeds for Oxygen Molecules at 298 K.

The result in Eq. (9.4-3) is a product of three factors. The factor $g(v)$ is the probability per unit volume in velocity space. The factor $4\pi v^2$ is the area of one surface of the spherical shell in Figure 9.11, and the factor dv is the thickness of the shell. The product $4\pi v^2 dv$ is the volume of the shell. The product $g(v)\,4\pi v^2 dv$ equals the probability per unit volume times the volume of the shell.

Figure 9.12 shows this probability distribution of speeds for oxygen molecules at 298 K. The most probable speed, the mean speed, and the root-mean-square speed are labeled on the speed axis. Compare this figure with Figure 9.7. The most probable value of a velocity component is zero, while the most probable speed is nonzero and the probability of zero speed is zero. This difference is due to the fact that the speed probability density is equal to the area of the spherical shell in velocity space (equal to $4\pi v^2$) times the probability density of the velocities lying in the spherical shell. Zero speed is improbable not because the velocity probability density is zero (it is at its maximum value), but because the area of the spherical shell vanishes at $v = 0$.

EXAMPLE 9.8

Obtain a formula for the *most probable speed*, v_p, by finding the value of the speed at which the first derivative of the probability density in Eq. (9.4-4) vanishes.

$$\frac{df_v}{dv} = \left(\frac{m}{2\pi k_B T}\right)^{3/2} 4\pi\left[2ve^{-mv^2/2k_BT} - v^2e^{-mv^2/2k_BT}\frac{2mv}{2k_BT}\right]$$

$$0 = e^{-mv^2/2k_BT}\left(2v - \frac{mv^3}{k_BT}\right) = e^{-mv^2/2k_BT}v\left(2 - \frac{mv^2}{k_BT}\right)$$

This first factor of this expression vanishes when $v \to \infty$, the second factor vanishes when $v = 0$, and the third factor vanishes when

$$v_p = \sqrt{\frac{2k_BT}{m}} \qquad (9.4\text{-}5a)$$

The extrema at $v = 0$ and at $v \to \infty$ correspond to minimum values of the speed probability distribution.

The most probable speed can also be written in terms of the molar mass, M, since $m = M/N_{Av}$ and $k_B = R/N_{Av}$:

$$v_p = \sqrt{\frac{2RT}{M}} \qquad (9.4\text{-}5b)$$

EXAMPLE 9.9

Find the most probable speed of oxygen molecules at 298 K.

$$v_p = \sqrt{\frac{2RT}{M}} = \left(\frac{2(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(298\text{ K})}{0.031999\text{ kg mol}^{-1}}\right)^{1/2} = 394\text{ m s}^{-1}$$

Exercise 9.13

Find the most probable speed of helium atoms at 298 K.

The *mean speed* is given by

$$\langle v\rangle = \int_0^\infty v f_v(v)\,dv = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\int_0^\infty v^3 e^{-mv^2/2k_BT}\,dv$$

$$\boxed{\langle v\rangle = \sqrt{\frac{8k_BT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}}} \tag{9.4-6}$$

Exercise 9.14

Look up the integral and verify Eq. (9.4-6).

EXAMPLE 9.10

Find the mean speed of oxygen molecules at 298 K.

$$\langle v\rangle = \sqrt{\frac{(8)\left(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}\right)(298\,\mathrm{K})}{\pi\left(0.0320\,\mathrm{kg\,mol^{-1}}\right)}} = 444\,\mathrm{m\,s^{-1}}$$

This speed corresponds to 993 miles per hour or 1598 kilometers per hour.

The *mean-square speed* is defined to be

$$\left\langle v^2\right\rangle = 4\pi\left(\frac{m}{2\pi k_BT}\right)^{3/2}\int_0^\infty v^4 e^{-mv^2/2k_BT}\,dv = \frac{3k_BT}{m} = \frac{3RT}{M} \tag{9.4-7}$$

where we have looked up the integral in the table of Appendix C. The *root-mean-square speed* v_{rms} is the square root of the mean-square speed:

$$\boxed{v_{\mathrm{rms}} = \left\langle v^2\right\rangle^{1/2} = \sqrt{\frac{3k_BT}{m}} = \sqrt{\frac{3RT}{M}}} \tag{9.4-8}$$

EXAMPLE 9.11

Find the value of the root-mean-square speed of oxygen molecules at 298 K.

$$v_{\mathrm{rms}} = \left(\frac{(3)\left(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}\right)(298\,\mathrm{K})}{\left(0.0320\,\mathrm{kg\,mol^{-1}}\right)}\right)^{1/2} = 482\,\mathrm{m\,s^{-1}}$$

Exercise 9.15

Find the mean speed and the root-mean-square speed of helium atoms at 298 K.

Exercise 9.16

Show that the two ratios $\langle v\rangle/v_p$ and v_{rms}/v_p have the same two values for all gases at all temperatures and find those values.

Exercise 9.17

Find the ratio of the probability densities for each of the following:

a. v_p and $\langle v\rangle$ for argon gas at 298.15 K.
b. v_p and $\langle v\rangle$ for argon gas at 500.0 K.
c. v_p and $\langle v\rangle$ for helium gas at 298.15 K.
d. v_p and v_{rms} for argon gas at 298.15 K.
e. v_p and v_{rms} for argon gas at 500.0 K.
f. v_p and v_{rms} for helium gas at 298.15 K.

PROBLEMS

Section 9.4: The Distribution of Molecular Speeds

9.20 The escape velocity at the earth's surface is $1.12 \times 10^4\ \text{m s}^{-1} = 2.5 \times 10^4$ miles per hour.

a. Find the fraction of helium atoms at 298 K having a speed exceeding v_{esc}. You can use the identity

$$\int_0^x t^2 e^{-at^2}\,dt = \frac{\sqrt{\pi}}{4a^{3/2}}\operatorname{erf}\left(\sqrt{a}x\right) - \frac{x}{2a}e^{-ax^2}$$

b. Find the temperature at which the mean speed of helium atoms equals the escape velocity.

9.21 **a.** Find the fraction of molecules that has speeds greater than $\sqrt{k_B T/m}$. Explain the relationship of this fraction to the fraction computed in Problem 9.17. You can use the identity in Problem 9.20.

b. Find the fraction of molecules that has kinetic energies greater than $k_B T/2$. Explain the relationship of this fraction to that of part a.

9.22 For N_2 molecules at 298.15 K, calculate the probability that v exceeds the speed of light, $2.997 \times 10^8\ \text{m s}^{-1}$ according to the Maxwell–Boltzmann probability distribution.

9.23 **a.** Find the temperature at which hydrogen atoms have an average translational energy equal to $1.0 \times 10^9\ \text{J mol}^{-1}$ (perhaps enough energy to initiate a fusion reaction).

b. What is the mean speed of hydrogen atoms at this temperature?

c. Find the temperature at which deuterium atoms have an average translational energy equal to $1.0 \times 10^9\ \text{J mol}^{-1}$.

9.24 Find the fraction of molecules in a gas that has:

a. speeds less than the most probable speed.

b. speeds between the most probable speed and the mean speed.

c. speeds between the most probable speed and the root-mean-square speed.

d. speeds greater than the root-mean-square speed.

e. Explain why these fractions are independent of the temperature and of the mass of the molecules.
Note: You can use the identity in Problem 9.20.

9.25 The speed of sound in air and in other gases is somewhat less than the mean speed of the gas molecules.

a. Explain why you think this is true.

b. How do you think that the speed of sound in air would depend on the temperature?

c. How do you think that the speed of sound in helium gas would compare with its speed in air? Why do you think a person's voice sounds different after a breath of helium?

9.26 Find the fraction of molecules in a gas that has speeds greater than 80.0% of the mean speed.

9.27 It is shown in the theory of hydrodynamics that the speed of sound, v_s, is given by

$$v_s^2 = \frac{V_m C_P}{M \kappa_T C_V}$$

where V_m is the molar volume, M is the molar mass, κ_T is the isothermal compressibility, C_P is the heat capacity at constant pressure, and C_V is the heat capacity at constant volume.

a. Find the speed of sound in N_2 gas at 298.15 K and 1.000 atm. Look up the value of $C_{P,m}$ in the appendix. Assume that V_m and κ_T can be approximated by assuming that N_2 is an ideal gas. Look up the speed of sound in air and compare it with your answer.

b. Assume that $C_{P,m}$ of a gas can be approximated by $\frac{7}{2}R$. Find a formula for the speed of sound in a gas as a function of temperature and find the speed of sound in N_2 gas at 298.15 K and 1.000 atm.

c. Find the speed of sound in helium at 2981.15 K and 1.000 atm.

d. Find the ratio of the speed of sound to the mean speed of N_2 molecules at 298.15 K.

e. Find the fraction of N_2 molecules at 298.15 K that have speeds greater than the speed of sound.

9.28 Find the value of each of the ratios:

a. The mean speed of helium atoms at 298.15 K divided by the mean speed of oxygen molecules at 298.15 K.

b. The root-mean-square speed of helium atoms at 373.15 K divided by the mean speed of helium atoms at 373.15 K.

c. The mean speed of nitrogen molecules at 400 K divided by the mean speed of nitrogen molecules at 200 K.

d. The mean speed of nitrogen molecules at 400 K divided by the most probable speed of nitrogen molecules at 400 K.

9.29 **a.** The standard deviation of an arbitrary probability distribution for the variable u is defined by Eq. (9.3-34). Find the expression for the standard deviation for the distribution of speeds of gas molecules.

b. Find the value of this standard deviation for oxygen molecules at 298 K.

9.30 Find the ratio of the mean speeds of O_2 and O_3 molecules:

a. at 298 K

b. at 1000 K

9.31 If oxygen molecules had mass 32 g instead of 32 amu, what would their mean speed be at 298 K?

9.32 **a.** Find a general expression for the median speed of molecules in a dilute gas. *Hint:* See the identity in Problem 9.20. Your expressions will contain a constant that you will have to evaluate numerically.

b. Find the median speed for oxygen molecules at 298 K.

9.5 The Pressure of a Dilute Gas

We now want to show that our model gas of point-mass particles obeys the ideal gas law. We assume that the box confining our model system is rectangular with walls that are perpendicular to the coordinate axes and that the walls are smooth, slick, flat, and impenetrable. A collision of a molecule with such a wall is called a *specular collision*, which means: (1) It is elastic. That is, the kinetic energy of the molecule is the same before and after the collision. (2) The only force exerted on the particle is perpendicular to the wall.

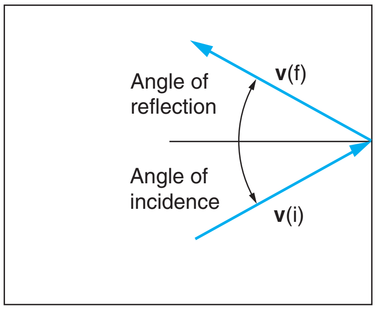

Figure 9.13 The Trajectory of a Particle Colliding Specularly with a Wall.

Consider a particle that strikes the wall at the right end of the box (perpendicular to the y axis), as shown in Figure 9.13. The values of v_x and v_z do not change because no force is exerted in these directions. Because the kinetic energy does not change, v_y^2 does not change, although the sign of v_y does change. Let $\mathbf{v}(i)$ be the initial velocity and $\mathbf{v}(f)$ be the final velocity:

$$v_x(f) = v_x(i), \qquad v_y(f) = -v_y(i), \qquad v_z(f) = v_z(i) \tag{9.5-1}$$

As the particle strikes the wall, the force exerted on the wall rises suddenly and drops to zero just as suddenly. This makes the force hard to analyze mathematically, so we deal with its time average. This seems physically reasonable, because any measuring instrument requires a period of time, called the *response time*, to adjust to a sudden change in the pressure. Consider the force exerted on the particle by the wall, which by Newton's third law is the negative of the force exerted on the wall by the particle. The time average of the y component of the force on the particle over a period of time from 0 to τ is given by

$$\langle F_y \rangle = \frac{1}{\tau}\int_0^{\tau} F_y(t)dt \quad \text{(definition of the time average of } F_y) \tag{9.5-2}$$

We use the notation $\langle \cdots \rangle$ to denote either a time average or a mean value. You must determine from the context which type of average is meant in a particular case.

We choose the period of time τ so that it includes the time at which the particle strikes the wall. From Newton's second law, Eq. (9.2-4), the force equals the mass times the acceleration:

$$\begin{aligned}\langle F_y \rangle &= \frac{1}{\tau}\int_0^{\tau} F_y dt = \frac{1}{\tau}\int_0^{\tau} m\frac{d^2y}{dt^2}dt = \frac{1}{\tau}\int_0^{\tau} m\frac{dv_y}{dt}dt = \frac{m}{\tau}\int_{v(0)}^{v(\tau)} dv_y \\ &= \frac{m}{\tau}\left[v_y(\tau) - v_y(0)\right] = \frac{m}{\tau}\left[v_y(f) - v_y(i)\right]\end{aligned} \tag{9.5-3}$$

Because $v_y(f) = -v_y(i)$,

$$\langle F_y \rangle = -\frac{2mv_y(i)}{\tau} \tag{9.5-4}$$

By Newton's third law the force on the wall, $\mathbf{F}_{\text{wall}}$, is equal to $-\mathbf{F}$, so that the average value of the force on the wall due to one particle is

$$\langle F_{\text{wall},y} \rangle = -\langle F_y \rangle = \frac{2mv_y}{\tau} \tag{9.5-5}$$

We use only initial velocities from now on and omit the (i) label.

The total time-average force on the area $\mathscr{A}$ of the wall is the sum of the contributions from all particles that strike this area in time τ. Consider first the particles whose velocities lie in the range $dv_x dv_y dv_z$, abbreviated by $d^3\mathbf{v}$. The fraction of all particles whose velocities lie in this range is

$$\text{(fraction)} = g(\mathbf{v})dv_x dv_y dv_z = g(\mathbf{v})d^3\mathbf{v} \tag{9.5-6}$$

where $\mathbf{v}$ is a velocity in the range $d^3\mathbf{v}$. All of the particles with velocities in this range are moving in the same direction with the same speed (within infinitesimal ranges). Those particles in this set that will strike an area $\mathscr{A}$ on the wall are contained in a prism with base area $\mathscr{A}$ and sides that are parallel to the direction of motion of the particles, as shown in Figure 9.14.

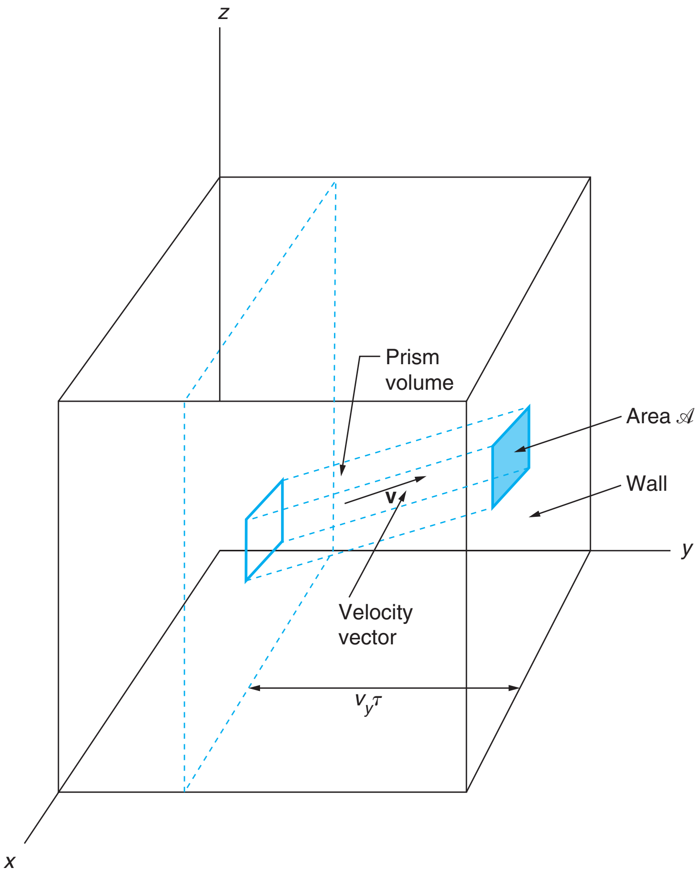

Figure 9.14 The Prism That Contains Molecules of a Certain Velocity That Will Strike Area A in Time τ.

The particles that are no farther from the wall in the y direction than a distance equal to $v_y\tau$ will strike the wall during the time interval τ (from the familiar relation, distance = rate × time). The distance in the y direction, not the distance along the surface of the prism, must be used because we are considering v_y, not the speed. The volume of the prism is equal to the area of its base times its altitude:

$$V_{\text{prism}} = \mathscr{A} v_y \tau \tag{9.5-7}$$

We assume that our system is uniform. The *number density*, $\mathscr{N}$, in any part of the system is equal to N/V where N is the number of particles and V is the volume of the system. The number of particles in the prism is

$$(\text{number in prism}) = \frac{N}{V}\mathscr{A} v_y \tau = \mathscr{N}\mathscr{A} v_y \tau \tag{9.5-8}$$

The number in the prism with velocities in the specified range is

$$\begin{pmatrix}\text{number in prism} \\ \text{with velocities in } d^3v \\ \text{striking } \mathscr{A} \text{ in time } \tau\end{pmatrix} = \mathscr{N}\mathscr{A} v_y \tau g(v)\, dv_x\, dv_y\, dv_z \tag{9.5-9}$$

Let the total time-average force on $\mathscr{A}$ be denoted by $\langle F_{\mathscr{A}} \rangle$. Each particle makes a contribution to this force that is given by Eq. (9.5-5), so that the collection of particles with velocities in the given range makes the contribution

$$\left(\begin{array}{l}\text{contribution to } \langle F_{\mathscr{A}} \rangle \text{ due} \\ \text{to particles with velocities} \\ \text{in the given range } dv_x\, dv_y\, dv_z\end{array}\right) = \frac{2mv_y}{\tau} = \mathscr{N}\mathscr{A}\, v_y \tau g(v)\, dv_x\, dv_y\, dv_z$$
$$= 2m\mathscr{N}\mathscr{A}\, v_y^2 g(v)\, dv_x\, dv_y\, dv_z \qquad (9.5\text{-}10)$$

Notice that τ cancels out of this equation. We now add up the contributions for molecules with different velocities by integrating over the velocity components. Only molecules with positive values of v_y will strike the wall at the right end of the box, whereas the components parallel to the wall can be positive or negative. The total time-average force on $\mathscr{A}$ is

$$\langle F_{\mathscr{A}} \rangle = 2m\mathscr{N}\mathscr{A} \int_{-\infty}^{\infty} \int_{0}^{\infty} \int_{-\infty}^{\infty} v_y^2 g(v)\, dv_x\, dv_y\, dv_z$$
$$= m\mathscr{N}\mathscr{A} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} v_y^2 g(v)\, dv_x\, dv_y\, dv_z \qquad (9.5\text{-}11)$$

The integrand is an *even function* of v_y, which means that if v_y is replaced by $-v_y$, the integrand is unchanged. The value of the integral over v_y from 0 to ∞ equals half of that of the integral from $-\infty$ to ∞, so we have replaced the lower limit by $-\infty$ and divided by 2. This integral is the same as the integral that gives the mean value of v_y^2, which equals $\langle v^2 \rangle /3$, so we can write

$$\langle F_{\mathscr{A}} \rangle = 2m\mathscr{N}\mathscr{A} \frac{1}{2} \left\langle v_y^2 \right\rangle = 2m\mathscr{N}\mathscr{A} \frac{1}{6} \left\langle v^2 \right\rangle$$
$$= \frac{1}{3} m\mathscr{N}\mathscr{A} \frac{3k_{\mathrm{B}}T}{m} = \mathscr{N}\mathscr{A} k_{\mathrm{B}}T \qquad (9.5\text{-}12)$$

The pressure is the force per unit area so that

$$P = \frac{\langle F_{\mathscr{A}} \rangle}{\mathscr{A}} = \mathscr{N} k_{\mathrm{B}}T = \frac{Nk_{\mathrm{B}}T}{V} = \frac{nRT}{V} \qquad (9.5\text{-}13)$$

We have derived the ideal gas law for our model system, so we believe that it does resemble a real dilute gas. It is also possible to assume that our system obeys the ideal gas law and then to derive the expression for the energy in Eq. (9.3-24).

EXAMPLE 9.12

For an O_2 molecule moving with $v_y = 444\ \mathrm{m\,s^{-1}}$, find the average impulse (force multiplied by the time over which the force is exerted) on a wall perpendicular to the y axis if the particle collides with the wall.

$$\langle F_y \rangle \tau = 2mv_y(i) = \frac{(2)(0.0320\ \mathrm{kg\,mol^{-1}})(444\ \mathrm{m\,s^{-1}})}{6.022 \times 10^{23}\ \mathrm{mol^{-1}}}$$
$$= 4.72 \times 10^{-23}\ \mathrm{kg\,m\,s^{-1}} = 4.72 \times 10^{-23}\ \mathrm{N\,s}$$

Exercise 9.18

Find the number of oxygen molecules with $v_y = 444\,\mathrm{m\,s^{-1}}$ that must strike an area of $1.000\,\mathrm{m}^2$ in 1.000 s in order for a force of 101325 N to be exerted on the area.

The Pressure of a Mixture of Gases

Now consider a model system that contains a mixture of several gaseous substances, each one represented by point-mass particles. We denote the number of substances by c. We continue to assume that the molecules have zero size and do not exert forces on each other, so the molecules of each substance will move just as though the other substances were not present. Because the pressure is the sum of the effects of individual molecules, the total pressure is the sum of the pressures exerted by each set of molecules:

$$P = P_1 + P_2 + P_3 + \cdots + P_c \tag{9.5-14}$$

where P_1 is the *partial pressure* of substance 1, defined to be the pressure that this substance would exert if it were alone in the container, and similarly for the other substances. Note that the partial pressure does not depend on the mass of the particles. Equation (9.5-14) is *Dalton's law of partial pressures*. Because each gas obeys the ideal gas law, the mixture of gases also obeys the ideal gas law,

$$P = \frac{n_1RT}{V} + \frac{n_2RT}{V} + \cdots + \frac{n_cRT}{V} = (n_1 + n_2 + \cdots + n_c)\frac{RT}{V} = \frac{nRT}{V} \tag{9.5-15}$$

where n is the total amount of all gases:

$$n = n_1 + n_2 + \cdots + n_c \tag{9.5-16}$$

PROBLEMS

Section 9.5: The Pressure of a Dilute Gas

9.33 In the discussion of this section, it was assumed that the system was contained in a rectangular box. Explain why the pressure of a gas is independent of the shape of the container.

9.34 For a helium atom moving with $v_y = 1255\,\mathrm{m\,s^{-1}}$, find the average impulse (force multiplied by the time over which the force is exerted) on a wall perpendicular to the y axis if the particle collides with the wall. Compare your value with that of Example 9.12. Comment on the fact that $444\,\mathrm{m\,s^{-1}}$ is the mean speed of O_2 molecules at 298.15 K while $1255\,\mathrm{m\,s^{-1}}$ is the mean speed of He atoms at 298.15 K.

9.35 Give a verbal explanation of the fact that the pressure of an ideal gas does not depend on the mass of the molecules.

9.36 Show that in a specular wall collision on a flat wall, the angle of incidence and the angle of reflection are equal. The angle of incidence is the angle between the line perpendicular to the surface and the initial velocity, and the angle of reflection is the angle between the line perpendicular to the surface and the final velocity.

9.37 **a.** Estimate the total force of the atmosphere on the outer surface of your body.

b. Estimate the mass (in pounds and in kilograms) such that its gravitational force at the surface of the earth is equal to the force in part a.

9.38 Derive the ideal gas law without using the velocity distribution function. *Hint:* Start with Eqs. (9.3-28) and (9.5-11).

9.39 Estimate the mass of the earth's atmosphere. Calculate the area of the earth. Make an estimate of the mean barometric pressure and the mean temperature of the atmosphere. Look up the mass of the earth and calculate the ratio of the atmosphere's mass to the earth's mass.

9.6 Effusion and Wall Collisions

Effusion is a process by which molecules of a gas pass through a small hole into a vacuum. The hole must be small enough so that the gas does not flow through the hole as a fluid, but passes as individual molecules. According to *Graham's law of effusion*, at a given temperature and a given pressure the rate of effusion of a gas is inversely proportional to the square root of its density.

Graham's law is named for Thomas Graham, 1805–1869, a British chemist who not only studied diffusion and effusion, but also determined the chemical formulas of the various species formed from phosphoric acid in aqueous solution.

Our analysis of effusion will be similar to that of the pressure in Section 9.5 except that we will now compute the number of molecules striking an area $\mathscr{A}$ instead of the force exerted on this area. If this area is a hole in the wall, we obtain the rate of effusion. If the area is a section of the wall, we obtain the rate of wall collisions. The number of molecules with velocities in the velocity interval $dv_x dv_y dv_z$ that will strike the area $\mathscr{A}$ in time τ is given by Eq. (9.5-9):

$$(\text{number striking } \mathscr{A} \text{ in time } \tau) = \mathcal{N}\mathscr{A} v_y \tau g(v) dv_x dv_y dv_z \tag{9.6-1}$$

The total number of molecules striking the area $\mathscr{A}$ in the time interval τ is

$$\begin{aligned}\begin{pmatrix}\text{total number}\\ \text{striking area}\\ \mathscr{A} \text{ in time } \tau\end{pmatrix} &= \mathcal{N}\mathscr{A}\tau \int_{-\infty}^{\infty}\int_{0}^{\infty}\int_{-\infty}^{\infty} v_y g(v)\, dv_x dv_y dv_z \\ &= \mathcal{N}\mathscr{A}\left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{3/2}\tau \int_{-\infty}^{\infty}\int_{0}^{\infty}\int_{-\infty}^{\infty} v_y e^{-mv^2/2k_\mathrm{B}T} dv_x dv_y dv_z \end{aligned}\tag{9.6-2}$$

This triple integral can be factored:

$$\begin{aligned}&\int_{-\infty}^{\infty}\int_{0}^{\infty}\int_{-\infty}^{\infty} v_y e^{-mv^2/2k_\mathrm{B}T} dv_x dv_y dv_z \\ &= \int_{-\infty}^{\infty} e^{-mv_x^2/2k_\mathrm{B}T} dv_x \int_{0}^{\infty} v_y e^{-mv_y^2/2k_\mathrm{B}T} dv_y \int_{-\infty}^{\infty} e^{-mv^2/2k_\mathrm{B}T} dv_z\end{aligned}$$

The integrations over v_x and v_z give factors of $\left(\frac{2\pi k_\mathrm{B}T}{m}\right)^{1/2}$ so that

$$\begin{pmatrix}\text{total number}\\ \text{striking area}\\ \mathscr{A} \text{ in time } \tau\end{pmatrix} = \mathcal{N} A \left(\frac{m}{2\pi k_\mathrm{B}T}\right)^{1/2}\tau \int_{0}^{\infty} v_y e^{-mv_y^2/2k_\mathrm{B}T} dv_y \tag{9.6-3}$$

The integral in this equation can be performed by the method of substitution. We let $w = v_y^2$, so that the integral becomes

$$\begin{aligned}\int_{0}^{\infty} v_y e^{-mv_y^2/2k_\mathrm{B}T} dv_y &= \frac{1}{2}\int_{0}^{\infty} e^{-mw/2k_\mathrm{B}T} dw \\ &= \frac{1}{2}\frac{2k_\mathrm{B}T}{m}\left(-e^{-mw/2k_\mathrm{B}T}\right)\Big|_{0}^{\infty} = \frac{k_\mathrm{B}T}{m}\end{aligned}\tag{9.6-4}$$

Therefore

$$\begin{pmatrix}\text{total number}\\ \text{striking area}\\ \mathscr{A}\text{ in time }\tau\end{pmatrix} = \mathscr{N}\mathscr{A}\tau\left(\frac{k_BT}{2\pi m}\right)^{1/2} = \frac{1}{4}\mathscr{N}\mathscr{A}\tau\left(\frac{8k_BT}{\pi m}\right)^{1/2} = \frac{1}{4}\mathscr{N}\mathscr{A}\tau\langle v\rangle \qquad (9.6\text{-}5)$$

The number of particles that strike the area $\mathscr{A}$ in time τ is proportional to the area $\mathscr{A}$, proportional to the length of time τ, proportional to $\mathscr{N}$, the number of particles per unit volume, and proportional to the mean speed of the particles. The number of molecules striking unit area per unit time is denoted by ν:

$$\nu = \frac{1}{4}\mathscr{N}\langle v\rangle = \frac{\mathscr{N}}{4}\left(\frac{8k_BT}{\pi m}\right)^{1/2} \qquad (9.6\text{-}6)$$

This equation for the rate of wall collisions also gives the rate of effusion per unit area in the case of a small hole in the wall. The effusion rate predicted by Eq. (9.6-6) is inversely proportional to the square root of the mass of the particles, and thus to the square root of the density, in agreement with Graham's law of effusion.

EXAMPLE 9.13

Estimate the number of molecules of air striking a person's eardrum in 1.00 s at 298 K and 1.00 atm. Assume air to be 79 mol% nitrogen and 21 mol% oxygen by moles, and assume that the area of the eardrum is 0.50 cm^2.

Solution

$\langle v(O_2)\rangle = 444\ \text{m s}^{-1}$ from Example 9.4 and $\langle v(N_2)\rangle = 475\ \text{m s}^{-1}$ by a similar calculation.

$$\mathscr{N}(N_2) = N(N_2)/V = P(N_2)/k_BT$$
$$= \frac{\left(101325\ \text{N m}^{-2}\ \text{atm}^{-1}\right)(0.79\ \text{atm})}{(1.3807\times10^{-23}\ \text{J K}^{-1})(298\ \text{K})} = 1.9\times10^{25}\ \text{m}^{-3}$$

where $P(N_2)$ is the partial pressure of N_2, $N(N_2)$ is the number of N_2 molecules and $\mathscr{N}(N_2)$ is the number density of N_2 molecules.

$$\mathscr{N}(O_2) = N(O_2)/V = 5.2\times10^{24}\ \text{m}^{-3}\ \text{by a similar calculation}$$
$$\nu(N_2) = \frac{1}{4}(1.9\times10^{25}\ \text{m}^{-3})(475\ \text{m s}^{-1}) = 2.3\times10^{27}\ \text{m}^{-2}\ \text{s}^{-1}$$
$$\nu(O_2) = 5.7\times10^{26}\ \text{m}^{-2}\ \text{s}^{-1}\ \text{by a similar calculation}$$
$$(\text{number per second}) = \nu(N_2) + \nu(O_2)(5.0\times10^{-5}\ \text{m}^2) = 1.4\times10^{23}\ \text{s}^{-1}$$

Exercise 9.19

a. Estimate the number of air molecules striking the palm of your hand in 24 hours.

b. A certain solid catalyst has a surface area of 55 m^2 per gram of catalyst. A mixture of gases with carbon monoxide mole fraction equal to 0.0050 passes over the catalyst at 350 K and 1.00 atm. Find the amount of CO in moles striking 1 gram of the catalyst per second.

PROBLEMS

Section 9.6: Effusion and Wall Collisions

9.40 Assume that one of the doors of a classroom is 36 inches by 80 inches (91 cm by 203 cm). Find the number of N_2 molecules and the number of moles of N_2 molecules striking one side of the door in 90 minutes. Assume that the partial pressure of N_2 is 0.78 atm and that the temperature is 25°C.

9.41 The equilibrium vapor pressure of a substance is the pressure of the vapor phase at equilibrium with the solid or liquid phase. The vapor pressure of solid tungsten (wolfram) at 4763 K is equal to 10.0 torr. A sample of solid at equilibrium with its vapor is maintained at this temperature in a container that has a circular hole of diameter 0.100 mm leading to a vacuum chamber. Find the loss of mass through the hole in 1.00 hour.

9.42 **a.** The equilibrium vapor pressure of water at 25°C is equal to 23.8 torr. If the relative humidity is 50.0%, calculate the number of water molecules per second striking an area of 1.00 cm^2 at 25°C.

b. Calculate the number of water molecules per second leaving an area of 1.00 cm^2 at 25°C. Calculate the net loss of mass per second at an area of 1.00 cm^2 at 25°C if the relative humidity is 50.0%.

9.43 In a certain vacuum system, a pressure of 1.0×10^{-10} torr is achieved. Assume that the air inside the vacuum system is 80 mol% N_2 and 20 mol% O_2.

a. Find the number density in molecules per cubic meter for each substance if the temperature is 298 K.

b. Find the number of molecules striking 1.00 cm^2 of wall per second at 298 K.

9.44 A spherical vessel of radius 10.0 cm contains argon at 0.980 atm pressure and 298.15 K. Calculate the number of argon atoms striking the inner surface of the container per second.

9.45 Assume that the mole fraction of carbon dioxide in the earth's atmosphere is 0.000306. The area of the earth's oceans is roughly $3.61 \times 10^8\ \mathrm{km}^2$. Estimate the number of moles of carbon dioxide molecules striking the earth's oceans in 1.00 s.

9.46 Calculate the number of N_2 molecules striking an area of 1.00 m^2 in 1.00 s if the pressure is 1.00 bar and the temperature is

a. 78 K

b. 298 K

c. 1000.0 K

9.47 A container with a volume of 1.00 L contains carbon monoxide gas, and a sample of a solid catalyst is suddenly placed into the container.

a. If the total surface area of the catalyst is 1.00 m^{-2}, and if the initial rate of collisions of CO molecules with the catalysts surface is $6.0 \times 10^{23}\ \mathrm{s}^{-1}$, find the initial pressure of the carbon monoxide.

b. If every CO molecule that strikes the catalyst surface sticks to the surface, how long will it take for the pressure of CO to drop to 50.0% of its initial value? Assume that enough surface sites are available for this to be the case.

9.48 Assume that in a certain automobile the exhaust gas has a carbon monoxide mole fraction of 0.0140 and a temperature of 500 K when it reaches the catalytic converter, which contains a solid platinum catalyst coated on a ceramic material with a large surface area. Calculate the number of carbon monoxide molecules and the amount of carbon monoxide in moles that strikes 50.00 m^2 of catalyst surface in 1.000 minute.

9.49 A 1.000-liter container full of neon gas and maintained at 298 K is placed in a large vacuum chamber, and a circular hole with a diameter of 20 micrometers is punched in the container. If the initial pressure in the container is 1013 Pa, find the time required for half of the neon gas to effuse from the container. *Hint:* Remember that the pressure will be dropping as the gas escapes.

9.50 Estimate the time required for a bicycle tire to go flat as a result of a circular hole of 50 μm diameter. State your assumptions.

9.7 The Model System with Potential Energy

Until now, we have assumed that the particles in our model gas have no forces acting on them except those due to collisions with the container. We now modify our model to include additional forces on the particles.

One-Body Forces

A one-body force is independent of the locations of other particles. Electrostatic forces on a charged particle due to an external electric field are one-body forces. Near the surface of the earth the force of gravity on a particle is also a one-body force. This gravitational force on an object corresponds to a potential energy

$$\mathcal{V}_g = mgz \tag{9.7-1}$$

where z is the vertical coordinate of the particle and m is its mass. The acceleration due to gravity is denoted by g. It is slightly dependent on latitude and is nearly equal to $9.80\,\mathrm{m\,s^{-2}}$ at the latitude of Washington, DC, USA, and Seoul, South Korea. We will use this value in our examples. The total energy of a particle subject to a gravitational force near the surface of the earth is

$$\varepsilon = \frac{m}{2}(v_x^2 + v_y^2 + v_z^2) + \mathcal{V}(x, y, z) = \frac{m}{2}v^2 + mgz \tag{9.7-2}$$

We now assert without proof that the Boltzmann probability distribution holds for this total energy:

$$\begin{pmatrix}\text{probability of a} \\ \text{state of energy } \varepsilon\end{pmatrix} \propto e^{-\varepsilon/k_\mathrm{B}T}dv = \exp\left(-\frac{mv^2/2 + \mathcal{V}}{k_\mathrm{B}T}\right) \tag{9.7-3}$$

where the symbol $\propto$ stands for "is proportional to."

EXAMPLE 9.14

Assume that the earth's atmosphere has a constant temperature of 298 K (not an accurate assumption). Estimate the pressure at 8900 m above sea level (roughly the altitude of Mount Everest). Assume that air is a single ideal gas with a molar mass of $0.029\,\mathrm{kg\,mol^{-1}}$.

Solution

Representing the high-altitude state as 2 and the sea-level state as 1, the probability ratio is

$$\frac{p_2}{p_1} = \frac{\mathcal{N}_2}{\mathcal{N}_1} = \frac{P_2}{P_1} = \frac{e^{-(\mathcal{K}_2 + \mathcal{V}_2)/k_\mathrm{B}T}}{e^{-(\mathcal{K}_1 + \mathcal{V}_1)/k_\mathrm{B}T}}$$

The average kinetic energy of a molecule depends only on the temperature, which we have assumed to be independent of altitude. The kinetic energy terms will cancel after averaging:

$$\frac{P_2}{P_1} = \exp\left(\frac{\mathcal{V}_2 - \mathcal{V}_1}{k_\mathrm{B}T}\right)$$

Assuming that the ideal gas law is valid, the pressure is proportional to the number of molecules per unit volume at constant temperature and is proportional to the population given by the Boltzmann distribution.

$$\mathcal{V}_2 - \mathcal{V}_1 = \frac{\left(0.029\,\mathrm{kg\,mol^{-1}}\right)\left(9.80\,\mathrm{m\,s^{2}}\right)(8900\,\mathrm{m})}{6.022 \times 10^{23}\,\mathrm{mol^{-1}}} = 4.2 \times 10^{-21}\,\mathrm{J}$$

If $P = 1.00\,\mathrm{atm}$ at sea level, and if we assume that air is an ideal gas:

$$\frac{P}{1.00\,\mathrm{atm}} = \exp\left(\frac{-4.2 \times 10^{-21}\,\mathrm{J}}{(1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}})(298\,\mathrm{K})}\right) = 0.36$$

Exercise 9.20

The altitude of Pike's Peak is 14,110 ft. Estimate the barometric pressure on Pike's Peak on a winter day when the temperature is −15°F.

Intermolecular Forces

We now modify our model to include two-body intermolecular forces. That is, the force on particle 1 due to particle 2 is unaffected by the positions of particle 3, particle 4, and so on. This is a good approximation for gases, and a fair approximation for liquids.[3] We assume also that the intermolecular forces are independent of the molecules' velocities, so that they can be derived from a potential energy. With our assumption the intermolecular potential energy $\mathscr{V}$ is a sum of two-body contributions.

$$\mathscr{V} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} u(r_{ij}) \tag{9.7-4}$$

The function $u(r_{ij})$ is called the *pair potential energy function* of particles i and j. We consider only monatomic gases, for which u depends only on r_{ij}, the distance between the centers of particles i and j. The limits on the double sum in Eq. (9.7-4) are chosen so that the contribution of a single pair of particles is counted only once.

The Lennard-Jones potential is named for J. E. Lennard-Jones, 1894–1954, a prominent British theoretical chemist.

A common approximate representation for the pair potential function is the *Lennard-Jones 6–12 potential function*:

$$u_{\mathrm{LJ}}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{9.7-5}$$

The parameter ε is equal to the depth of the minimum in the curve and the parameter σ is equal to the intermolecular separation at which the potential energy is equal to zero. The designation 6–12 denotes the choice of the exponents in the formula. This function is sometimes referred to simply as the Lennard-Jones potential function and is depicted in Figure 9.15. Table A.14 of Appendix A gives values of σ and ε for a few substances. The minimum in the function occurs at $r = 2^{1/6}\sigma$. If r is greater than this value, there is an attraction, and if r is smaller than this value, there is a repulsion. More accurate potential energy functions have been obtained, but the Lennard-Jones potential function remains widely used.[4]

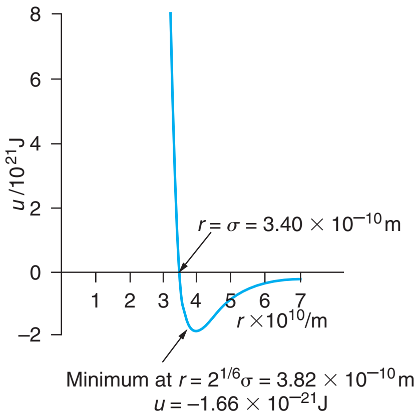

Figure 9.15 The Lennard-Jones Representation of the Intermolecular Potential of a Pair of Argon Atoms.

EXAMPLE 9.15

a. Show that for the Lennard-Jones potential,

$$u_{\mathrm{LJ}}(\sigma) = 0 \tag{9.7-6}$$

b. Show that the value of r at the minimum in the Lennard-Jones potential is

$$r_{\mathrm{min}} = 2^{1/6}\sigma = (1.12246)\sigma \tag{9.7-7}$$

---

[3] D. R. Williams and L. J. Schaad, *J. Chem. Phys.*, **47**, 4916 (1967). See C. A. Parish and C. E. Dykstra, *J. Chem. Phys.*, **101**, 7618 (1994) for a three-body potential for helium atoms.

[4] See for example D. E. Moon, *J. Chem. Phys.*, **100**, 2838 (1994).

Solution

a.

$$u(\sigma) = 4\varepsilon\left[\left(\frac{\sigma}{\sigma}\right)^{12} - \left(\frac{\sigma}{\sigma}\right)^{6}\right] = 4\varepsilon(1-1) = 0$$

b. At an extremum, the derivative du/dr is equal to zero:

$$\frac{du}{dr} = 4\varepsilon\left[-12\sigma^{12}\frac{1}{r^{13}} + 6\sigma^{6}\frac{1}{r^{7}}\right] = 0$$

$$0 = 4\varepsilon\left(6\sigma^{6}\frac{1}{r^{7}}\right)\left(-\frac{2\sigma^{6}}{r^{6}} + 1\right)$$

This expression equals zero if $r \to \infty$ or if

$$r = 2^{1/6}\sigma = 1.12246\sigma$$

The minimum is at $r = r_{\text{min}} = 2^{1/6}\sigma$. There is a relative maximum at $r \to \infty$.

Exercise 9.21

a. Show that

$$u_{\text{LJ}}(r_{\text{min}}) = -\varepsilon \tag{9.7-8}$$

b. The force in the r direction is given by $-du/dr$. Show that the force on one particle due to another particle at distance r is

$$F_{\text{r}} = 4\varepsilon\left(12\frac{\sigma^{12}}{r^{13}} - 6\frac{\sigma^{6}}{r^{7}}\right) \tag{9.7-9}$$

c. Show that $F_{\text{r}} = 0$ if $r = 2^{1/6}\sigma$.

In a liquid or solid the average separation of the molecules from their nearest neighbors is approximately equal to the intermolecular distance at the minimum in u. Energy is required either to compress a liquid or solid or to pull its molecules away from each other, which results in a nearly constant volume. In a gas at ordinary pressures, the average nearest-neighbor distance is roughly 10 times as great as in a liquid, and the average intermolecular forces are relatively small.

A simpler but less realistic representation of the pair potential function is the *square well potential*

$$u(r) = \begin{cases} \infty & (0 < r < d) \\ -u_0 & (d < r < c) \\ 0 & (r > c) \end{cases} \tag{9.7-10}$$

This representation is shown in Figure 9.16. If optimum values of d and c are chosen, this function can approximate the actual intermolecular potential for some purposes.

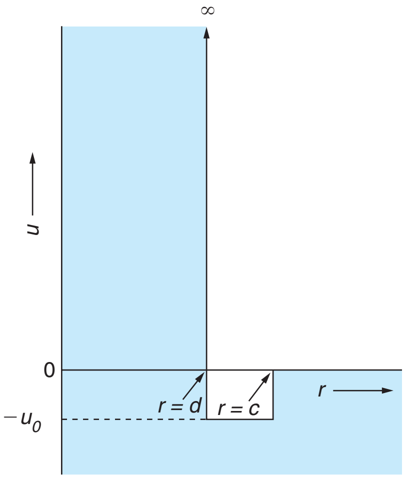

Figure 9.16 The Square-Well Representation of the Intermolecular Potential of a Pair of Atoms.

PROBLEMS

Section 9.7: The Model System with Potential Energy

9.51 **a.** Construct an accurate graph of the Lennard-Jones 6–12 potential function for two argon atoms.

b. Find the value of r for which $u_{\mathrm{LJ}}(r) = \frac{3}{2}k_{\mathrm{B}}T$ for 273 K, 373 K, and 473 K. Compare your values with the effective hard-sphere diameter of argon at these temperatures from Table A.15.

9.52 Find the value of the Lennard-Jones representation of the interatomic potential function of argon at interatomic distances equal to each of the effective hard-sphere diameters of argon at different temperatures in Table A.15 of Appendix A. Explain the temperature dependence of your values.

9.53 **a.** Estimate the average distance between nearest-neighbor atoms in gaseous argon at 1.000 atm and 87.5 K, its normal boiling temperature. Do this by calculating the side of a cube containing one argon atom.

b. Calculate the value of the Lennard-Jones potential function for two argon atoms at this separation.

c. Calculate the minimum value of the Lennard-Jones potential function for two argon atoms. Calculate the ratio of the value in part b to this value.

9.54 Another approximate representation for intermolecular pair potentials is the *exponential-6 potential function*

$$u(r) = be^{-ar} - cr^{-6}$$

where a, b, and c are parameters to be chosen to fit data for each substance. The function has a nonphysical maximum and approaches negative infinity as r approaches zero. For values of r smaller than the value at the maximum, this expression must be replaced by a different representation. The usual procedure is to define u to be positively infinite in this region. Find the values of a, b, and c in the 6-exponential representation of the interatomic potential of argon that matches the Lennard-Jones representation such that $c = 4\varepsilon\sigma^6$ and such that the minimum is at the same value of r as the minimum of the Lennard-Jones representation.

9.55 Assume that air is 80% nitrogen and 20% oxygen, by moles, at sea level. Calculate the percentages and the total pressure at an altitude of 20 km, assuming a temperature of −20°C at all altitudes. Calculate the percent error in the total pressure introduced by assuming that air is a single substance with molar mass 0.029 kg mol^{-1}.

9.56 Calculate the difference in the density of air at the top and bottom of a vessel 1.00 m tall at 273.15 K at sea level. State any assumptions.

9.57 Estimate the difference in barometric pressure between the ground floor of a building and the 41st floor, assumed to be 400 feet higher. State any assumptions.

9.58 A helium-filled balloon is filled with helium at sea level and at a temperature of 20°C. The design of the balloon is such that the pressure inside the balloon remains equal to the external atmospheric pressure (the volume can change).

a. If the volume of the balloon at sea level is 1000 m^3 find the mass of helium required to fill the balloon and the mass that can be lifted (including the mass of the balloon).

b. Assuming that the atmosphere has a uniform temperature, find the volume of the balloon at an altitude of 10.0 km and find the mass that it can lift, assuming that the same amount of helium is in the balloon as in part a.

9.8 The Hard-Sphere Gas

The simplest representation of the pair potential function is the *hard-sphere potential*:

$$u(r) = \begin{cases} \infty & (0 < r < d) \\ 0 & (r > d) \end{cases} \tag{9.8-1}$$

which is depicted in Figure 9.17. The parameter d is the distance of closest approach of the centers of the two spheres and is thus equal to the diameter of one molecule.

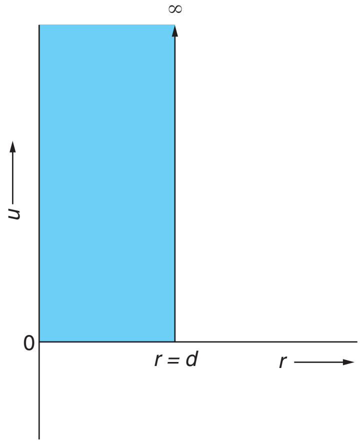

Figure 9.17 The Hard-Sphere Representation of the Intermolecular Potential of a Pair of Atoms.

Table A.15 in the appendix gives the values of the effective hard-sphere diameters of several substances.

Consider a model system consisting of N identical hard spheres in a container of volume V. We now obtain an approximate equation of state for this model system. We first pretend that all of the particles in the system are stationary except particle number 1. This moving particle has access to a volume that is smaller than V because of the presence of the other particles. Figure 9.18 shows the volume due to particle 2 into which the center of particle 1 cannot penetrate. The radius of this *excluded volume* is the sum of the radii of the two molecules, equal to the diameter of one molecule. Its volume is 8 times as large as the volume of one particle. If the gas contains N particles the total volume from which particle 1 is excluded is $N - 1$ times the volume in Figure 9.18:

$$V_{\text{exc}} = (N-1)\left(\frac{4}{3}\pi d^3\right) \approx N\frac{4}{3}\pi d^3 \tag{9.8-2a}$$

where we neglect unity compared with N.

If all of the particles are moving, the excluded volume in Figure 9.18 represents not only the volume from which particle 1 is excluded because of particle 2, but also the volume from which particle 2 is excluded because of particle 1. We assign half of this volume to each particle and write for the net excluded volume for a single particle

$$V_{\text{exc}} = \frac{N}{2}\left(\frac{4}{3}\pi d^3\right) = N\frac{2}{3}\pi d^3 \tag{9.8-2b}$$

We take as our approximate equation of state that of an ideal gas with a volume equal to the volume in which each particle can actually move,

$$P(V - V_{\text{exc}}) = Nk_{\text{B}}T = nRT \tag{9.8-3}$$

where k_{B} is Boltzmann's constant, n is the amount of the gas measured in moles, and R is the ideal gas constant. We divide Eq. (9.8-3) by n and write

$$P(V_{\text{m}} - b) = RT \tag{9.8-4}$$

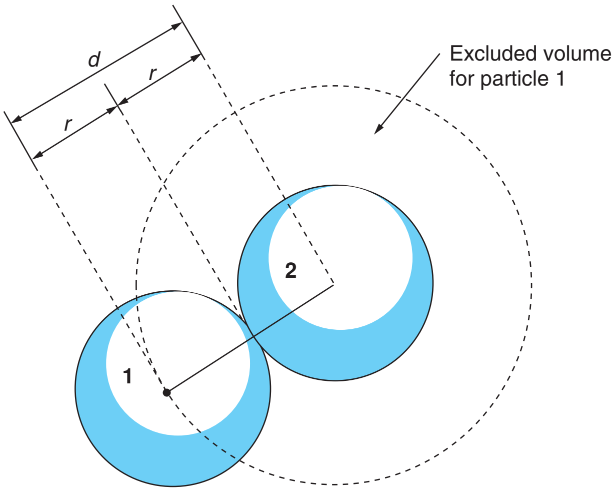

Figure 9.18 The Excluded Volume of a Pair of Hard Spheres.

where $V_{\mathrm{m}} = /n$, the molar volume, where we define the constant b,

$$b = \frac{V_{\mathrm{exc}}}{n} = \frac{N}{n}\frac{2}{3}\pi d^3 = N_{\mathrm{Av}}\frac{2}{3}\pi d^3 \tag{9.8-5}$$

and where N_{Av} is Avogadro's constant.

If we write Eq. (9.8-4) in the form

$$P = \frac{RT}{V_{\mathrm{m}} - b} \tag{9.8-6}$$

we can see that the pressure of our hard-sphere gas is greater than that of an ideal gas with the same values of V_{m} and T. Since our hard-sphere system has only repulsive forces, this agrees with our earlier assertion that repulsive forces make a positive contribution to the pressure. Equation (9.8-4) resembles the van der Waals equation of state of Eq. (9.3-1) except for the absence of the term containing the parameter a. The parameter a represents the effect of attractive forces, which make a negative contribution to the pressure. The argument has been advanced that attractive forces must slow a particle down just before it strikes a wall because other particles will be only on the side of the particle away from the wall as it strikes the wall. Similarly, repulsive forces accelerate a particle as it strikes the wall.

EXAMPLE 9.16

Assume that the parameter b in Eq. (9.8-6) can be identified with the van der Waals parameter b. Calculate the radius of an argon atom from the value of the van der Waals parameter b in Table A.3.

Solution

From Table A.3, $b = 3.219 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}$

$$b = N_{\mathrm{Av}}\frac{2}{3}\pi d^3$$

$$d^3 = \frac{3(3.219 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}})}{2\pi(6.022 \times 10^{23}\ \mathrm{mol^{-1}})} = 2.55 \times 10^{-29}\ \mathrm{m^3}$$

$$d = 2.94 \times 10^{-10}\ \mathrm{m}$$

From Table A.15, $d = 3.61 \times 10^{-10}$ m. This value is calculated from viscosity data taken at 293 K. The values differ because atoms and molecules are not actually hard spheres, and different kinds of measurements give different effective hard-sphere sizes.

The virial equation of state of Eq. (1.3-3) is a widely used equation of state for nonideal gases. Classical statistical mechanics provides formulas for calculating the virial coefficients of a nonideal monatomic gas. We present the following formula for the second virial coefficient without derivation:

$$B_2 = -\frac{N_{\mathrm{Av}}}{2}\int_0^{\infty} e^{-u(r)/k_{\mathrm{B}}T} - 14\pi r^2 dr \tag{9.8-7}$$

where r is the intermolecular distance and $u(r)$ is the pair potential energy function.

EXAMPLE 9.17

Obtain a formula for the second virial coefficient of a hard-sphere gas.

Solution

For the hard-sphere gas with molecular diameter d,

$$
\begin{aligned}
u(r) &= \infty \quad \text{if } r < d \\
u(r) &= 0 \quad \text{if } r > d \\
e^{-u(r)/k_BT} - 1 &= -1 \quad \text{if } r < d \\
e^{-u(r)/k_BT} - 1 &= 0 \quad \text{if } r > d
\end{aligned}
$$

$$B_2 = -\frac{N_{Av}}{2}\int_0^d -14\pi r^2 dr = \frac{2\pi N_{Av} d^3}{3}$$

Exercise 9.22

Write Eq. (9.8-6) in the form

$$\frac{PV_m}{RT} = \frac{1}{1 - b/V_m}$$

and use the identity

$$\frac{1}{1-x} = 1 + x + x^2 + x^3 + \cdots \quad (|x| < 1)$$

to transform Eq. (9.8-6) into the form of the virial equation of state. Show that the same formula results for the second virial coefficient as in the previous example.

Exercise 9.23

a. For a hard-sphere gas with molecules of radius 1.8×10^{-10} m find the pressure of the gas at a temperature of 298.15 K and a molar volume of 0.0244 m^3 mol^{-1}.

b. Find the pressure of the gas using the ideal gas law under the same conditions. Express the deviation of the pressure from the ideal pressure as a percentage of the ideal pressure.

The equation of state of a hard-sphere fluid has been the subject of considerable research, and far better approximate equations than Eq. (9.8-4) have been obtained.[5] One such equation of state is found in Problem 9.64. Much additional research on gases and liquids has used the technique of *molecular dynamics*, in which solutions to the classical equations of motion for a system of several hundred particles are numerically simulated by a computer program. Energies, pressures, etc., are then calculated by averaging over the particles' positions and velocities. As we would expect, the molecular dynamics calculations indicate that there is no gas–liquid condensation in the hard-sphere system. However, there is considerable evidence from these calculations that a gas–solid phase transition occurs.[6] This result was originally somewhat surprising because of the absence of attractive forces.

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[5] R. Hoste and W. Van Dael, *J. Chem. Soc. Faraday Trans.*, 2, **80**, 477 (1984).

[6] H. Reiss and A. D. Hammerich, *J. Phys. Chem.*, **90**, 6252 (1986).

Molecular Collisions in a Hard-Sphere Gas

We now want to study the rate of molecular collisions in our model hard-sphere gas of a single substance. In this model system a molecule moves at a constant velocity between collisions. We first pretend that only particle number 1 is moving while the others are stationary and distributed uniformly throughout the container. The mean number of stationary particles per unit volume is given by

$$\frac{N-1}{V} \approx \frac{N}{V} = \mathscr{N} \tag{9.8-8}$$

where we neglect unity compared with N and where $\mathscr{N}$ is the number density of molecules in the gas, equal to N/V. The mean number N' of particles in a volume V' is given by

$$N' = \mathscr{N}V' \tag{9.8-9}$$

As the moving particle travels along, it "sweeps out" a cylindrical volume as shown in Figure 9.19. The radius of this *collision cylinder* is equal to twice the radius of the molecules and is equal to d. We call d the *collision diameter*. The cross-sectional area of the collision cylinder is called the *collision cross section*

$$(\text{collision cross section}) = \pi d^2 \tag{9.8-10}$$

If the center of any stationary molecule lies in this cylinder it will be struck by the moving particle. The length of the cylinder that contains on the average one stationary particle is equal to the average distance between collisions, called the *mean free path*

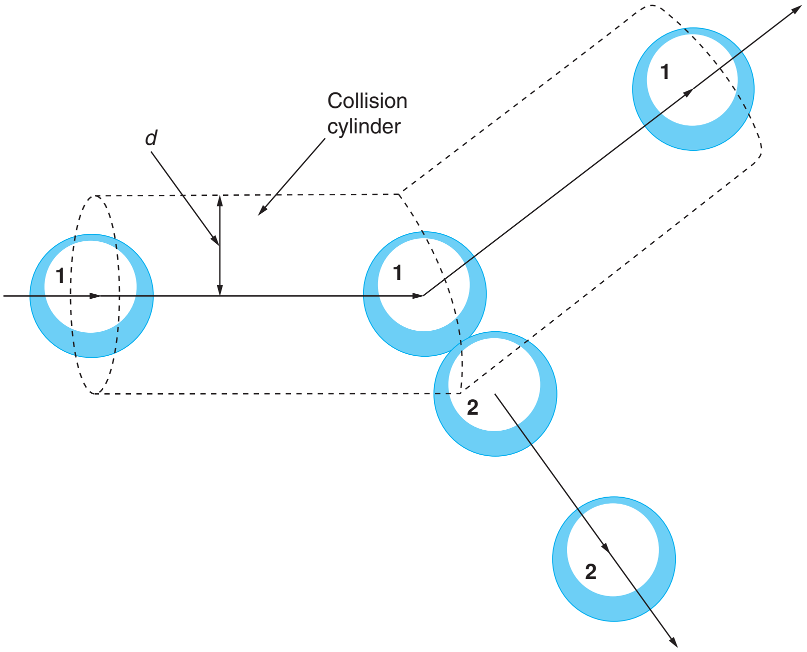

Figure 9.19 A Portion of the Collision Cylinder of Particle 1.

and denoted by λ. This volume is

$$\text{(volume containing one particle)} = \lambda\pi d^2 \tag{9.8-11}$$

and must equal V/N, the average volume per molecule:

$$\lambda\pi d^2 = \frac{V}{N} = \frac{1}{\mathcal{N}} \tag{9.8-12}$$

The mean free path is therefore given in this approximation by

$$\lambda = \frac{1}{\pi d^2 \mathcal{N}} \quad \text{(approximate equation)} \tag{9.8-13}$$

Equation (9.8-13) is a crude approximation because all of the particles are actually moving. When two particles collide they might initially be moving toward each other, they might initially be moving roughly at right angles to each other, or they might be moving in the same general direction. We assume that the "average" collision occurs with the particles moving initially at right angles to each other as in Figure 9.20. If prior to the collision x is the distance of one particle from the collision site and y is the distance of the other from this site, the separation of the two particles is given by the theorem of Pythagoras:

$$r = (x^2 + y^2)^{1/2} \tag{9.8-14}$$

The *relative speed* is defined as the magnitude of dr/dt.

We assume that both particles are moving at the same speed so that x and y must be equal to each other in order for the collision to occur. Therefore

$$r = \sqrt{2}x \tag{9.8-15}$$

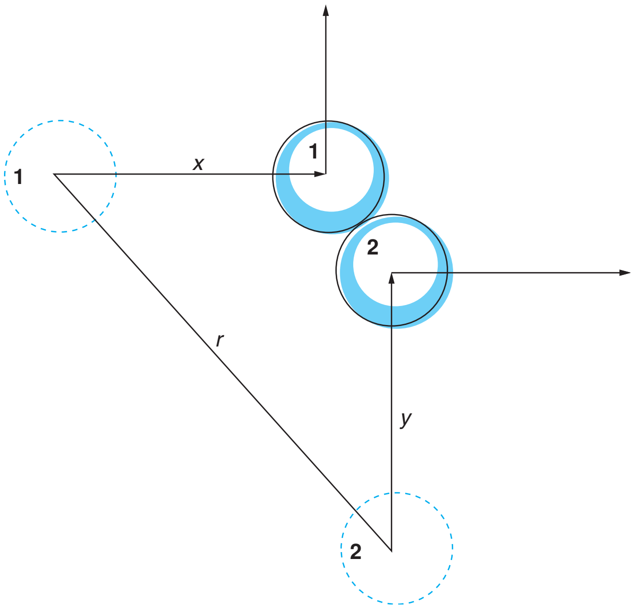

Figure 9.20 An "Average" (Right-Angle) Collision of Two Hard Spheres of the Same Type.

The relative speed is the rate of change of r and is larger than the speed of each particle by a factor of $\sqrt{2}$:

$$v_{\mathrm{rel}} = \left|\frac{dr}{dt}\right| = \sqrt{2}\left|\frac{dx}{dt}\right| \tag{9.8-16}$$

If both particles are moving at the mean speed, we identify their relative speed as the *mean relative speed*, denoted by $\langle v_{\mathrm{rel}}\rangle$:

$$\langle v_{\mathrm{rel}}\rangle = \sqrt{2}\langle v\rangle = \sqrt{2}\sqrt{\frac{8k_{\mathrm{B}}T}{\pi m}} = \sqrt{\frac{16k_{\mathrm{B}}T}{\pi m}} \tag{9.8-17}$$

Our derivation is crude, but Eq. (9.8-17) is the correct formula for the mean relative speed.

If we assume that particle 1 is approaching the other particles at a mean speed of $\sqrt{2}\,\langle v\rangle$ instead of $\langle v\rangle$ the mean free path is shorter by a factor of $1/\sqrt{2}$:

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 \mathcal{N}} \tag{9.8-18}$$

We will use this equation rather than Eq. (9.8-13). The *mean collision time* τ_{coll} is given by the familiar relation: time = distance/speed:

$$\tau_{\mathrm{coll}} = \frac{\lambda}{\langle v\rangle} = \sqrt{\frac{\pi m}{8k_{\mathrm{B}}T}}\frac{1}{\sqrt{2}\pi d^2 \mathcal{N}} \tag{9.8-19}$$

Note that the mean speed enters in this formula, not the mean relative speed. However, incorporation of the $\sqrt{2}$ factor in the formula for the mean free path allows us to write

$$\tau_{\mathrm{coll}} = \sqrt{\frac{\pi m}{16k_{\mathrm{B}}T}}\frac{1}{\pi d^2 \mathcal{N}} = \frac{1}{\langle v_{\mathrm{rel}}\rangle \pi d^2 \mathcal{N}} \tag{9.8-20}$$

The *mean molecular collision rate* z is the reciprocal of the mean collision time:

$$z = \frac{1}{\tau_{\mathrm{coll}}} = \pi d^2 \mathcal{N}\sqrt{\frac{16k_{\mathrm{B}}T}{\pi m}} = \pi d^2 \mathcal{N}\langle v_{\mathrm{rel}}\rangle \tag{9.8-21}$$

Notice how reasonable this equation is. The rate of collisions of a molecule is proportional to the collision cross section, to the number density of molecules, and to the mean relative speed. Under ordinary conditions, a gas molecule undergoes billions of collisions per second.

EXAMPLE 9.18

For nitrogen gas at 298 K and a molar volume of 24.45 L (approximately corresponding to 1.00 atm pressure):

a. Find the mean free path.

b. Find the mean collision time and the mean molecular collision rate.

Solution

a.

$$\mathcal{N} = \frac{N}{V} = \frac{6.022 \times 10^{23}\,\mathrm{mol^{-1}}}{0.02445\,\mathrm{m^3\,mol^{-1}}} = 2.463 \times 10^{25}\,\mathrm{m^{-3}}$$

$$\langle v \rangle = \left(\frac{8(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298.15\,\mathrm{K})}{\pi(0.0280\,\mathrm{kg\,mol^{-1}})} \right)^{1/2} = 475\,\mathrm{m\,s^{-1}}$$

$$\langle v_{\mathrm{rel}} \rangle = \sqrt{2}\langle v \rangle = 671\,\mathrm{m\,s^{-1}}$$

$$\lambda = \frac{1}{\sqrt{2}\pi(3.7 \times 10^{-10}\,\mathrm{m^3})^2(2.463 \times 10^{25}\,\mathrm{m^{-3}})} = 6.7 \times 10^{-8}\,\mathrm{m}$$

b.

$$\tau_{\mathrm{coll}} = \frac{\lambda}{\langle v \rangle} = \frac{6.7 \times 10^{-8}\,\mathrm{m}}{475\,\mathrm{m\,s^{-1}}} = 1.4 \times 10^{-10}\,\mathrm{s}$$

$$z = \frac{1}{1.4 \times 10^{-10}\,\mathrm{s}} = 7.1 \times 10^{9}\,\mathrm{s^{-1}}$$

Remember the approximate size of the collision rate and mean free path for an ordinary gas. A gas molecule ordinarily undergoes several billion collisions per second and moves several tens of nanometers between collisions.

Exercise 9.24

For helium gas at a molar volume of 24.45 L:

a. Find the length of a cube containing on the average one atom.

b. Find the mean free path.

c. Why is the mean free path so much larger than the length of the cube of part a?

To obtain a formula for the *total rate of collisions* per unit volume we multiply the mean molecular collision rate by the number of molecules per unit volume, but we must correct for the fact that this would count each collision twice. For example, the collision between molecule number 1 and molecule number 37 would be included once for molecule 1 and once for molecule 37. We correct for this double counting by dividing by 2:

$$Z = \frac{1}{2}z\mathcal{N} = \frac{1}{2}\pi d^2 \langle v_{\mathrm{rel}} \rangle \mathcal{N}^2 = \pi d^2 \sqrt{\frac{4k_{\mathrm{B}}T}{\pi m}}\mathcal{N}^2 \qquad (9.8\text{-}22)$$

where the total collision rate per unit volume is denoted by Z.

Notice the following important physical facts: (1) the total collision rate per unit volume is proportional to the square of the number density, (2) it is proportional to the collision cross section, and (3) it is proportional to the mean speed and thus to the square root of the absolute temperature. For example, doubling the number density quadruples Z, while doubling the absolute temperature increases Z by a factor of $\sqrt{2}$.

EXAMPLE 9.19

Calculate the total rate of collisions in 1.000 mol of nitrogen gas confined in a volume of 24.45 L at 298 K.

Solution

Using the values from Example 9.18:

$$Z = \frac{1}{2}z\mathscr{N} = \frac{1}{2}(7.1 \times 10^{9}\ \mathrm{s^{-1}})(2.463 \times 10^{25}\ \mathrm{m^{-3}}) = 8.7 \times 10^{34}\ \mathrm{m^{-3}\ s^{-1}}$$

$$(\text{Total rate}) = (8.7 \times 10^{34}\ \mathrm{m^{-3}\ s^{-1}})(0.02445\ \mathrm{m^{3}}) = 2.1 \times 10^{33}\ \mathrm{s^{-1}}$$

The total number of collisions per second in 1 mol of an ordinary gas is about a billion times larger than Avogadro's constant, because each molecule collides about a billion times per second.

Collisions in a Multicomponent Hard-Sphere Gas

We now modify our model system to contain more than one substance. We first consider collisions between two molecules of the same substance. If other substances are present a molecule might collide with other types of molecules between two collisions with others of its own kind. The effect of such collisions will be to put bends in the collision cylinder. The results for a one-component gas can be applied to the collisions between molecules of the same substance in a multicomponent gas if we interpret the mean free path between collisions as the sum of the lengths of the portions of the collision cylinder between collisions with molecules of other substances.

We now consider the rate of collisions of unlike molecules. The radius of the collision cylinder (the collision diameter) for collisions between molecules of substance 1 and substance 2 is denoted by d_{12} and is equal to the sum of the radii of the molecules, or half the sum of their diameters:

$$d_{12} = \frac{1}{2}(d_1 + d_2) \tag{9.8-23}$$

Assume that molecule 1 is of substance 1 and is moving at $\langle v_1 \rangle$, the mean speed of molecules of substance 1, and that molecule 2 is of substance 2 and is moving at $\langle v_2 \rangle$, the mean speed of molecules of type 2. Assume again that the average collision takes place at right angles. Figure 9.20 must be modified, as shown in Figure 9.21. In order for the molecules to collide the distances from the location of the collision must be proportional to the speeds of the molecules:

$$x = t_c \langle v_1 \rangle, \quad y = t_c \langle v_2 \rangle \tag{9.8-24}$$

where $\langle v_1 \rangle$ is the mean speed of particles of type 1, $\langle v_2 \rangle$ is the mean speed of particles of type 2, and where t_c is the time yet to elapse before the collision occurs. The molecular

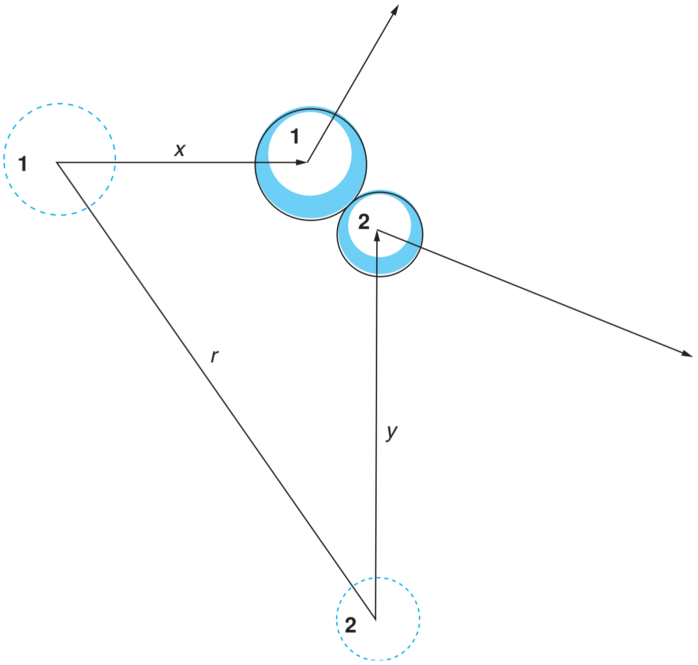

Figure 9.21 An “Average” (Right-Angle) Collision of Two Hard Spheres of Different Types.

separation is given by the theorem of Pythagoras:

$$r = t_c\left[\langle v_1\rangle^2 + \langle v_2\rangle^2\right]^{1/2} \tag{9.8-25}$$

We denote the *mean relative speed* by $\langle v_{12}\rangle$:

$$\langle v_{\text{rel}}\rangle = \langle v_{12}\rangle = \sqrt{\langle v_1\rangle^2 + \langle v_2\rangle^2} = \sqrt{\frac{8k_BT}{\pi m_1} + \frac{8k_BT}{\pi m_2}}$$

$$\boxed{\langle v_{12}\rangle = \sqrt{\frac{8k_BT}{\pi\mu_{12}}}} \tag{9.8-26}$$

where m_1 and m_2 are the two molecular masses and where μ_{12} is called the *reduced mass* of particles 1 and 2:

$$\boxed{\frac{1}{\mu_{12}} = \frac{1}{m_1} + \frac{1}{m_2}} \tag{9.8-27}$$

$$\boxed{\mu_{12} = \frac{m_1m_2}{m_1 + m_2}} \tag{9.8-28}$$

Our derivation is crude, but Eq. (9.8-26) is the correct expression for the mean relative speed. For a pair of identical particles, μ is equal to $m/2$, so that Eq. (9.8-26) is valid for that case as well as for two different substances.

EXAMPLE 9.20

Calculate the mean relative speed of nitrogen and oxygen molecules at 298 K.

Solution

Let nitrogen be substance 1 and oxygen be substance 2.

$$\langle v_{12}\rangle = \sqrt{\frac{8k_{\mathrm{B}}T}{\pi\mu_{12}}} = \sqrt{\frac{8RT}{\pi N_{\mathrm{Av}}\mu_{12}}}$$

$$N_{\mathrm{Av}}\mu_{12} = \frac{(0.0280\,\mathrm{kg\,mol^{-1}})(0.0320\,\mathrm{kg\,mol^{-1}})}{0.0280\,\mathrm{kg\,mol^{-1}} + 0.0320\,\mathrm{kg\,mol^{-1}}} = 0.0149\,\mathrm{kg\,mol^{-1}}$$

$$\langle v_{12}\rangle = \sqrt{\frac{8(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(298\,\mathrm{K})}{\pi(0.0149\,\mathrm{kg\,mol^{-1}})}} = 650\,\mathrm{m\,s^{-1}}$$

When we take account of the fact that the molecules of substance 2 are moving, the mean free path between collisions of a single particle of substance 1 with particles of substance 2 is given by

$$\lambda_{1(2)} = \frac{\langle v_1\rangle}{\langle v_{12}\rangle}\frac{1}{\pi d_{12}^2\mathcal{N}_2} = \sqrt{\frac{m_2}{m_1+m_2}}\frac{1}{\pi d_{12}^2\mathcal{N}_2} \tag{9.8-29}$$

We interpret $\lambda_{1(2)}$ as the sum of the lengths of the straight portions of the collision cylinder between bends caused by collisions of other types than 1–2 collisions. The mean free path of a molecule of substance 2 between collisions with molecules of substance 1 is denoted by $\lambda_{2(1)}$ and is obtained by switching the indices 1 and 2 in Eq. (9.8-29). Note that $\lambda_{2(1)}$ is not necessarily equal to $\lambda_{1(2)}$.

The formula for the *mean rate of collisions* of one molecule of substance 1 with molecules of substance 2 is analogous to Eq. (9.8-21):

$$z_{1(2)} = \frac{1}{\tau_{1(2)}} = \frac{\langle v_1\rangle}{\lambda_{1(2)}} = \sqrt{\frac{8k_{\mathrm{B}}T}{\pi\mu_{12}}}\pi d_{12}^2\mathcal{N}_2 \tag{9.8-30}$$

The rate of collisions of a molecule of substance 2 with molecules of substance 1 is obtained by switching the indices 1 and 2 in Eq. (9.8-30). The rate $z_{2(1)}$ is not necessarily equal to $z_{1(2)}$.

The *total rate per unit volume of collisions* between molecules of substance 1 and molecules of substance 2 is equal to the collision rate of Eq. (9.8-30) times the number density of molecules of substance 1, and is also equal to the collision rate of Eq. (9.8-29) times the number density of molecules of type 2:

$$Z_{12} = z_{1(2)}\mathcal{N}_1 = z_{2(1)}\mathcal{N}_2 = \sqrt{\frac{8k_{\mathrm{B}}T}{\pi\mu_{12}}}\pi d_{12}^2\mathcal{N}_1\mathcal{N}_2 = \langle v_{12}\rangle\pi d_{12}^2\mathcal{N}_1\mathcal{N}_2 \tag{9.8-31}$$

There is no need to divide by 2 as in Eq. (9.8-22). The two molecules in a given collision are of different substances so that there is no double counting. This equation should be easy to remember because all four factors are things to which the rate should be proportional. The most important physical fact shown in Eq. (9.8-31) is this: *The total rate of collisions between molecules of two substances is proportional to the number density of each substance*.

Exercise 9.25

Assume that 0.800 mol of nitrogen (substance 1) and 0.200 mol of oxygen (substance 2) are contained in 24.45 L at 298 K.

a. Find $\lambda_{1(2)}$, $\lambda_{2(1)}$, $\lambda_{1(1)}$, and $\lambda_{2(2)}$.
b. Find $z_{1(2)}$, $z_{2(1)}$, $z_{1(1)}$, and $z_{2(2)}$.
c. Find Z_{11}, Z_{22}, and Z_{12}.
d. Find the total number of collisions per second.

PROBLEMS

Section 9.8: The Hard-Sphere Gas

9.59 **a.** Write an expression for the excluded volume of a pair of hard spheres of different sizes.

b. Obtain an equation of state for a mixture of two different hard-sphere substances.

c. Compare your equation of state with the van der Waals equation of state using the mixing rules in Problem 1.38.

9.60 Calculate the pressure of carbon dioxide gas at 298.15 K and a molar volume of 24.00 L mol^{-1}, assuming (a) the ideal gas law, (b) the van der Waals equation of state, and (c) Eq. (9.8-6), taking the same value of the parameter b as for the van der Waals equation of state.

9.61 What would the pressure of nitrogen gas have to be at 25°C for a nitrogen molecule to undergo 1.00×10^6 collisions per second?

9.62 For N_2 gas at 298.15 K and 1.000 atm, calculate the ratio of the total volume of the molecules to the volume of the gas, (a) using the value of the hard-sphere diameter from Table A.15 of Appendix A, and (b) using the value of molecular diameter calculated from the value of the van der Waals parameter b.

9.63 Calculate the coefficient of the r^{-6} term in the Lennard-Jones potential, $4\varepsilon\sigma^6$, for He, Ne, N_2, O_2, Ar, and CO_2. Make a graph of this quantity versus the number of electrons in the atom or molecule. Comment on your result in view of the interpretation that the London attraction is due to synchronized fluctuating dipoles in the electrons of the two attracting atoms or molecules.

9.64 An approximate equation of state for the hard-sphere fluid is due to Carnahan and Starling:

$$\frac{PV}{Nk_BT} = \frac{1 + y + y^2 - y^3}{(1 - y)^3}$$

where

$$y = \frac{\pi N d^3}{6V} = \frac{\pi \mathcal{N} d^3}{6}$$

Manipulate this equation of state into the virial equation of state and find the expressions for the second and third virial coefficients. Compare your formula for the second virial coefficient with that of Exercise 9.22.

9.65 Evaluate the second virial coefficient of helium, using the value of the hard-sphere diameter in Table A.15 of the appendix. Compare your value with those in Table A.4 of Appendix A.

9.66 For a mixture of 2.000 mol of CO and 1.000 mol of O_2 at 292 K and 1.000 atm, calculate:

a. the number of collisions with O_2 molecules suffered by one CO molecule in 1.000 s, taking $d = 2.94 \times 10^{-10}$ m for CO;

b. the number of collisions with CO molecules suffered by one O_2 molecule in 1.000 s;

c. the length of time required for one CO molecule to have as many collisions with O_2 molecules as there are O_2 molecules in the system.

9.67 A mixture of 1.000 mol of methane and 2.000 mol of oxygen is held at a total pressure of 1.000 bar and a temperature of 298.15 K. The effective hard-sphere diameter of methane molecules is 414 pm and that of oxygen molecules is 361 pm. Assume that no reaction has taken place.

a. Calculate the mean number of collisions per second that a methane molecule undergoes with oxygen molecules.

b. Calculate the mean number of collisions per second that an oxygen molecule undergoes with methane molecules. Explain why this quantity is not equal to your result for part a.

c. Calculate the total number of methane–oxygen collisions per second in the system.

9.68 Assume that in a certain automobile the exhaust gas has a carbon monoxide mole fraction of 0.0140 and a temperature of 500 K when it reaches the catalytic converter.

a. Find the mean free path between CO–CO collisions of one CO molecule in the exhaust gas. (Collisions with other types of molecules can intervene.)

b. Find $z_{1(1)}$, the mean collision rate of CO–CO collisions for one CO molecule in the exhaust gas of this automobile.

9.69 Assume that the mole fraction of carbon dioxide in the earth's atmosphere is 0.000306.

a. Estimate the mean free path between CO_2-CO_2 collisions in the atmosphere at sea level if the temperature is 298 K (collisions with molecules of other substances can intervene, so that the free path in question can have bends in it).

b. Estimate the number of collisions with other CO_2 molecules per second undergone by a CO_2 molecule under the conditions in part a.

9.70 Assume that a certain region of interstellar space contains 1 hydrogen atom (not molecule) per cubic meter at a temperature of 5 K. Estimate the mean time between collisions for a hydrogen atom. You will have to estimate a value for the atomic diameter.

9.71 A stoichiometric mixture for the combustion of carbon monoxide with oxygen is prepared at 25°C and a total pressure of 1.000 atm.

a. Calculate the total number of oxygen–carbon monoxide collisions per cubic meter per second, assuming that no reaction takes place.

b. If every such collision led to reaction, how long would it take for half of the material to react? How do you think this compares with the actual half-life of the reaction at this temperature?

9.72 **a.** Find the mean speed of atoms in gaseous argon at 85 K, the normal boiling temperature of argon.

b. Find the rate of collisions of one argon atom with other argon atoms in pure gaseous argon at 85 K and 1.00 atm. The effective hard-sphere diameter of argon atoms is 3.16×10^{-10} m.

c. Find the mean free path of argon under the conditions of part b.

9.73 Estimate the mean free path for hydrogen atoms under the conditions of Problem 9.70

9.9 The Molecular Structure of Liquids

A great deal of research has been carried out on the properties of liquids, but a single comprehensive theory of the liquid state does not exist. The theories that do exist are much more complicated than gas kinetic theory, and we present only a few elementary comments. We note a simple but important fact: *The structure and properties of a liquid are primarily determined by its potential energy, whereas the properties of a gas are primarily determined by its kinetic energy.* For example, consider liquid argon. The Lennard-Jones pair potential function for argon was shown in Figure 9.15. The minimum is at 380 pm (3.8 Å). The potential energy of a pair of atoms at this distance must be increased either to separate them or to push them closer together.

Substances such as argon consist of spherical atoms. In a solid lattice of spheres, 12 nearest-neighbor spheres can surround a given sphere. Each of these nearest neighbors touches the central sphere and touches four of the other nearest neighbors. Solid argon has a nearest-neighbor distance equal to 372 pm. This distance is slightly smaller than the distance at the minimum of the Lennard-Jones pair potential, 380 pm, as we might expect due to the attractions of molecules beyond the shell of nearest neighbors. Although the density of liquid argon is smaller than that of the solid, the nearest neighbors are at very nearly the same average distance as in the solid. On the average there are fewer nearest neighbors, because the nearest neighbors are disordered and voids exist between them.

Exercise 9.26

Estimate the number of nearest neighbors around an argon atom in the liquid by multiplying 12, the number of nearest neighbors in the solid, by the ratio of the density of the liquid to the density of the solid. The density of solid argon is equal to $1.82\ \mathrm{g\ mL^{-1}}$, and that of liquid argon is equal to $1.40\ \mathrm{g\ mL^{-1}}$.

Since molecules in the liquid are surrounded by other molecules their motions are very different from those of gaseous molecules. The nearest neighbors form a "cage" in which a given molecule is confined. Instead of moving considerable distances between occasional collisions, a molecule of a liquid is involved in frequent collisions as it undergoes a kind of rattling motion. Intermolecular forces do not depend on velocities, so the velocity distribution of Section 9.4 is valid for a liquid or solid as well as for a gas. The mean speed is given by Eq. (9.4-6):

$$\langle v\rangle = \sqrt{\frac{8k_{\mathrm{B}}T}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} \tag{9.9-1}$$

For example, the mean speed of water molecules in liquid water at 100°C is the same as in water vapor at the same temperature. The input of energy required to vaporize the liquid changes the potential energy, not the kinetic energy.

Since the molecules in a liquid are much closer together than in a gas, and since they are moving just as rapidly on the average as in a gas at the same temperature, the rate of collisions in a liquid is much greater than in a gas. There is some ambiguity in defining a collision between two molecules in a liquid, because the molecules are not exactly like hard spheres and there is no unique instant of contact between them. However, if some definition of a collision is adopted, the rate of collisions between liquid molecules can be estimated.[7]

EXAMPLE 9.21

Estimate the collision frequency of an argon atom in liquid argon at its normal boiling temperature, 85 K. Assume that the atom is moving at the mean speed for this temperature. Estimate the time between collisions as the time required to travel twice the distance from the minimum in the potential function of Figure 9.15 to a value of r such that the potential energy is equal to the kinetic energy of a particle moving at the mean relative speed.

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[7] P. K. Davis, *J. Chem. Phys.*, **57**, 517 (1972).

Solution

$$\langle v\rangle = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(85\,\mathrm{K})}{\pi(0.039948\,\mathrm{kg\,mol^{-1}})}} = 212\,\mathrm{m\,s^{-1}}$$

The kinetic energy of an argon atom moving at this speed is 1.49×10^{-21} J. To find the value of r that corresponds to this value of the potential energy function, we set

$$1.49 \times 10^{-21}\,\mathrm{J} = 4\varepsilon\left[(\sigma/r')^{12} - (\sigma/r')^{6}\right]$$

where r' is the value of r that we seek. This equation must be solved by numerical approximation, using a spreadsheet or a simple computer program. With values of ε and σ from Table A.14, we find that $r' = 3.3 \times 10^{-10}$ m. The minimum of the potential energy is at 3.8×10^{-10} m. Twice the distance from r' to this value of r is 1.0×10^{-10} m. The time required to traverse this distance at $212\,\mathrm{m\,s^{-1}}$ is equal to 4.7×10^{-13} s, giving an estimate of the collision rate equal to $2.1 \times 10^{12}\,\mathrm{s^{-1}}$.

As seen in the previous example, collision rates of a molecule in a typical liquid are several hundred times larger than in a typical gas.

PROBLEMS

Section 9.9: The Molecular Structure of Liquids

9.74 The density of ice is $0.917\,\mathrm{g\,mL^{-1}}$ at 0°C, and that of liquid water is $1.000\,\mathrm{g\,mL^{-1}}$. Ice is completely hydrogen-bonded with four nearest neighbors for each water molecule. Estimate the average number of nearest neighbors in liquid water at 0°C. Explain your answer, and explain why liquid water is denser than ice.

9.75 **a.** Calculate the density of solid xenon from the Lennard-Jones parameters, assuming that the interatomic distance is 2% smaller than the minimum in the pair potential function.

b. The density of liquid xenon is $3.52\,\mathrm{g\,mL^{-1}}$. Estimate the number of nearest-neighbor atoms in the liquid.

9.76 **a.** If 1.000 mol of argon atoms is in a perfect crystal lattice such that each atom has 12 nearest neighbors at the interatomic distance equal to the distance at the minimum in the Lennard-Jones potential function, calculate the energy required to turn the crystal into a gas, neglecting all interactions except those of nearest neighbors. Assign half of the interaction energy of a pair to each member of the pair, so that each atom has to break six attractions in the sublimation process. Compare this energy with the actual energy of sublimation at 0 K, $8.49\,\mathrm{kJ\,mol^{-1}}$.

b. Calculate the energy of vaporization of argon, assuming that each argon atom has approximately 10.5 nearest neighbors.

c. Calculate the energy of fusion of argon.

Summary of the Chapter

The first model system designed to represent a dilute gas consists of noninteracting point-mass molecules that obey classical mechanics. We obtained the Maxwell–Boltzmann probability distribution for molecular velocities:

$$g(v) = \left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{3/2} e^{-mv^2/2k_{\mathrm{B}}T}$$

The probability distribution for molecular speeds is

$$f_v(v) = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2} v^2 e^{-mv^2/2k_B T}$$

The mean speed of molecules in our model gas is given by

$$\langle v\rangle = \sqrt{\frac{8\pi k_B T}{3m}} = \sqrt{\frac{8\pi RT}{3M}}$$

Equations were derived for the most probable speed and the root-mean-square speed. The rate of wall collisions per unit area per unit time is given by

$$v = \frac{1}{4}\frac{N}{V}\langle v\rangle = \frac{1}{4}\mathscr{N}\langle v\rangle$$

The model system obeys the ideal gas law and Dalton's law of partial pressures.

A second model system was the hard-sphere gas. We derived an approximate equation of state for this system and discussed molecular collisions using this model system. We obtained formulas for the mean free paths between collisions and for collision rates, for both one-component and multicomponent systems. An important result was that the total rate of collisions in a one-component gas was proportional to the square of the number density and to the square root of the temperature. In a multicomponent gas, the rate of collisions between molecules of two different substances was found to be proportional to the number densities of both substances and to the square root of the temperature.

A few elementary ideas about the molecular structure of liquids were presented. In a liquid, the shell of nearest neighbors contains voids, so that fewer nearest neighbors are present than in the solid. In a typical liquid, a molecule undergoes roughly 100 times as many collisions per second as does a molecule in a typical gas.

ADDITIONAL PROBLEMS

9.77 Assume that a certain sample of air at 25°C contains dust particles with diameter 5.0 μm and density 2500 kg m^{-3}.

a. Find the most probable speed, the mean speed, and the root-mean-square speed of the dust particles, treating them as though they were molecules.

b. Assuming that the dust particles are described by a Boltzmann distribution, find the ratio of the concentration of dust particles at a height of 1.000 m to the concentration at a height of 0.00 m.

c. Find the rate of collisions of one dust particle with other dust particles if their number density is 1.0×10^9 m^{-3}.

d. Find the total rate of collisions per cubic meter of pairs of dust particles.

e. Find the rate of collisions of one dust particle with nitrogen molecules.

f. Assume that a dust particle is stationary and calculate the rate at which nitrogen molecules strike its surface. Compare your answer with that of part e, and explain any difference.

9.78 At 25°C and 1.000 atm, methane gas has a mean free path of 5.33×10^{-8} m.

a. Calculate the effective hard-sphere diameter of methane molecules.

b. Calculate the mean number of collisions per second undergone by one methane molecule at this temperature and pressure.

c. Calculate the total number of collisions per cubic meter per second in methane gas at this temperature and pressure.

d. Keeping the volume of the container and the temperature fixed, enough oxygen gas is added to make the total pressure 2.000 atm. Find the total number of collisions of each kind per cubic meter per second. The effective hard-sphere diameter of oxygen is 0.361 nm.

9.79 Consider a spherical water droplet in a cloud at 25°C. The radius of the droplet is 10.0 μm. The equilibrium vapor pressure of water at this temperature is 23.756 torr.

a. Calculate the rate at which water molecules strike the surface of the droplet, assuming that the air is saturated with water vapor (the partial pressure equals the equilibrium vapor pressure).

b. Assume that the air is supersaturated (the water vapor is supercooled) with a water partial pressure of 30.0 torr. Find the rate at which water molecules strike the surface of the droplet.

c. Calculate the rate at which the mass of the droplet in part b is growing. State any assumptions.

9.80 The number of three-body collisions is far smaller than the number of two-body collisions in a dilute gas. Consider three-body collisions in a sample of pure argon at 1.000 bar and 300 K. Assume that a three-body collision occurs when a third body collides with a pair of molecules in the act of colliding,

a. Estimate the number density of colliding pairs by estimating the time during which two colliding molecules are close enough together to be struck by a third body. Take this time as the time for a molecule moving at the mean relative speed to travel a distance equal to the collision diameter.

b. Estimate the rate of three-body collisions by estimating the rate of collisions between colliding pairs and third bodies. Take an effective hard-sphere diameter of the colliding pair to be twice that of a single molecule.

9.81 Uranium hexafluoride has a vapor pressure at 56°C equal to 765 torr, so UF_6 is a gas at 60°C and 1.000 atm. Various diffusion and thermal diffusion processes were used in the Manhattan Project of the United States in World War II to separate gaseous $^{235}UF_6$ molecules from $^{238}UF_6$ molecules.

a. Find the mean speed of $^{235}UF_6$ molecules at 60.0°C. Round off atomic masses in amu to the nearest integer.

b. Find the mean speed of $^{238}UF_6$ molecules at 60.0°C. Round off atomic masses in amu to the nearest integer.

c. The effective hard-sphere diameter of UF_6 molecules is 570 pm. Find the mean free path of UF_6 molecules at 60°C and 1.000 atm.

d. Find the number of collisions that one UF_6 molecule undergoes in 1.000 s at 60.0°C and 1.000 atm.

9.82 **a.** Calculate the most probable speed and the mean speed for ozone (O_3) molecules at 298.15 K.

b. On a smoggy day in Los Angeles, ozone can reach 0.5 parts per million by moles (mole fraction = 0.5×10^{-6}). Estimate the number of ozone molecules that would strike your face during 8 hours of exposure to this air. State any assumptions.

c. Estimate the number of collisions per second with other ozone molecules undergone by an ozone molecule at this concentration. Estimate the mean free path between such collisions. Assume what you think is a reasonable effective hard-sphere diameter for ozone and state any other assumptions.

9.83 Label each of the following statements as either true or false. If a statement is true only under special circumstances, label it as false.

a. If a given sample of a pure gas is isothermally expanded to twice its original volume, the total rate of collisions in the entire sample drops to one-fourth of its original value.

b. If a given sample of a pure gas is isothermally expanded to twice its original volume, the rate of collisions per unit volume drops to one-fourth of its original value.

c. The mean speed of water molecules at 100°C has the same value in the liquid as in the vapor.

d. The ratio of the most probable speed to the mean speed has the same value for all gases at all temperatures.

e. The ratio of the mean speed to the root-mean-square speed has the same value for all gases at all temperatures.

f. Ordinary gases behave nearly like ideal gases because the molecules are far enough part on the average that the intermolecular forces are small.

g. In a typical gas under ordinary conditions, the average distance between neighboring molecules is roughly 10 times as great as the distance between neighboring molecules in the liquid.

h. The mean free path in an ordinary gas is roughly equal to the average distance between neighboring molecules.

i. Because the temperature on the Kelvin scale cannot be negative, a state of higher energy cannot have a greater population than a state of lower energy.

j. The mean value of a velocity component is equal to the mean speed of the molecules of a dilute gas.

k. The most probable value of a velocity component is equal to the most probable speed of the molecules of a dilute gas.

l. The mean molecular kinetic energy of a gas at a fixed temperature is independent of the molecular mass of the gas.

9.84 Assume that a certain sample of polluted air has the following composition by moles: nitrogen, 76.08%; oxygen, 20.41%; water vapor, 2.57%; argon 0.910%; carbon dioxide, 0.0306%; ozone, 0.0004%; carbon monoxide, 0.0005%. The air is maintained at a temperature of 300 K and a pressure of 1.000 bar.

a. Find the number of collisions a single ozone molecule undergoes with carbon monoxide molecules.

b. Find the number of ozone–carbon monoxide collisions per cubic meter per second.

c. Find the number of ozone–oxygen collisions per cubic meter per second.

d. Find the number of nitrogen–nitrogen collisions per cubic meter per second.

10

Transport Processes

PRINCIPAL FACTS AND IDEAS

1. The macroscopic description of nonequilibrium states of fluid systems requires independent variables to specify the extent to which the system deviates from equilibrium and dependent variables to express the rates of processes.
2. The three principal transport processes are heat conduction, diffusion, and viscous flow.
3. Each transport process is described macroscopically by an empirical linear law.
4. Molecular theories of transport processes in dilute gases are based on gas kinetic theory.
5. Transport processes in liquids are visualized as the motion of molecules from one "cage" to another with the cages being made up of neighboring molecules.
6. The electrical conductivity of solutions of ions can be understood on the basis of ionic motion in an electric field.

10.1 The Macroscopic Description of Nonequilibrium States

In earlier chapters we were able to calculate changes in thermodynamic state functions for nonequilibrium processes that began with equilibrium or metastable states and ended with equilibrium states. In this chapter we present a nonthermodynamic analysis of three nonequilibrium processes: heat conduction, diffusion, and viscous flow. These processes are called *transport processes*, since in each case some quantity is transported from one location to another. We will discuss only systems that do not deviate too strongly from equilibrium, excluding turbulent flow, shock waves, supersonic flow, and the like.

In order to discuss the macroscopic nonequilibrium state of a fluid system, we will first assume that we can use intensive thermodynamic variables such as the temperature, pressure, density, concentrations, and chemical potentials. In order to justify this assumption we visualize the following process: A small portion of the system is suddenly removed from the system and allowed to relax adiabatically to equilibrium at fixed volume. Once equilibrium is reached, intensive thermodynamic variables are well defined and can be measured. The measured values are assigned to a point inside the volume originally occupied by this portion of the system and to the time at which the subsystem was removed. We imagine that this procedure is performed repeatedly at different times and different locations in the system. Interpolation procedures are carried out to obtain smooth functions of position and time to represent the temperature, pressure, and concentrations:

$$T = T(x, y, z, t) = T(\mathbf{r}, t) \tag{10.1-1}$$

$$P = P(x, y, z, t) = P(\mathbf{r}, t) \tag{10.1-2}$$

$$c_i = c_i(x, y, z, t) = c_i(\mathbf{r}, t) \quad (i = 1, 2, \ldots, s) \tag{10.1-3}$$

where c_i is the molar concentration of substance i. The position vector with components x, y, and z is denoted by $\mathbf{r}$.

The values of these intensive variables at a point are not sufficient for a complete description of the nonequilibrium state at that point. We also need a measure of how strongly the variables depend on position. We use the gradients of these variables for this purpose. The *gradient* of a scalar function $f(x, y, z)$ is defined by Eq. (B-43) of Appendix B. It is a vector derivative that points in the direction of the most rapid increase of the function and has a magnitude equal to the derivative with respect to distance in that direction. The gradient of the temperature is denoted by ∇T:

$$\nabla T = \mathbf{i}\frac{\partial T}{\partial x} + \mathbf{j}\frac{\partial T}{\partial y} + \mathbf{k}\frac{\partial T}{\partial z} \tag{10.1-4}$$

where $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ are unit vectors in the directions of the x, y, and z axes. The *gradient operator* ∇ is sometimes called "del." The concentration gradient of substance number i is

$$\nabla c_i = \mathbf{i}\frac{\partial c_i}{\partial x} + \mathbf{j}\frac{\partial c_i}{\partial y} + \mathbf{k}\frac{\partial c_i}{\partial z} \tag{10.1-5}$$

Gradients of other variables are defined in the same way. Gradients can also be expressed in other coordinate systems. Appendix B contains the formulas for the gradient in spherical polar coordinates and cylindrical polar coordinates. When possible we will discuss cases in which variables depend on only one Cartesian coordinate, so that only one term in equations like Eq. (10.1-5) is nonzero. We assume that the time derivatives of the temperature, pressure, and concentrations are dependent variables, so that it is not necessary to specify the time derivatives to specify the state of the system.

EXAMPLE 10.1

Assume that the concentration of substance number 2 is represented by the function

$$c_2 = c_2(z, t) = c_0 + a\cos(bz)e^{-t/\tau}$$

where c_0, a, b, and τ are constants and where t represents the time. Write the expressions for ∇c_2 and for $\partial c_2/\partial t$.

Solution

$$\nabla c_2 = -\mathbf{k}ab\sin(bz)e^{-t/\tau}$$
$$\frac{\partial c_2}{\partial t} = at\cos(bz)e^{-t/\tau}$$

where **k** is the unit vector in the z direction.

If a fluid system is flowing the flow velocity is also needed to specify the state of the system. The flow velocity **u** is a vector quantity that depends on position and time:

$$\mathbf{u} = \mathbf{u}(\mathbf{r}, t) = \mathbf{u}(x, y, z, t) = \mathbf{i}u_x(\mathbf{r}, t) + \mathbf{j}u_y(\mathbf{r}, t) + \mathbf{k}u_z(\mathbf{r}, t) \tag{10.1-6}$$

Just as with the temperature, pressure, and concentration, we need a specification of how strongly the flow velocity depends on position. Each term in Eq. (10.1-6) can be differentiated with respect to x, y, and z, so the gradient of **u** has nine components. We will avoid a full discussion of this gradient and focus on single terms. For example, the derivative $\partial u_y/\partial z$ gives the rate of change of the y component of the velocity in the z direction. This quantity is called the *rate of shear*, or the rate at which one layer of the fluid is sliding (shearing) past an adjacent layer.

PROBLEMS

Section 10.1: The Macroscopic Description of Nonequilibrium States

10.1 Write a formula for the gradient of each of the following functions, where a, b, and c represent constants.

a. $f = e^{-x^2+y^2+z^2}$

b. $f = r\cos(\theta)$ (transform to Cartesian coordinates or use Eq. (B-46) in Appendix B).

c. $f = \sin(bx)\cos(cy)$

d. $f = e^{-az^2}\sin(bx)$

10.2 Assume that in a two-component solution the temperature is given by

$$T = T_0 + B\cos(a_1 z)\,e^{-t/b_1}$$

and the concentration of component 2 is given by

$$c_2 = c_0 + C\sin(a_2 z)\,e^{-t/b_2}$$

where B, C, a_1, a_2, b_1, and b_2 are constants and where t represents the time.

a. Write the expressions for the gradient of the temperature and the gradient of the concentration of component 2.

b. Write the expressions for the time derivatives of the temperature and the concentration of component 2.

10.2 Transport Processes

In a transport process, some quantity is transported from one place to another. The principal transport processes are heat conduction, diffusion, and viscous flow. In heat conduction, energy in the form of heat is transported. In diffusion, substances are transported. In viscous flow, momentum is transported.

Variables to Specify the Rates of Transport Processes

The rates of nonequilibrium processes could be specified by time derivatives of intensive variables, but other variables are customarily used. The rate of heat flow is customarily specified by the *heat flux*, which is a vector $\mathbf{q}$ in the direction of the flow of heat and with magnitude equal to the quantity of heat in joules per square meter per second passing through a plane perpendicular to the direction of heat flow. The rate of diffusion of substance i is specified by its *diffusion flux*, which is a vector $\mathbf{J}_i$ that has the direction of the average velocity of the molecules of substance i and a magnitude equal to the net amount of the substance in moles per square meter per second passing through a plane perpendicular to the direction of diffusion. In precise discussions of diffusion one must specify whether the plane is stationary in the laboratory or is stationary with respect to the center of mass of a small portion of the fluid in the system, etc. We will assume that our plane is stationary in the laboratory.

The rate of viscous flow is specified in a different way. Figure 10.1 shows an idealized apparatus for the measurement of viscosity, which is the resistance of a fluid to shearing flow. The fluid is confined between two large horizontal plates. The top plate is dragged along parallel to its surface in the y direction, and the lower plate is fixed to a stationary object with infinite mass. The moving plate puts a frictional force on the layer of fluid next to it, transferring momentum to it, and this layer of fluid puts a frictional force on another layer, transferring momentum to it, and so on. The momentum is eventually transferred to the stationary object, which does not accelerate due to its infinite mass. The speed of each layer is a little smaller than the speed of the layer that puts a force on it, corresponding to a nonzero value to the rate of shear $\partial u_y/\partial z$. In Figure 10.1, arrows are used to indicate the magnitude of the flow velocity at different heights. This kind of flow is called *laminar flow* (flow in layers). A flow that is not laminar is called *turbulent flow*. We do not attempt to discuss turbulent flow. Although we could use the momentum flux as a rate variable, it is customary to use as a rate variable the force per unit area that must be exerted on the moving plate by an external agent to keep it

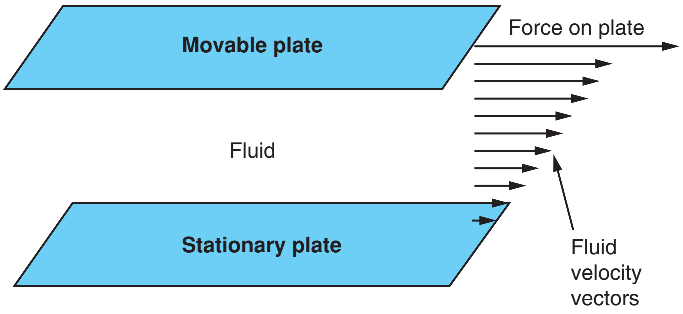

Figure 10.1 An Idealized Viscosity Experiment.

at a steady speed. Since Newton's second law relates force and the rate of change of velocity (and thus the rate of change of momentum) the same information is contained in either choice.

Driving Forces and Linear Laws

To a first approximation each rate variable depends on a single state variable that we call the *driving force* for that variable. The temperature gradient is the driving force for heat conduction, the concentration gradient of substance i is the driving force for diffusion of that substance, and the rate of shear is the driving force for viscous flow. The empirical formulas that describe these phenomena specify that the rate of the process is directly proportional to the driving force, so that these formulas are called *linear laws*. In a thorough treatment of irreversible thermodynamics, more carefully defined driving forces are used and the possibility is included that the driving force for one transport process can make a contribution to the rate of another transport process. An example is thermal diffusion, in which a diffusion flow is driven by a temperature gradient. We will not discuss this and other *cross-effects*, although there is a considerable literature involving them.

Fourier's Law of Heat Conduction

Fourier's law is named for Jean Baptiste Joseph Fourier, 1768–1830, a famous French mathematician and physicist who also invented Fourier series and Fourier transforms.

The flow of heat in a solid, liquid, or gas system is described by a linear law known as *Fourier's law of heat conduction*:

$$\mathbf{q} = -\kappa \nabla T \quad \text{(Fourier's law)} \tag{10.2-1}$$

where κ is a coefficient called the *thermal conductivity*. If the temperature varies only in the z direction, this equation is

$$q_z = -\kappa \frac{\partial T}{\partial z} \tag{10.2-2}$$

Fourier's law is called a *linear law* because the rate is directly proportional to (linearly dependent on) the gradient of the temperature, ∇T, which is the driving force. The thermal conductivity κ can depend on the composition, the temperature, the pressure, and on the identities of the substances present, but does not depend on the temperature gradient. Fourier's law is also called a *phenomenological law*, which means that it is not derived theoretically but simply describes a phenomenon. Fourier's law holds quite accurately for gases, liquids, and solids. Table A.16 in Appendix A gives the values of the thermal conductivity for several substances.

EXAMPLE 10.2

A cubical cell 0.100 m on a side is filled with benzene. The top surface is maintained at 25.0°C and the bottom surface is maintained at 15.0°C. After some time, the system will reach a *steady state* in which the state of the system does not change with time although heat is flowing. Calculate the amount of heat flowing through the benzene per hour after a steady state is achieved, neglecting convection.

Solution

Since the top of the vessel is at a higher temperature than the bottom, we assume that convection can be neglected. The thermal conductivity of pure benzene at 20°C and 1.00 atm pressure is equal to 0.151 J $\mathrm{m^{-1}s^{-1}\ K^{-1}}$. Assuming that the temperature depends only on z, the vertical coordinate, the temperature gradient is

$$\frac{dT}{dz} \approx \frac{\Delta T}{\Delta z} = \frac{10.0\ \mathrm{K}}{0.100\ \mathrm{m}} = 100\ \mathrm{K\ m^{-1}}$$

We have used an average value for the gradient by replacing dT/dz by the quotient of finite differences $\Delta T/\Delta z$. Fourier's law now gives the result

$$q_z = -\kappa\left(\frac{\Delta T}{\Delta z}\right) = -(0.151\ \mathrm{J\ m^{-1}\ s^{-1}\ K^{-1}})(100\ \mathrm{K\ m^{-1}}) = -15.1\ \mathrm{J\ m^{-2}\ s^{-1}}$$

The cross-sectional area is 0.0100 $\mathrm{m^2}$, so the total amount of heat flowing in 1.00 hour is

$$q = \left|-\left(15.1\ \mathrm{J\ m^{-2}\ s^{-1}}\right)\left(0.0100\ \mathrm{m^2}\right)(3600\ \mathrm{s})\right| = 544\ \mathrm{J}$$

Exercise 10.1

A bar of aluminum with length 0.400 m and uniform cross-sectional area $1.00 \times 10^{-4}\ \mathrm{m^2}$ is placed between two large objects as in Figure 3.9. One object is maintained at 30.0°C and the other is maintained at 20.0°C. Calculate the amount of heat in joules that is conducted through the bar in 15.0 minutes.

Fick's Law of Diffusion

Diffusion in solids, liquids, and gases is described by a second linear law, Fick's law of diffusion:

$$\mathbf{J}_i = -D_i \nabla c_i \quad \text{(Fick's law)} \tag{10.2-3}$$

where c_i is the concentration of substance i and where D_i is a coefficient called the *diffusion coefficient* of substance i. It depends on temperature, pressure, composition, and on the identities of all substances that are present, but not on the concentration gradient. If the concentration varies only in the z direction, Fick's law is

$$J_{iz} = -D_i\left(\frac{\partial c_i}{\partial z}\right) \tag{10.2-4}$$

Fick's law is named for Adolf Fick, 1829–1901, a German physiologist.

According to Fick's law, the driving force for diffusion is the concentration gradient, ∇c_i. The thermodynamically correct driving force for diffusion is the chemical potential gradient. Larger values of the chemical potential correspond to larger values of the concentration, so the gradient of the concentration is related to the gradient of the chemical potential. Fick's law is a good approximation for most gaseous, liquid and solid systems.

Table A.17 in the appendix gives the values of several diffusion coefficients. Many liquid substances with "ordinary size" molecules have diffusion coefficients roughly equal to $10^{-9}\ \mathrm{m^2\,s^{-1}} = 10^{-5}\ \mathrm{cm^2\,s^{-1}}$. Diffusion coefficients for gases are somewhat larger than this value and are more variable in size, and those for solids are much smaller. Diffusion of one solid into another occurs only if the solids are soluble in each other. For example, if finely machined blocks of gold and silver are clamped together and left for several years at room temperature, a significant amount of each substance will diffuse into the other.

EXAMPLE 10.3

Calculate the value of the steady-state diffusion flux of sucrose in water at 25°C if the concentration of sucrose at the top of a cell of height 0.100 m is maintained at $0.060\ \mathrm{mol\ L^{-1}}$ and at the bottom of the cell is maintained at $0.0300\ \mathrm{mol\ L^{-1}}$.

Solution

From Table A.17 of Appendix A,

$$D = 0.5226 \times 10^{-9}\ \mathrm{m^2\,s^{-1}}$$

$$J_z = D\frac{\partial c}{\partial z} \approx D\frac{\Delta c}{\Delta z} = (0.5226 \times 10^{-9}\ \mathrm{m^2\,s^{-1}})\left(\frac{0.0300\ \mathrm{mol\ L^{-1}}}{0.100\ \mathrm{m}}\right)\left(\frac{1000\ \mathrm{L}}{1\ \mathrm{m^3}}\right)$$

$$\approx -1.57 \times 10^{-7}\ \mathrm{mol\,m^{-2}\,s^{-1}} = -1.57 \times 10^{-11}\ \mathrm{mol\,cm^{-2}\,s^{-1}}$$

The Equation of Continuity

We now derive a one-dimensional version of the equation of continuity. Consider a thin horizontal slab in a fluid system in which properties depend on the vertical coordinate z but not on x or y, as depicted in Figure 10.2.

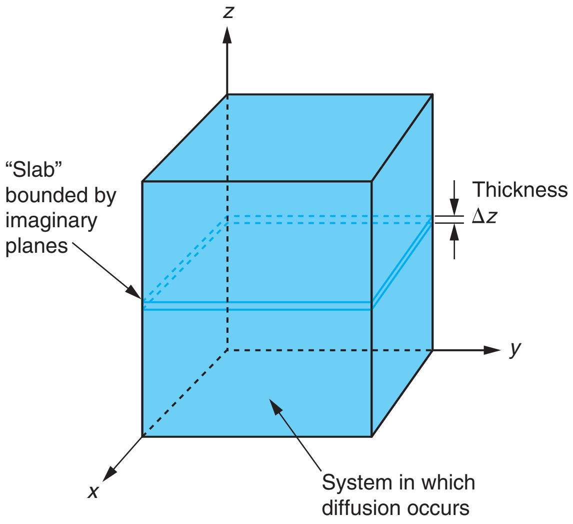

Figure 10.2 A Slab-Shaped Portion of a Fluid System.

The bottom of the slab is located at $z = z'$. The area of the large face of the slab is $\mathscr{A}$ and the thickness of the slab is Δz. Assume that substance number i is diffusing in the positive z direction. The net amount of substance i entering the slab per second from below is

$$\text{influx} = \mathscr{A} J_{iz}(z') \tag{10.2-5}$$

where $J_{iz}(z')$ is the diffusion flux of substance i evaluated at z'. The net amount leaving the slab per second through its top surface is proportional to the diffusion flux evaluated at $z' + \Delta z$ (the top of the slab):

$$\text{efflux} = \mathscr{A} J_{iz}(z' + \Delta z) \tag{10.2-6}$$

The rate of change of n_i, the amount of substance i in the slab, is equal to the influx minus the efflux:

$$\frac{dn_i}{dt} = \mathscr{A}\left[J_{iz}(z') - J_{iz}(z' + \Delta z)\right] \tag{10.2-7}$$

The molar concentration of substance i, denoted by c_i, is the amount of substance i per unit volume. The volume of the slab is $\mathscr{A}\Delta z$, so that the rate of change of c_i is

$$\frac{\partial c_i}{\partial t} = \frac{(dn_i/dt)}{\mathscr{A}\Delta z} = \frac{J_{iz}(z') - J_{iz}(z' + \Delta z)}{\Delta z} \tag{10.2-8}$$

We write $\partial c_i/\partial t$ as a partial derivative because it is taken at a fixed value of z. Now we take the limit that Δz approaches zero so that the right-hand side of Eq. (10.2-8) becomes the negative of a derivative. The result is the one-dimensional version of the *equation of continuity*:

$$\frac{\partial c_i}{\partial t} = -\frac{\partial J_{iz}}{\partial z} \quad \text{(equation of continuity in one dimension)} \tag{10.2-9}$$

The physical content of this equation is the conservation of matter. It is equivalent to saying that rate of change in the concentration is just the difference between what arrives (the influx) and what leaves (the efflux). The three-dimensional version of the equation of continuity is

$$\frac{\partial c_i}{\partial t} = -\left(\frac{\partial J_{ix}}{\partial x} + \frac{\partial J_{iy}}{\partial y'} + \frac{\partial J_{iz}}{\partial z}\right) = -\nabla \cdot \mathbf{J}_i \quad \text{(equation of continuity)} \tag{10.2-10}$$

where $\nabla \cdot \mathbf{J}_i$ is the *divergence* of $\mathbf{J}_i$, defined in Eq. (B-44) of Appendix B. The divergence is a measure of the rate at which "*stream lines*" of a vector quantity diverge from each other. If it is positive, the stream lines move away from each other and the concentration of the substance decreases as one follows the flow. This physical interpretation of the divergence explains why the name was chosen.

Exercise 10.2

Derive Eq. (10.2-10) by considering a small cube in a fluid system instead of a thin slab.

Fick's Second Law of Diffusion

We substitute Eq. (10.2-4) into Eq. (10.2-9) to obtain Fick's second law of diffusion for the one-dimensional case:

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial z}\left(D_i \frac{\partial c_i}{\partial z}\right) \quad \text{(Fick's second law of diffusion in one dimension)} \tag{10.2-11}$$

If D_i is independent of position we obtain the *diffusion equation* for one dimension:

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial z^2} \quad \text{(the diffusion equation in one dimension)} \tag{10.2-12}$$

If the concentration depends on all three coordinates and if D_i is constant, the diffusion equation is

$$\frac{\partial c_i}{\partial t} = D_i\left[\frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2} + \frac{\partial^2 c_i}{\partial z^2}\right] = D_i \nabla^2 c_i \quad \text{(the diffusion equation in three dimensions)} \tag{10.2-13}$$

The Laplacian is named for Pierre Simon, Marquis de Laplace, 1749–1827, a great French mathematician and astronomer who proposed that the solar system condensed from a rotating gas cloud.

The operator ∇^2 ("del squared") is called the *Laplacian operator*.

The one-dimensional diffusion equation in Eq. (10.2-12) contains partial derivatives and is called a *partial differential equation*. The solution of such an equation requires not only the equation, but also specification of *initial conditions*. For example, if a solution initially containing a solute (substance 2) at concentration c_0 in a solvent (substance 1) is placed in the bottom half of a cell and pure solvent is carefully layered above it in the top half of the cell, the initial condition is

$$c_2(z, 0) = \begin{cases} c_0 & \text{if } z < 0 \\ 0 & \text{if } z > 0 \end{cases}$$

where $z = 0$ is the center of the cell. The solution of Eq. (10.2-2) for this initial condition in an infinitely long cell is[1]

$$c_2(z, t) = \frac{c_0}{2}\left[1 - \operatorname{erf}\left(\frac{z}{2\sqrt{D_2 t}}\right)\right] \tag{10.2-14}$$

where erf$(\cdots)$ denotes the *error function*, introduced in Chapter 9 and described in Appendix C. This solution is shown in Figure 10.3 for three values of t and for a value

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[1] See D. P. Shoemaker, C. W. Garland, and J. W. Nibler, *Experiments in Physical Chemistry*, 6th ed., McGraw-Hill, New York, 1996, for a solution pertaining to a cell of finite length.

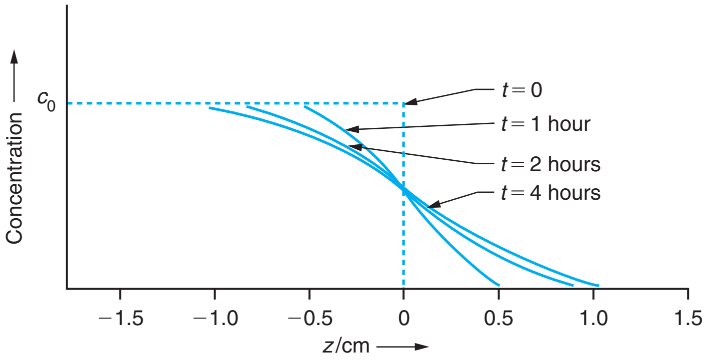

Figure 10.3 Concentration as a Function of Position in a Diffusing System According to Eq. (10.2-14).

of D_2 equal to $1.0 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$, a typical value for ordinary liquids. This figure illustrates the fact that ordinary liquids require several hours to diffuse 1 cm.

Exercise 10.3

Show by substitution that the function of Eq. (10.2-14) satisfies Eq. (10.2-12). You will need the identity

$$\frac{d}{dx}\left(\int_0^x f(u)du\right) = f(x) \tag{10.2-15}$$

Another case that can be mathematically analyzed is approximated when the bottom half of a cell is filled with pure solvent and a very thin layer of solute is layered carefully on it, followed by more pure solvent to fill the cell. An idealized representation of this initial condition is

$$c_2(z,0) = \begin{cases} \infty & \text{if } z = 0 \\ 0 & \text{if } z \neq 0 \end{cases}$$

For an infinitely long cell, a solution of Eq. (10.2-12) corresponding to this initial condition is

$$c_2(z,t) = \frac{n_0}{2\sqrt{\pi D_2 t}} e^{-z^2/4D_2 t} \tag{10.2-16}$$

where n_0 is the total amount of substance 2 initially present per unit cross-sectional area. This function is a *Gaussian function*, or *Gaussian distribution*, as introduced in Chapter 9. It is shown in Figure 10.4 for a value of D_2 equal to $1.0 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$ and for three values of the time.

Exercise 10.4

a. Show by substitution that the function in Eq. (10.2-16) satisfies Eq. (10.2-12).

b. Show that the same amount of substance 2 is present at any time by showing that

$$\int_{-\infty}^{\infty} c_2(z,t)\, dz = n_0$$

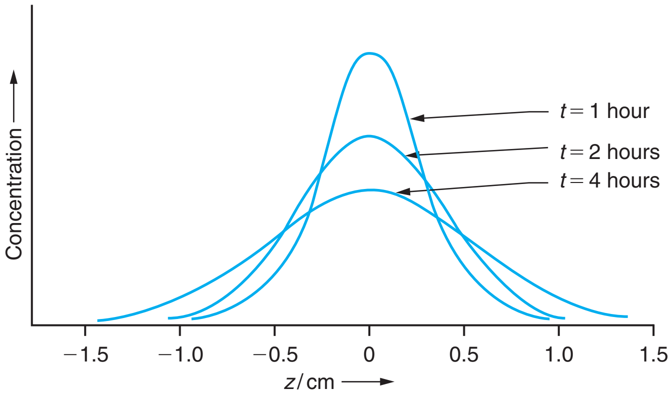

Figure 10.4 Concentration as a Function of Position in a Diffusing System with an Initial Thin Layer of Solute, as in Eq. (10.2-16).

Since all of the molecules of substance 2 started out at $z = 0$, we can use Eq. (10.2-16) to study their average displacement in the z direction. Consider a thin slab of the system lying between z' and $z' + dz$, where z' is some value of z. The fraction of the molecules of substance 2 in the slab at time t is

$$\text{(fraction in slab)} = \frac{c_2(z',t)dz}{\int_{-\infty}^{\infty} c_2(z,t)dz} = \frac{c_2(z',t)dz}{n_0} \tag{10.2-17}$$

The mean value of the coordinate z at time t is given by

$$\langle z(t)\rangle = \frac{1}{n_0}\int_{-\infty}^{\infty} zc_2(z,t)dz = 0 = \frac{1}{n_0}\frac{n_0}{2\sqrt{\pi D_2 t}}\int_{-\infty}^{\infty} ze^{-z^2/4D_2t}dz = 0 \tag{10.2-18}$$

The mean value $\langle z(t)\rangle$ vanishes because the integrand is an *odd function*. If $f(x)$ is an odd function, then $f(-x) = -f(x)$. The fact that $\langle z(t)\rangle = 0$ corresponds to the fact that for every molecule that has moved in the positive z direction, another has moved the same distance in the negative z direction.

The *root-mean-square value* of the z coordinate is a measure of the magnitude of the distance traveled in the z direction by an average molecule. The root-mean-square value is the square root of the *mean-square value*, $\langle z^2\rangle$:

$$z_{\text{rms}} = \left\langle z^2\right\rangle^{1/2} = \left[\frac{1}{n_0}\int_{-\infty}^{\infty} z^2 c_2(z,t)dz\right]^{1/2}$$

$$= \left[\frac{1}{n_0}\frac{n_0}{2\sqrt{\pi D_2 t}}\int_{-\infty}^{\infty} z^2 e^{-z^2/4D_2t}dz\right]^{1/2}$$

$$\boxed{z_{\text{rms}} = [2D_2 t]^{1/2}} \tag{10.2-19}$$

where we have looked up the integral in Appendix C. The root-mean-square displacement is proportional to the square root of the elapsed time and to the square root of the diffusion coefficient. This behavior is similar to that of a *random walk*,[2] which is

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[2] L. E. Reichl, *A Modern Course in Statistical Physics*, University of Texas Press, Austin, 1980, p. 151ff.

a model process such that an object repeatedly takes steps of fixed length in randomly chosen directions. The displacement is proportional to the square root of the elapsed time, not to the elapsed time, since as time passes there are more chances for the object to reverse direction.

Exercise 10.5

Look up the integral and show that Eq. (10.2-19) is correct.

Although we obtained the root-mean-square distance traveled by a diffusing molecule by considering a special case in which all of the molecules started out at the same value of z, the molecules diffuse in the same way for other initial conditions, and we can use Eq. (10.2-19) for any kind of initial conditions and for the x and y directions as well.

EXAMPLE 10.4

Find the root-mean-square distance in three dimensions diffused by glucose molecules in 30.0 minutes in water at 25°C.

Solution

The root-mean-square distance traveled in three dimensions is

$$r_{\text{rms}} = \left\langle x^2 \right\rangle + \left\langle y^2 \right\rangle + \left\langle z^2 \right\rangle^{1/2} = 3\left\langle z^2 \right\rangle^{1/2} = \sqrt{6D_2 t} \qquad (10.2\text{-}20)$$

where we use the fact that all three directions are equivalent. From Table A.17 of Appendix A, the value of the diffusion coefficient of glucose at 25°C is $0.673 \times 10^{-9}\ \text{m}^2\ \text{s}^{-1}$.

$$r_{\text{rms}} = 6D_2 t^{1/2} = \sqrt{6\left(0.673 \times 10^{-9}\ \text{m}^2\ \text{s}^{-1}\right)(30.0\ \text{min})(60\ \text{s min}^{-1})}$$

$$= 2.70 \times 10^{-3}\ \text{m} = 0.270\ \text{cm} = 2.70\ \text{mm}$$

Newton’s Law of Viscous Flow

Consider the arrangement that is shown in Figure 10.1. There is a force per unit area denoted by P_{zy} that is exerted on the upper plate to keep it moving at a constant speed. The first subscript on P_{zy} indicates that the plate is perpendicular to the z direction, and the second subscript indicates that the force is in the y direction. The y component of the velocity depends on z as indicated in Figure 10.1, corresponding to shearing flow.

Newton’s law of viscous flow is named for Sir Isaac Newton, 1642–1727, the great British mathematician and physicist who is famous for Newton’s laws of motion and for being one of the inventors of calculus.

Newton’s law of viscous flow is the linear law for viscous flow:

$$P_{zy} = \eta\left(\frac{\partial u_y}{\partial z}\right) \quad \text{(Newton's law of viscous flow)} \qquad (10.2\text{-}21)$$

The coefficient η is called the *viscosity coefficient* or the *viscosity*. It depends on the temperature and the identity of the substance but does not depend on the rate of shear if Newton’s law is obeyed. Table A.18 of Appendix A gives values for viscosity coefficients for a few liquids and gases. Equation (10.2-21) holds not only for the force exerted on the fluid by the upper plate, but also for the force exerted on one layer of the fluid by the adjacent layer.

Newton's law is formulated so that the rate of shear $(\partial u_y/\partial z)$ plays the role of a driving force while the force per unit area plays the role of a rate variable. This seems like a role reversal, but defining Newton's law in this way corresponds to a viscosity coefficient that is larger for more viscous fluids. Newton's law is valid only for *laminar flow*, which means flow in layers. Flow that is not laminar is called *turbulent flow*, and Newton's law does not hold for turbulent flow. There are some liquids, such as blood and polymer solutions, that do not obey Newton's law even for laminar flow. These fluids are called *non-Newtonian fluids* or *thixotropic fluids* and can be described by a viscosity coefficient that depends on the rate of shear.

EXAMPLE 10.5

The viscosity coefficient of water at 20°C equals $0.001002\ \mathrm{kg\ m^{-1}\ s^{-1}}$ (0.001002 Pa s). For an apparatus like that in Figure 10.1, find the force per unit area required to keep the upper plate moving at a speed of $0.250\ \mathrm{m\ s^{-1}}$ if the tank is 0.0500 m deep.

Solution

The rate of shear has an average value of

$$\frac{\Delta u_y}{\Delta z} = \frac{0.250\ \mathrm{m\ s^{-1}}}{0.0500\ \mathrm{m}} = 5.00\ \mathrm{s^{-1}}$$

so that

$$\begin{aligned} P_{zy} &= \left(0.001002\ \mathrm{kg\ m^{-1}\ s^{-1}}\right)\left(5.00\ \mathrm{s^{-1}}\right) \\ &= 5.01 \times 10^{-3}\ \mathrm{kg\ m^{-1}\ s^{-2}} = 5.01 \times 10^{-3}\ \mathrm{N\ m^{-2}} \end{aligned}$$

Poiseuille's Equation for Viscous Flow in a Tube

This equation describes the rate of laminar flow of a liquid through a straight tube or pipe of length L and radius R. We assume that the tube is parallel to the z axis and we assume that the velocity depends only on r, the perpendicular distance from the center of the tube. Consider a portion of the fluid that is contained in an imaginary cylinder of radius r that is concentric with the tube walls, as depicted in Figure 10.5.

When a steady state has been reached there is no net force on the fluid since it does not accelerate. The frictional force due to viscosity at the surface of the cylinder balances the hydrostatic force pushing the liquid through the cylinder. From Newton's law of viscous flow,

$$\frac{F_{\mathrm{f}}}{\mathscr{A}} = \eta\left|\frac{du_z}{dr}\right| \tag{10.2-22}$$

where F_{f} is the magnitude of the frictional force on the liquid in the imaginary cylinder and $\mathscr{A}$ is the area of its surface (excluding the area of its ends). This area is the circumference times the length of the cylinder:

$$\mathscr{A} = 2\pi rL$$

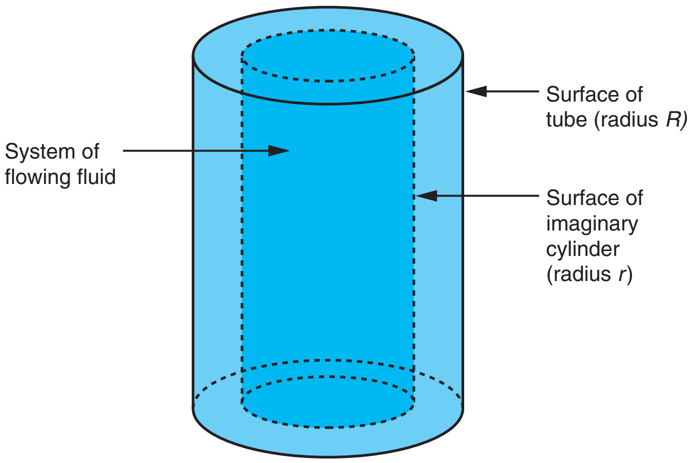

Figure 10.5 Flowing Fluid in a Tube.

The magnitude of the hydrostatic force on the liquid in the imaginary cylinder is equal to the difference of the pressure at its ends times the cross-sectional area of the cylinder:

$$F_{\mathrm{h}} = (P_2 - P_1)\pi r^2$$

where P_2 is the pressure at one end of the tube and P_1 is the pressure at the other end. Equating the magnitudes of $F_{\mathrm{h}}/\mathscr{A}$ and $F_{\mathrm{f}}/\mathscr{A}$ gives

$$\frac{(P_2 - P_1)r}{2L\eta} = \left|\frac{du_z}{dr}\right| = \frac{du_z}{dr}$$

We assume that u_z is negative and conclude that du_z/dr is positive since the magnitude of the flow velocity is larger in the center of the tube. We multiply both sides of this equation by dr and integrate from $r = R$ to $r = r'$, where R is the radius of the tube and r' is some value of r inside the tube:

$$\int_R^{r'} \frac{du_z}{dr} dr = \int_{u_z(R)}^{u_z(r')} du_z = \frac{P_2 - P_1}{2L\eta} \int_R^{r'} r dr$$

If the liquid does not slip on the tube walls $u_z(R)$ will vanish, and the integration yields

$$\boxed{u_z(r) = \frac{P_2 - P_1}{4L\eta}\left(r^2 - R^2\right)} \qquad (10.2\text{-}23)$$

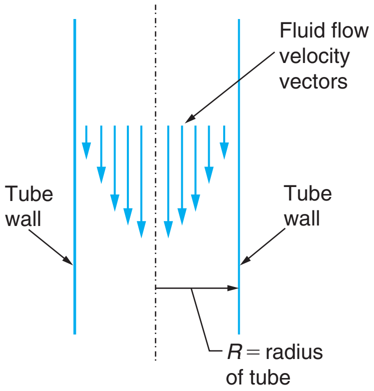

Figure 10.6 The Fluid Velocity in a Tube with Laminar Flow.

where we replace r' by r. This parabolic dependence of the flow velocity on position is represented in Figure 10.6. The length of each arrow in the figure is proportional to the flow velocity at its location.

The total rate of flow of the liquid through the tube can be computed by considering a cylindrical shell of thickness dr and radius r concentric with the walls of the tube and then adding up the contributions of all such shells. The volume of the fluid in this shell that flows out of the tube in 1 s (the contribution of the shell to the volume rate of flow) is equal to the cross-sectional area of the shell times a length equal to the distance traveled in 1 s. Since the circumference of a shell of radius r is equal to $2\pi r$ and since its thickness is dr,

$$(\text{contribution of the shell to } dV/dt) = 2\pi r dr\, |u_z(r)|$$

The total volume rate of flow is the integral over all such shells:

$$\frac{dV}{dt} = 2\pi \int_0^R r\, |u_z(r)|\, dr = 2\pi \frac{P_2 - P_1}{4L\eta} \int_0^R \left(R^2 r - r^3\right) dr$$

$$\boxed{\frac{dV}{dt} = \frac{(P_2 - P_1)\,\pi R^4}{8L\eta} \quad \text{(Poiseuille's equation)}} \tag{10.2-24}$$

Poiseuille's equation is named for Jean Leonard Marie Poiseuille, 1797–1869, a French physician who studied the circulation of blood.

This is Poiseuille's equation for the rate of flow of an incompressible liquid undergoing laminar flow in a tube of radius R. A different version holds for the flow of a gas.[3] Some people are surprised that the rate of flow is proportional to the fourth power of the radius of the pipe. You can think of two powers of R as coming from the dependence of the cross-sectional area on the radius and two powers of R as coming from the dependence of the mean speed on the radius. The mean speed of the fluid is equal to dV/dt divided by the cross-sectional area of the tube:

$$|\langle u_z \rangle| = \frac{1}{\pi R^2}\frac{dV}{dt} = \frac{(P_2 - P_1) R^2}{8L\eta} \tag{10.2-25}$$

EXAMPLE 10.6

Assume that the lower portion of a buret (including the stopcock) consists of a tube of length 7.00 cm and a radius of 0.500 mm. The upper portion is a tube of uniform diameter that is large enough so that the upper tube does not inhibit the flow. The distance from the 0.00-mL mark to the constriction of the lower part is 57.00 cm and the distance from the 50.00-mL mark to the constriction is 4.50 cm. If the buret is filled with water at 20.0°C, find the volume rate of flow and the mean speed of flow when the meniscus is at the 0.00-mL mark. Assume laminar flow.

Solution

The viscosity of water at 20°C is equal to $0.001002\ \mathrm{kg\ m^{-1}\ s^{-1}}$. The density of water at 20°C is $998.23\ \mathrm{kg\ m^{-3}}$. The value of $P_2 - P_1$ is equal to the hydrostatic pressure:

$$P_2 - P_1 = hg\rho = (0.5700\ \mathrm{m})\left(9.80\ \mathrm{m\ s^{-2}}\right)\left(998.2\ \mathrm{kg\ m^{-3}}\right) = 5576\ \mathrm{Pa}$$

$$\frac{dV}{dt} = \frac{(5576\ \mathrm{Pa})(\pi)(0.000500\ \mathrm{m})^4}{(8)(0.0700\ \mathrm{m})\left(0.001002\ \mathrm{kg\ m^{-1}\ s^{-1}}\right)} = 1.95 \times 10^{-6}\ \mathrm{m^3\ s^{-1}}$$
$$= 1.95\ \mathrm{mL\ s^{-1}}$$

$$|\langle u_z \rangle| = \frac{1}{\pi R^2}\frac{dV}{dt} = \frac{1.95 \times 10^{-6}\ \mathrm{m^3\ s^{-1}}}{\pi (0.000500\ \mathrm{m})^2} = 2.48\ \mathrm{m\ s^{-1}}$$

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[3] D. P. Shoemaker, C. W. Garland, and J. W. Nibler, *Experiments in Physical Chemistry*, 6th ed., McGraw-Hill, New York, 1996, p. 126ff.

Exercise 10.6

The inside diameter of the buret in Example 10.6 is equal to 0.80 cm. Calculate the speed of the meniscus when the meniscus is at the 0.00-mL mark.

EXAMPLE 10.7

The blood pressure difference across a capillary in a human body is approximately 22 torr. Assume that a human body contains 1×10^{10} capillaries with an average length of 8×10^{-4} m and an average diameter of 7×10^{-6} m. Although blood is a non-Newtonian fluid and contains red blood cells with diameter near 7×10^{-6} m, assume that a Newtonian viscosity of 0.004 kg $\mathrm{m^{-1}\ s^{-1}}$ can be used ("Blood is thicker than water"). Estimate the volume of blood flowing through the human circulatory system in 1.00 minute, assuming Poiseuille's equation and assuming that the resistance to flow in the arteries and veins is negligible compared with that in the capillaries. The actual volume is approximately 5 liter per minute, which corresponds roughly to the entire volume of blood in the body circulating each minute.

Solution

$$\frac{dV}{dt} = \frac{(P2 - P1)\pi R^4}{8L\eta} \times (\text{number of capillaries})$$

$$= \frac{(22\ \text{torr})\left(\dfrac{101325\ \text{Pa}}{760\ \text{torr}}\right)\pi(3.5 \times 10^{-6}\ \text{m})^4}{8(8 \times 10^{-4}\ \text{m})(0.004\ \text{kg m}^{-1}\ \text{s}^{-1})}(1 \times 10^{10}) = 5.4 \times 10^{-4}\ \text{m}^3\ \text{s}^{-1}$$

$$= (5.4 \times 10^{-4}\ \text{m}^3\ \text{s}^{-1})\left(\frac{60\ \text{s}}{1\ \text{min}}\right)\left(\frac{1\ \text{min}}{1\ \text{m}^3}\right) = 32\ \text{L min}^{-1}$$

This value is too large by a factor of 6, which is not surprising because the red blood cells have a diameter roughly equal to the capillary diameter and the flow cannot be assumed to be laminar.

If the flow of a fluid is turbulent the problem is much more complicated and we will not attempt to discuss it. There is a dimensionless quantity called the *Reynolds number* that can be used to determine whether flow through a tube is likely laminar. The Reynolds number is denoted by $\mathscr{R}$ and is defined for flow in a cylindrical tube by

$$\mathscr{R} = \frac{R\langle u\rangle\rho}{\eta} \quad \text{(definition of Reynolds number)} \tag{10.2-26}$$

where R is the radius of the tube, ρ is the density of the fluid, η is the viscosity of the fluid, and $\langle u\rangle$ is the mean speed of flow in the tube. It is found experimentally that flow in a tube is probably laminar if the Reynolds number is smaller than 2000, no matter what the values of the individual quantities in Eq. (10.2-26) are. If the tube is long, smooth, and straight, the flow might be laminar if the Reynolds number is as large as 3000, but it is best to assume that the flow is not laminar if $\mathscr{R}$ exceeds 2000. If calculation indicates that a flow is not laminar, Poiseuille's equation cannot be used.

EXAMPLE 10.8

Calculate the Reynolds number for the flow of water in Example 10.6. Is the flow laminar?

Solution

$$\mathscr{R} = \frac{R\langle u\rangle\rho}{\eta} = \frac{(0.500 \times 10^{-3}\ \mathrm{m})(2.48\ \mathrm{m\ s^{-1}})(998.2\ \mathrm{kg\ m^{-3}})}{(0.001002\ \mathrm{kg\ m^{-1}\ s^{-1}})} = 1234$$

The flow is probably laminar.

Exercise 10.7

Estimate the Reynolds number for the flow of blood in a typical human capillary. Is the flow laminar? The average diameter of a red blood cell is roughly 7μm, which is the same as the assumed diameter of the capillaries. Comment on this fact.

EXAMPLE 10.9

Water flows through a tube of length 0.420 m and radius 0.00520 m. If the pressure difference is 0.0500 atm and the temperature is 20°C, find the volume of water that flows in 1.000 hour, assuming laminar flow.

Solution

$$\frac{dV}{dt} = \frac{(P_2 - P_1)\pi R^4}{8L\eta} = \frac{(0.0500\ \mathrm{atm})(101325\ \mathrm{Pa\ atm^{-1}})\pi(0.00520\ \mathrm{m})^4}{8(0.420\ \mathrm{m})(0.001002\ \mathrm{kg\ m^{-1}\ s^{-1}})}$$

$$= 3.457 \times 10^{-3}\ \mathrm{m^3\ s^{-1}} = 3.457\ \mathrm{L\ s^{-1}}$$

$$V = (3.457 \times 10^{-3}\ \mathrm{m^3\ s^{-1}})(3600\ \mathrm{s}) = 12.4\ \mathrm{m^3}$$

Exercise 10.8

Estimate the Reynolds number for the flow in the previous example. Is the answer to this example usable? What is the maximum value of the pressure difference that would correspond to laminar flow?

Stokes' Law

Stokes' law was derived from the laws of hydrodynamics by George Gabriel Stokes, 1819–1903, an Anglo-Irish mathematician and physicist who pioneered the science of hydrodynamics.

If a spherical object moves through a fluid or if the fluid flows past it, there is a frictional force on the object. If the flow is laminar and if the object moves with a velocity $\mathbf{v}$ through a fluid with viscosity η, Stokes' law is

$$\boxed{\mathbf{F}_\mathrm{f} = -6\pi\eta r\mathbf{v} \quad \text{(Stokes' law)}} \qquad (10.2\text{-}27)$$

where $\mathbf{F}_f$ is the frictional force on the object and r is the radius of the object. The negative sign indicates that the frictional force is in the opposite direction to the velocity of the object.

EXAMPLE 10.10

An iron sphere of density 7.874 g mL^{-1} is falling at a steady speed in glycerol at 20°C. The density of glycerol is 1.2613 g mL^{-1} and its viscosity at this temperature is 1.49 kg m^{-1} s^{-1} (1.49 Pa s). If the radius of the sphere is 5.00 mm, find the speed, assuming that Stokes' law is valid.

Solution

If the sphere has a constant speed the frictional force must be equal in magnitude to the gravitational force, which (corrected for buoyancy) is equal to

$$\begin{aligned}|\mathbf{F}_g| &= \frac{4\pi r^3}{3}(\rho_{\text{Fe}} - \rho_{\text{gly}})g \\ &= \frac{4\pi}{3}\left(5.00 \times 10^{-3}\ \text{m}\right)^3\left(7874\ \text{kg m}^{-3} - 1261.3\ \text{kg m}^{-3}\right)\left(9.80\ \text{m s}^{-2}\right) \\ &= 0.0339\ \text{kg m s}^{-2} = 0.0339\ \text{N} \\ v &= \frac{|\mathbf{F}_g|}{6\pi\eta r} = \frac{0.0339\ \text{kg m s}^{-2}}{6\pi\left(1.49\ \text{kg m}^{-1}\ \text{s}^{-1}\right)\left(5.00 \times 10^{-3}\ \text{m}\right)} = 0.242\ \text{m s}^{-1}\end{aligned}$$

The Reynolds number can be approximately applied to motion of a spherical object through a liquid by replacing the radius of the tube by the radius of the object and replacing the mean flow speed with the speed of the object through the liquid.

EXAMPLE 10.11

Obtain an approximate Reynolds number for the falling sphere in Example 10.10. Comment on your result.

Solution

$$\mathscr{R} = \frac{R\langle u\rangle\rho}{\eta} = \frac{\left(5.00 \times 10^{-3}\ \text{m}\right)\left(0.242\ \text{m s}^{-1}\right)\left(1261.3\ \text{kg m}^{-3}\right)}{1.49\ \text{kg m}^{-1}\ \text{s}^{-1}} = 1.02$$

The flow is almost certainly laminar.

Exercise 10.9

a. Find the speed of the iron sphere in Example 10.10 if it is falling in water at 20°C instead of glycerol assuming that Stokes' law is valid. The viscosity of water at 20°C is 0.001002 kg m^{-1} s^{-1} and its density is 998.2 kg m^{-3}. Find the value of the Reynolds number and decide if Stokes' law is valid.

b. Find the speed of an iron sphere falling in glycerol at 20°C if the radius of the sphere is 5.00 cm. Calculate the Reynolds number and comment on your result.

c. Estimate the diameter of the largest iron sphere for which Stokes' law is valid if it is falling in glycerol at 20°C.

PROBLEMS

Section 10.2: Transport Processes

10.3 One end of a bar of aluminum is maintained at 100.0°C and the other is maintained at 20.0°C. The length of the bar is 0.500 m, and its cross-sectional area is $1.00\,\mathrm{cm}^2 = 0.000100\,\mathrm{m}^2$. The thermal conductivity of aluminum is equal to $237\,\mathrm{J\,s^{-1}\,m^{-1}\,K^{-1}} = 237\,\mathrm{watt\,m^{-1}\,K^{-1}}$. How much heat is transferred through the bar in 1.00 minute?

10.4 The thermal conductivity of copper at 300 K is equal to $398\,\mathrm{J\,s^{-1}\,m^{-1}\,K^{-1}}$. A bar of copper with cross-sectional area $1.00\,\mathrm{cm}^2$ and length 10.00 cm is maintained with one end at 305.0 K and the other end at 295.0 K. Find the rate at which heat is conducted through the bar.

10.5 **a.** Show that the concentration expression in Problem 10.2 can satisfy Fick's second law of diffusion, Eq. (10.2-13).

b. Find the expression for the constant b_2 in terms of a_2 and D_2, the diffusion coefficient, assuming Fick's law to be valid. What is the physical interpretation of the constant a_2?

c. If $D_2 = 1.00 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$ and if $a_2 = 10.0\,\mathrm{m^{-1}}$, find the value of b_2.

10.6 At 25.4°C, the diffusion coefficient of methane in glycerol equals $9.5 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$.

a. Find the root-mean-square displacement in one direction of a methane molecule in 60 minutes and in 120 minutes.

b. Find the total root-mean-square distance traveled in 90 minutes by a methane molecule in glycerol at 25.4°C.

10.7 **a.** A uniform tube with cross-sectional area $1.00 \times 10^{-5}\,\mathrm{m^2}$ and length 0.100 m connects two large vessels in which effective stirring is maintained. Each contains a solution of 1,1,1-trichloroethane (methyl chloroform) in carbon tetrachloride, and a uniform temperature of 25.00°C is maintained in the entire system. If one vessel contains a solution of concentration $0.500\,\mathrm{mol\,L^{-1}}$ and the other contains a solution of concentration $0.100\,\mathrm{mol\,L^{-1}}$, and if a steady state has been achieved, find the rate in $\mathrm{mol\,s^{-1}}$ at which 1,1,1-trichloroethane is being transported through the tube. The diffusion coefficient at 25.0°C is equal to $1.4 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$.

b. Find the root-mean-square distance in one direction traveled by a 1,1,1-trichloroethane molecule in 30.0 minutes. How long is required for an average molecule to traverse the length of the tube?

10.8 Two large containers are connected by a tube of length 10.0 cm and inside diameter 0.60 cm. Chamber A is filled with an aqueous solution of glucose with molar concentration $0.500\,\mathrm{mol\,L^{-1}}$ and container B is filled with a solution of glucose with molar concentration $0.100\,\mathrm{mol\,L^{-1}}$. The two containers have effective stirrers operating in them, but we can assume that the liquid in the connecting tube is not stirred. Calculate the amount of glucose that diffuses through the tube in 10.0 minutes. The diffusion coefficient of glucose in water at this temperature is equal to $6.73 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$.

10.9 Estimate the time required for molecules of a *neurotransmitter* to diffuse across a *synapse* (the gap between two nerve cells) by calculating the time required for $\langle x^2\rangle^{1/2}$ to equal 50 nm, a typical synapse spacing, if $D = 5 \times 10^{-10}\,\mathrm{m^2\,s^{-1}}$.

10.10 The diffusion coefficient of 1,1,1-trichloroethane (TCE) in carbon tetrachloride at 25°C is equal to $1.36 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$. Find the time required for the root-mean-square displacement of TCE molecules in one dimension to equal 1.00 cm at 25°C.

10.11 Liquid water at 20°C is flowing through a tube of radius 5.00 mm with a speed at the center of the tube (at $r = 0$) equal to $4.55\,\mathrm{cm\,s^{-1}}$.

a. Find the speed at $r = 2.00\,\mathrm{mm}$.

b. Find $P_2 - P_1$ if the length of the tube is 0.500 m.

c. Find dV/dt, the volume rate of flow through the tube.

d. Find the value of the Reynolds number. Is the flow laminar?

10.12 Find the root-mean-square distance in the z direction traveled by glucose molecules in 1.00 hour in a dilute aqueous solution at 25°C.

10.13 A lead sphere of radius 0.500 cm is falling at a steady speed in water at 25.0°C. The density of lead is $11.35\,\mathrm{g\,mL^{-1}}$. Find its speed. Comment on whether you think your value is reasonable. If not, what could be the reason that it is not?

10.14 A glass marble is falling at a steady speed in a swimming pool at 20.0°C. If the density of the marble is $2.2 \times 10^3\,\mathrm{kg\,m^{-3}}$ and the radius of the marble is 0.0075 m, find its speed, assuming laminar flow. If the flow is not laminar, do you think the speed would be greater or less than expected with laminar flow?

10.15 An Ostwald viscometer consists of a capillary tube through which a fixed volume of a liquid is allowed to flow under hydrostatic pressure. If in a certain viscometer the fixed volume of water requires 215.3 s to flow at 20°C, calculate the time required for this volume of sulfuric acid to flow at 20°C. Use the fact that the hydrostatic force in a given viscometer is proportional to the density of the liquid. The density of sulfuric acid is 1.834 g mL^{-1} and that of water is 0.9982 g mL^{-1} at 20°C.

10.16 In a certain Ostwald viscometer (see Problem 10.15), a fixed volume of water required 183.5 s to flow at 20°C. If the same volume of mercury flows in 20.78 s at 20°C, find the viscosity of mercury at 20°C. The density of water is 0.99823 g mL^{-1}, and that of mercury is 13.5462 g mL^{-1}.

10.17 In experiments with a certain Ostwald viscometer, a time of 56.8 s is required for the specified volume of water to flow at 20.0°C. Find the time required for the same volume of ethanol to flow. The density of ethanol is 0.7893 g mL^{-1} at this temperature, and that of water is 0.9982 g mL^{-1}. The viscosity of water is $1.002 \times 10^{-3}\ \mathrm{kg\ m^{-1}\ s^{-1}}$ at this temperature and that of ethanol is $1.200 \times 10^{-3}\ \mathrm{kg\ m^{-1}\ s^{-1}}$.

10.18 The *poise* ($\mathrm{g\ cm^{-1}\ s^{-1}}$) is the cgs unit of viscosity. The viscosity of dry air is given in poise as a function of temperature by the following formula:[4]

$$\eta = \frac{(1345.8 \times 10^{-7})T^{3/2}}{T + 110.4}$$

where units are disregarded in the formula. Estimate the steady-state speed of a basketball falling in air at 25°C, assuming laminar flow. The circumference of a standard U.S. basketball is 30 inches, and its mass is between 20 and 22 ounces. Does your answer seem reasonable? If not, explain why it is not.

10.19 **a.** A certain garden hose is advertised to be able to deliver 550 gallons of water per hour. If the hose if 50 feet long and has an inside diameter of 5/8 inch, estimate the water pressure necessary to deliver this much water, assuming laminar flow.

b. Calculate the Reynolds number for the flow in part a, and determine whether the flow is laminar.

10.20 Water at 298.15 K is flowing through a tube of length 50.0 cm and radius 0.400 cm. The pressure difference between the two ends is 0.750 atm.

a. Find the volume of water that flows through the tube in 1.00 minute assuming laminar flow.

b. Calculate the Reynolds number and determine whether the flow is laminar.

10.21 **a.** Using the equation of continuity, show for a diffusing system in a steady state that the concentration gradient must be uniform if the diffusion coefficient is a constant and if the cross-sectional area of the system is uniform.

b. Argue that the temperature gradient must be uniform in a system of uniform cross section with a uniform thermal conductivity if a steady state occurs.

10.3 The Gas Kinetic Theory of Transport Processes in Hard-Sphere Gases

An elementary molecular theory for nonequilibrium processes in a hard-sphere gas can be based on the gas kinetic theory that was presented in Chapter 9. We will apply this theory to self-diffusion and give the results of its application to heat conduction and viscous flow.

Self-Diffusion in a Hard-Sphere Gas

For diffusion to take place there must be at least two substances present. *Self-diffusion* is a model diffusion process in which the molecules of the two substances have all of their properties in common but can somehow be distinguished from each other. This

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[4] Tables of Thermal Properties of Gases, Table 1-B, U.S. Natl. Bur. Stand. Circ. 564, U.S. Government Printing Office, Washington, DC, 1955.

situation can be approximated in the laboratory by using two substances that differ only by isotopic substitution. Diffusion of such actual substances is called *tracer diffusion*.

We now define a gaseous model system that contains two kinds of hard spherical molecules with the same size and mass. The system is at a uniform temperature and pressure and is contained in a rectangular box with four vertical sides. The concentrations of the two substances depend on the vertical coordinate z but not on the horizontal coordinates x and y. The sum of the two concentrations is independent of position so that the pressure is uniform. Figure 10.7 depicts this model system. In the interior of the system we place three imaginary horizontal planes. The center plane is located at $z = z'$, the upper plane is located at $z' + \lambda$, and the lower plane is located at $z' - \lambda$, where λ is the mean free path between collisions of a molecule with any kind of molecule.

We assume that all molecules passing upward through the center plane last suffered collisions at the lower plane and were equilibrated at that location. Molecules passing downward through the center plane are assumed to have been equilibrated at the upper plane. This assumption is not correct for every molecule since the z component of every free path is not equal to the mean free path and since equilibration might not be complete at each collision. It should be roughly valid on the average.

The number of molecules of substance 1 passing upward through the center plane per unit area per unit time is given by Eq. (9.6-6):

$$\nu_1(\text{up}) = \frac{1}{4}\mathcal{N}_1(z' - \lambda)\langle v \rangle \tag{10.3-1}$$

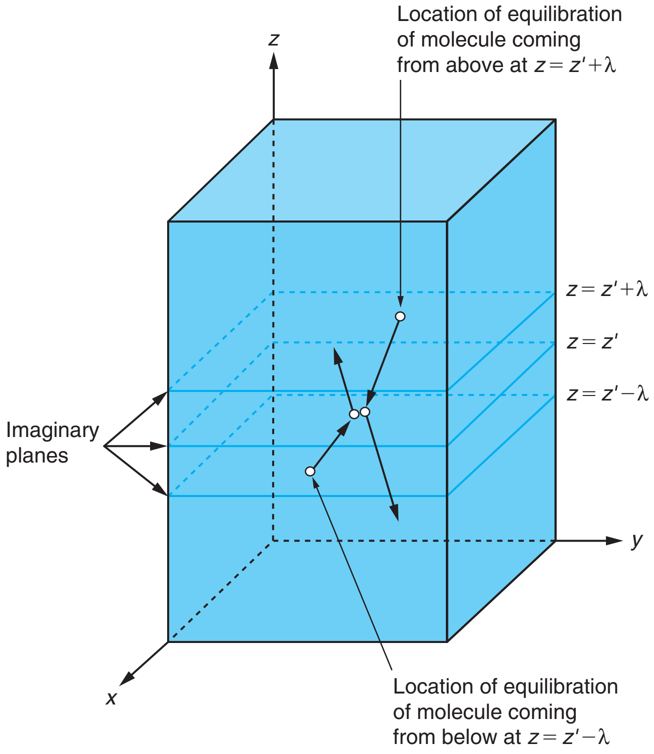

Figure 10.7 The Model System Showing Three Imaginary Planes for Analysis of Self-Diffusion in a Hard-Sphere Gas.

where $\langle v \rangle$ is the mean speed of the molecules and where the number density $\mathscr{N}_1(z' - \lambda)$ is evaluated at $z' - \lambda$, the location of the lower plane. Since the temperature of the system is uniform, the mean speed is independent of position. The rate of molecules of substance 1 passing downward through unit area of the center plane is given by Eq. (9.6-6) with $\mathscr{N}_1$ evaluated at $z' + \lambda$:

$$\nu_1(\text{down}) = \frac{1}{4}\mathscr{N}_1(z' + \lambda)\langle v \rangle \tag{10.3-2}$$

The mean speed of the molecules has the same value in both of these equations since the temperature is uniform. The diffusion flux equals the net amount (in moles) of the substance passing unit area per second:

$$J_{1z} = \frac{1}{N_{\text{Av}}}\left[\nu_1(\text{up}) - \nu_1(\text{down})\right] \tag{10.3-3}$$

where the divisor of Avogadro's constant is needed to express the flux in moles instead of molecules. The expressions for the upward and downward rates are substituted into Eq. (10.3-3):

$$\begin{aligned} J_{1z} &= \frac{\langle v \rangle}{4N_{\text{Av}}}\left[\mathscr{N}_1(z' - \lambda) - \mathscr{N}_1(z' + \lambda)\right] = \frac{\langle v \rangle}{4}\left[c_1(z' - \lambda) - c_1(z' + \lambda)\right] \\ &= -\frac{\langle v \rangle}{4}\left[\frac{c_1\big(z' + \lambda\big) - c_1\big(z' - \lambda\big)}{2\lambda}\right]2\lambda \end{aligned}$$

where the molar concentration c_1 is equal to $\mathscr{N}_1/N_{\text{Av}}$ and where we have in the last equation multiplied and divided by 2λ.

If c_1 is approximately a linear function of z, the quotient of finite differences is nearly equal to a derivative, and we write

$$J_{1z} = -\frac{\langle v \rangle \lambda}{2}\frac{\partial c_1}{\partial z} \tag{10.3-4}$$

Comparison of this equation with Fick's law as given in Eq. (10.2-4) gives

$$D_1 = \frac{\langle v \rangle \lambda}{2} \tag{10.3-5}$$

Notice how reasonable this equation is. The diffusion coefficient is proportional to the mean speed of the molecule and to the mean free path.

The mean free path between collisions with any kind of molecule is given by Eq. (9.8-18):

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 \mathscr{N}_{\text{tot}}} \tag{10.3-6}$$

where d is the effective hard-sphere diameter of the molecules and where $\mathscr{N}_{\text{tot}}$ is the total number density

$$\mathscr{N}_{\text{tot}} = \mathscr{N}_1 + \mathscr{N}_2 \tag{10.3-7}$$

The total number density occurs in the formula because we include collisions with both types of molecules. From the formulas for the mean speed and the mean free path in

Chapter 9 we have

$$D_1 = \frac{1}{2}\left(\frac{8k_BT}{\pi m}\right)^{1/2}\frac{1}{\sqrt{2}\pi d^2\mathcal{N}_{\text{tot}}} = \frac{1}{\pi d^2\mathcal{N}_{\text{tot}}}\left(\frac{k_BT}{\pi m}\right)^{1/2} \quad \begin{array}{l}\text{(approximate}\\ \text{expression)}\end{array} \tag{10.3-8}$$

where we have used Eq. (9.4-6) for the mean speed and Eq. (9.8-18) for the mean free path.

Our result can be improved by taking into account the fact that all molecules do not arrive at a given plane having had their last collision at the same location. When this is done, the resulting expression for the diffusion coefficient has the same dependence on density, temperature, mass, and hard-sphere diameter as the expression of Eq. (10.3-8), but differs by 18% from that expression:[5]

$$D_1 = \frac{3\pi}{16}\lambda\langle v\rangle = \frac{3}{8d^2\mathcal{N}_{\text{tot}}}\left(\frac{k_BT}{\pi m}\right)^{1/2} \quad \begin{array}{l}\text{(more accurate}\\ \text{expression)}\end{array} \tag{10.3-9}$$

We will use this equation for numerical calculations instead of Eq. (10.3-8).

Table A.19 in the appendix gives some experimental values for self-diffusion coefficients, obtained from tracer diffusion experiments. When these data are used to calculate effective hard-sphere diameters the calculated hard-sphere diameters depend on temperature, with smaller diameters corresponding to higher temperatures. This is explained by the fact that the actual intermolecular repulsive potential is not infinitely steep like the hard-sphere potential. When two molecules strike together more strongly, as they more often do at higher temperature, the distance of closest approach is smaller and the effective hard-sphere diameter is smaller.

EXAMPLE 10.12

Calculate the self-diffusion coefficient of N_2 gas at 298 K and 1.00 atm.

Solution

We use the ideal gas law to calculate the number density:

$$\mathcal{N}_{\text{tot}} = \frac{N}{V} = \frac{P}{k_BT} = \frac{101325\ \text{N m}^{-2}}{\left(1.3807\times10^{-23}\ \text{J K}^{-1}\right)(298\ \text{K})} = 2.46\times10^{25}\ \text{m}^{-3}$$

From Table A.15, $d = 3.7\times10^{-10}$ m.

$$D_1 = \frac{3}{8d^2\mathcal{N}_{\text{tot}}}\left(\frac{k_BT}{\pi m}\right)^{1/2} = \frac{3}{8d^2\mathcal{N}_{\text{tot}}}\left(\frac{RT}{\pi M}\right)^{1/2}$$

$$= \frac{3}{8\left(3.7\times10^{-10}\ \text{m}\right)^2\left(2.46\times10^{25}\ \text{m}^{-3}\right)}\left(\frac{\left(8.3145\ \text{J K}^{-1}\ \text{mo1}^{-1}\right)(298\ \text{K})}{\pi\left(0.028\ \text{kg mol}^{-1}\right)}\right)^{1/2}$$

$$= 1.9\times10^{-5}\ \text{m}^2\ \text{s}^{-1}$$

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[5] R. D. Present, *Kinetic Theory of Gases*, McGraw-Hill, 1958, Section 8-3.

Exercise 10.10

Evaluate the self-diffusion coefficient of argon at 1.00 atm and 0°C from the value of the hard-sphere diameter in Table A.15 in the appendix for this temperature. Compare your result with the experimental value of the self-diffusion coefficient in Table A.19 in the appendix.

Exercise 10.11

Find the effective hard-sphere diameter of argon atoms from each of the self-diffusion coefficient values in Table A.19. Comment on your results. Compare your results with the values in Table A.15 in the appendix.

Thermal Conduction in the Hard-Sphere Gas

An analysis of heat conduction that is very similar to that for self-diffusion can be carried out for a system of hard spheres having a uniform pressure but a temperature that depends on z.[6] We again consider the same three imaginary planes in the system as before and assume that the molecules reaching the central plane were equilibrated at the temperature of the upper plane or the temperature of the lower plane. We assume that the heat capacity per molecule is constant and write for the mean molecular kinetic energy

$$\langle \varepsilon \rangle = c_{\mathrm{V}} T = \frac{C_{\mathrm{V,m}}}{N_{\mathrm{Av}}} T$$

where c_{V} is the heat capacity per molecule. The net (upward) energy flux is given by

$$q_z = \nu\varepsilon(z' - \lambda) - \nu\varepsilon(z' + \lambda) = \frac{1}{4}\mathcal{N}\langle v\rangle \left[\varepsilon(z' - \lambda) - \varepsilon(z' + \lambda)\right]$$

where ν is the rate per unit area of molecules reaching the center plane, as discussed in Chapter 9.

$$\varepsilon(z' - \lambda) - \varepsilon(z' + \lambda) \approx \frac{\partial \varepsilon}{\partial z}(2\lambda) = \frac{\partial \varepsilon}{\partial T}\frac{\partial T}{\partial z}(2\lambda) = \frac{C_{\mathrm{V,m}}}{N_{\mathrm{Av}}}\frac{\partial T}{\partial z}(2\lambda)$$

$$q_z \approx \frac{1}{4}\mathcal{N}\langle v\rangle(2\lambda)\frac{C_{\mathrm{V,m}}}{N_{\mathrm{Av}}}\frac{\partial T}{\partial z} = \kappa\frac{\partial T}{\partial z}$$

$$\kappa = \frac{1}{2}\mathcal{N}\langle v\rangle\lambda\frac{C_{\mathrm{V,m}}}{N_{\mathrm{Av}}} \tag{10.3-10}$$

If the same corrections are applied that were used to derive Eq. (10.3-9), a more accurate expression is obtained:

$$\kappa = \frac{25\pi}{64}c_{\mathrm{V}}\lambda\langle v\rangle\mathcal{N} \tag{10.3-11a}$$

$$\kappa = \frac{25}{32}\frac{c_{\mathrm{V}}}{d^2}\left(\frac{k_{\mathrm{B}}T}{\pi m}\right)^{1/2} = \frac{25}{32}\frac{c_{\mathrm{V}}}{d^2}\left(\frac{RT}{\pi M}\right)^{1/2} \quad \text{(more accurate expression)} \tag{10.3-11b}$$

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[6] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1954, p. 9ff.

We will apply this expression only to a monatomic gas. For a diatomic or polyatomic gas the thermal conductivity is more complicated, since it is not an adequate approximation to assume that rotational and vibrational motions are equilibrated at the upper and lower planes.

EXAMPLE 10.13

Calculate the thermal conductivity of argon gas at 20°C from its hard-sphere diameter in Table A.15 in the appendix. Compare your value with that in Table A.16 in the appendix.

Solution

$$\kappa = \frac{25}{32}\left(\frac{3}{2}\right)\frac{1.3807 \times 10^{-23}\ \mathrm{J\ K^{-1}}}{(3.61 \times 10^{-10}\ \mathrm{m})^2}\left(\frac{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(293.15\ \mathrm{K})}{\pi(0.039948\ \mathrm{kg\ mol^{-1}})}\right)^{1/2}$$

$$= 0.0173\ \mathrm{J\ s^{-1}\ m^{-1}K}$$

The value in Table A.16 is 0.01625 J $\mathrm{s^{-1}\ m^{-1}K}$.

Exercise 10.12

Calculate the effective hard-sphere diameter of helium at 20°C and 1.00 atm from its thermal conductivity in Table A.16 of the appendix. Compare your result with the value in Table A.15 in the appendix.

The Viscosity of the Hard-Sphere Gas

If a fluid has a velocity in the y direction that depends on z, the y component of the momentum is transported in the z direction as each layer of fluid puts a frictional force on the next layer. An analysis similar to that of self-diffusion and thermal conductivity can be carried out for a hard-sphere gas. The net flow of the momentum is computed and the result is an expression for the *viscosity coefficient*:[7]

$$\eta = \frac{5\pi}{32} m\lambda\langle v\rangle\mathcal{N} = \frac{5}{16}\frac{1}{d^2}\sqrt{\frac{mk_\mathrm{B}T}{\pi}} \qquad (10.3\text{-}12)$$

This equation is at the level of accuracy of Eqs. (10.3-9) and (10.3-11).

All three transport coefficients are proportional to the mean speed of the molecules and to the mean free path, which means that they are proportional to the square root of the temperature at constant density. A gas becomes more viscous when the temperature is raised (opposite to the behavior of a liquid). The coefficient of viscosity and the coefficient of thermal conductivity are independent of the number density. This behavior was predicted by kinetic theory before it was observed experimentally.

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[7] R. D. Present, *Gas Kinetic Theory*, McGraw-Hill, New York, 1958, Section 11-2.

EXAMPLE 10.14

Calculate the viscosity coefficient of O_2 gas at 292 K from its hard-sphere diameter. Compare your result with the value in Table A.18 in the appendix.

Solution

$$m = \frac{0.03200\ \text{kg mol}^{-1}}{6.02214 \times 1023\ \text{mol}^{-1}} = 5.3137 \times 10^{-26}\ \text{kg}$$

$$\eta = \frac{5}{16}\frac{1}{(3.58 \times 10^{-10}\ \text{m})^2}\left(\frac{(5.3137 \times 10^{-26}\ \text{kg})(1.3807 \times 10^{-23}\ \text{J K}^{-1})(292\ \text{K})}{\pi}\right)^{1/2}$$
$$= 2.013 \times 10^{-5}\ \text{kg m}^{-1}\ \text{s}^{-1}$$

The value in Table A.18 is 2.018 g $\times 10^{-5}$ kg m^{-1} s^{-1}. This relatively close agreement is not surprising since the effective hard-sphere diameters are presumably obtained from viscosity data, probably using a somewhat more accurate formula than Eq. (10.3-12).

Exercise 10.13

Calculate the hard-sphere diameter of water molecules at 100°C from the coefficient of viscosity in Table A.18. Compare your result with the hard-sphere diameter in Table A.15.

Exercise 10.14

Certain useful dimensionless ratios of physical constants are called *dimensionless groups*. Show that for a monatomic hard-sphere gas each of the following ratios equals a dimensionless constant and find each constant:

$$\frac{\eta}{m\mathcal{N}D},\quad \frac{c_V\eta}{\kappa m},\quad \frac{Dc_V\mathcal{N}}{\kappa}$$

PROBLEMS

Section 10.3: The Gas Kinetic Theory of Transport Processes in Hard-Sphere Gases

10.22 **a.** Calculate the self-diffusion coefficient of helium gas at STP (273.15 K, 1.000 atm) from the hard-sphere diameter.

b. Calculate the self-diffusion coefficient of argon gas at STP from the hard-sphere diameter.

c. Calculate the self-diffusion coefficient of argon gas at 0.100 atm and 273.15 K from the hard-sphere diameter. Comment on the comparison with the result of part b.

d. Calculate and compare the rms distances traveled in one direction in 60.0 minutes by He and Ar atoms diffusing at STP in self-diffusion experiments.

10.23 **a.** Calculate the self-diffusion coefficient of carbon dioxide gas at 1.000 bar and 298.15 K from the hard-sphere diameter.

b. Calculate the self-diffusion coefficient of O_2 gas at 1.000 bar and 373.15 K from the hard-sphere diameter.

10.24 Calculate the effective hard-sphere diameter of argon atoms from the value of its self-diffusion coefficient at 273 K in Table A.19. Compare it with the value from Table A.15.

10.25 Show that for fixed pressure, the self-diffusion coefficient of a hard-sphere gas is proportional to $T^{3/2}$. Explain in words why the temperature dependence is different for constant pressure than for constant number density.

10.26 For diffusion in a two-substance hard-sphere gas in which the substances have different masses and sizes and in which neither substance is dilute, one uses the linear equation

$$\mathbf{u}_1 - \mathbf{u}_2 = \frac{1}{x_1 x_2} D_{12} \nabla x_1$$

instead of Fick's law. In this equation, $\mathbf{u}_1$ is the mean drift velocity of molecules of component 1 and $\mathbf{u}_2$ is the same quantity for component 2. The quantities x_1 and x_2 are the two mole fractions and D_{12} is called the mutual diffusion coefficient. For a mixture of hard spheres[8]

$$D_{12} = \frac{3}{8\pi^{1/2}} \frac{1}{d_{12}^2 \mathcal{N}_{\mathrm{tot}}} \left(\frac{k_B T}{2\mu} \right)^{1/2}$$

where μ is the reduced mass, $\mathcal{N}_{\mathrm{tot}}$ is the total number density, and d_{12} is the mean collision diameter

$$d_{12} = \frac{d_1 + d_2}{2}$$

Find the mutual diffusion coefficient for helium and argon at 273.15 K and 1.000 atm pressure. Compare with the self-diffusion coefficient of each substance from Problem 10.22.

10.27 Gaseous argon has a viscosity of 2.099×10^{-5} Pa s $= 2.099 \times 10^{-5}$ kg m^{-1} s^{-1} at 0°C and 1.000 atm.

a. Estimate its viscosity at 100°C and 1.000 atm.

b. Estimate its viscosity at 0°C and 0.500 atm.

c. Estimate its viscosity at 100°C and 0.500 atm.

10.28 Liquid uranium hexafluoride has a vapor pressure at 56°C equal to 765 torr, so UF_6 is a gas at 60°C and 1.000 atm. Various diffusion and thermal diffusion processes were used in World War II to separate gaseous $^{235}UF_6$ molecules from $^{238}UF_6$ molecules. Calculate the mutual diffusion coefficient of these substances at 60°C and 1.000 atm. Calculate the self-diffusion coefficient of ^{238}U at this temperature and pressure. Make a reasonable estimate of the effective hard-sphere diameter of UF_6 and see Problem 10.26 for the necessary equation.

10.29 Calculate the mutual diffusion coefficient for helium and carbon dioxide at 298.15 K and 1.000 bar. (See Problem 10.26 for equations.)

10.30 At 20.0°C, the viscosity of ammonia gas is equal to 9.82×10^{-6} kg m^{-1} s^{-1}. Find the effective hard-sphere diameter of ammonia molecules at this temperature.

10.31 From values of the viscosity in Table A.18, calculate the effective hard-sphere diameter of gaseous water at 100°C and at 200°C. Explain any temperature dependence.

10.32 For a temperature of 293 K and a pressure of 1.00 atm, calculate the viscosities of helium gas and of carbon dioxide gas from the hard-sphere diameters. Explain why the values compare as they do.

10.33 Find the value of each of the ratios:

a. The self-diffusion coefficient of helium divided by the self-diffusion coefficient of argon at the same pressure and temperature.

b. The viscosity of helium divided by the viscosity of argon at the same pressure and temperature.

c. The viscosity of helium at 1.00 atm and 298.15 K divided by the viscosity of helium at 0.100 atm and 298.15 K.

d. The thermal conductivity of argon divided by the thermal conductivity of xenon at the same pressure and temperature.

10.4 Transport Processes in Liquids

In Section 9.9 the molecular environment of a molecule in a liquid was described as a cage made up of neighboring molecules, in which the molecule is confined by repulsive intermolecular forces. If a molecule were absolutely confined to such a cage there could be no diffusion or viscous flow, and this is almost the case in solids. In a liquid there are voids among the neighbors. There is a chance that, after colliding many times with the neighboring molecules in a given cage, a molecule can push past some neighbors

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[8] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1954, pp. 14, 518.

into an adjacent cage. Whereas a molecule in a typical gas might undergo a collision every 10^{-10} to 10^{-9} s, a molecule in a typical liquid might undergo a collision with its neighbors every 10^{-13} to 10^{-11} s (see Example 9.21). However, only a small fraction of the collisions leads to motion into another cage. The molecule might move to a new cage every 10^{-11} to 10^{-9} second.

EXAMPLE 10.15

a. If a substance has $D = 1.0 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}$, find the root-mean-square distance diffused in 1.00 hour.

b. In the random walk model an object repeatedly takes a step of fixed length in a randomly chosen direction. The root-mean-square distance traveled in one dimension is equal to the square root of the number of steps, N, times the length of a step, denoted by a: $d_{\mathrm{rms}} = \sqrt{N}a$. If a molecule moves 6×10^{-10} m each time it moves to a new cage and if it requires 1 hour to diffuse the distance found in the previous example, estimate the time required to move to a new cage.

Solution

a. From Eq. (10.2-20) for motion in three dimensions

$$r_{\mathrm{rms}} = \sqrt{6D_2t} = \sqrt{6(1.0 \times 10^{-9}\,\mathrm{m^2\,s^{-1}})(3600\,\mathrm{s})} = 0.0046\,\mathrm{m} = 0.46\,\mathrm{cm}$$

b. We calculate the number of steps in 1.00 hour:

$$r_{\mathrm{rms}} = 0.0046\,\mathrm{m} = N^{1/2}(6 \times 10^{-10}\,\mathrm{m})$$

$$N = \left(\frac{0.0046\,\mathrm{m}}{6 \times 10^{-10}\,\mathrm{m}}\right)^2 = 5.9 \times 10^{13}\ \text{steps in 1.00 hour}$$

$$\text{time for one step} = \frac{3600\,\mathrm{s}}{5.9 \times 10^{13}} = 6.1 \times 10^{-11}\,\mathrm{s}$$

In some approximate theories of liquid transport it is found that the motion of a molecule or ion through a fluid is on the average impeded by an effective frictional force that is approximately proportional to the negative of the average velocity of the molecules or ions:

$$\mathbf{F}_{\mathrm{f}} = -f\mathbf{v} \tag{10.4-1}$$

where $\mathbf{F}_{\mathrm{f}}$ is the frictional force, $\mathbf{v}$ is the velocity of the molecule or ion, and where f is called the *friction coefficient*. This equation is similar to Stokes' law, Eq. (10.2-27), which applies to a macroscopic sphere moving through a continuous fluid. We now write the analogue of Eq. (10.2-27):

$$f = 6\pi\eta r_{\mathrm{eff}} \tag{10.4-2}$$

and use this relation to define r_{eff} as an *effective radius* of the molecule or ion. Reasonable values for effective radii of molecules and hydrated ions are obtained from experimental data. Macromolecules (molecules of large molecular mass) and colloidal particles (particles roughly 3 to 1000 nm in diameter) nearly obey Stokes' law, and their effective radii are nearly equal to their actual radii.

Brownian motion is named for Robert Brown, 1773–1858, the most prominent British botanist of his time. He observed a jittery motion of pollen grains and showed that this phenomenon was not due to biological motility by observing it in mineral particles, including some taken from the Sphinx. Brown is also credited with discovering the cell nucleus around 1833.

Around 1905 Einstein devised a theory of *Brownian motion*, the irregular motion of colloidal particles suspended in a liquid. Einstein assumed that a colloidal particle is bombarded randomly by the molecules of the solvent and was able to show for a spherical colloidal particle that the mean-square displacement of the particle in the z direction in a time t is given by

$$\left\langle z^2 \right\rangle = \frac{k_\mathrm{B} T}{3\pi\eta r} t \tag{10.4-3}$$

where k_B is Boltzmann's constant, T is the absolute temperature, r is the radius of the particle, and η is the viscosity of the solvent. Comparison of this equation with Eq. (10.2-19) shows that the diffusion coefficient of a macromolecular or colloidal substance is given by

$$\boxed{D_2 = \frac{k_\mathrm{B} T}{f} = \frac{k_\mathrm{B} T}{6\pi\eta r_\mathrm{eff}} \quad \text{(macromolecular or colloidal substance)}} \tag{10.4-4}$$

Jean Baptiste Perrin, 1870–1942, was a French physicist.

Using a dark-field microscope, Perrin was able in 1908 to measure repeatedly the displacements of colloidal particles and verified Eq. (10.4-3) experimentally. For many skeptics this was considered to be the definitive verification of the existence of atoms and molecules, since Einstein's derivation of Eq. (10.4-3) depended on the assumption that the colloidal particle was bombarded randomly by solvent molecules. Perrin was able to obtain an approximate value of Boltzmann's constant from Eq. (10.4-3), and thus calculated a value of Avogadro's constant using the known value of the ideal gas constant.

EXAMPLE 10.16

The diffusion coefficient of hemoglobin in water at 20°C is equal to $6.9 \times 10^{-11}\ \mathrm{m^2\ s^{-1}}$. Assuming the hemoglobin molecule to be spherical, calculate its effective radius. The viscosity coefficient of water at this temperature is equal to $1.002 \times 10^{-3}\ \mathrm{kg\ m^{-1}\ s^{-1}}$.

Solution

$$r = \frac{k_\mathrm{B} T}{6\pi\eta D} = \frac{\left(1.3807 \times 10^{-23}\ \mathrm{J\ K^{-1}}\right)(293\ \mathrm{K})}{6\pi\left(1.002 \times 10^{-3}\ \mathrm{kg\ m^{-1}\ s^{-1}}\right)\left(6.9 \times 10^{-11}\ \mathrm{m^2\ s^{-1}}\right)}$$

$$= 3.1 \times 10^{-9}\ \mathrm{m} = 3100\ \mathrm{pm} = 31\ \text{Å}$$

Exercise 10.15

a. Estimate the molar volume of hemoglobin from the molecular size in the previous example.

b. Human hemoglobin has a density of $1.335\ \mathrm{g\ mL^{-1}}$ (a little larger than typical protein densities, which run around $1.25\ \mathrm{g\ mL^{-1}}$). It has a molar mass of $68\ \mathrm{kg\ mol^{-1}}$. Calculate its molar volume and compare with your answer from part a.

The Temperature Dependence of Diffusion and Viscosity Coefficients in Liquids

Diffusion coefficients and viscosities in liquids depend more strongly on temperature than on gases. It is found experimentally that diffusion coefficients in liquids are usually well described by the formula

$$D = D_0 e^{-E_{\mathrm{a,d}}/RT} \tag{10.4-5}$$

where R is the ideal gas constant and T is the absolute temperature. The quantity D_0 is a parameter that is nearly temperature-independent, and $E_{\mathrm{a,d}}$ is called the molar *activation energy* for diffusion. Liquid viscosities are usually well described by the formula

$$\eta = \eta_0 e^{E_{\mathrm{a},\eta}/RT} \tag{10.4-6}$$

where $E_{\mathrm{a},\eta}$ is the molar activation energy for viscous flow.

An elementary explanation of Eq. (10.4-5) is as follows: If a molecule in a liquid pushes past some of its nearest neighbors and moves into the next cage, the potential energy of the system rises as the molecule passes between the “cage” molecules, as depicted in Figure 10.8.

If we identify ε_{a} as a minimum energy required to break out of a cage (a molecular activation energy), then from the Boltzmann probability distribution of Eq. (9.3-42) we see that the probability for a molecule to have this energy is

$$(\text{probability}) \propto e^{-\varepsilon_{\mathrm{a}}/k_{\mathrm{B}}T} = e^{-E_{\mathrm{a}}/RT} \tag{10.4-7}$$

where k_{B} is Boltzmann’s constant and where the molar activation energy $E_a = N_{\mathrm{Av}}\varepsilon_{\mathrm{a}}$. It is therefore reasonable that a diffusion coefficient in a liquid would obey Eq. (10.4-5) with E_{ad} roughly equal to the molar activation energy required to move into the next cage.

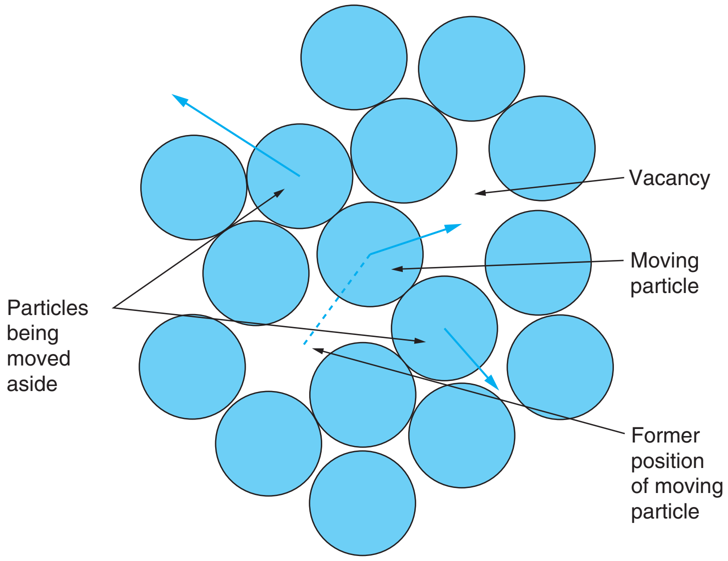

Figure 10.8 Motion of a Molecule into a Vacancy in a Liquid.

In order for shearing flow to take place, layers of a liquid must flow past each other. This requires disruption of cages and also raises the potential energy of the system. The activation energy per molecule is similar to the activation energy of diffusion. Note that the sign of the exponent in Eq. (10.4-6) is opposite from that in Eq. (10.4-5). This is because the rate of shear is proportional to the Boltzmann probability factor in Eq. (10.4-7), making the viscosity coefficient inversely proportional to it. The activation energy for viscosity is often roughly equal to the activation energy for self-diffusion in the same liquid, giving further plausibility to this argument.

EXAMPLE 10.17

Following are data on the viscosity of liquid carbon tetrachloride:

$T/°\mathrm{C}$	0	15	20	30	40	50	60
η/cP	1.329	1.038	0.969	0.843	0.739	0.651	0.585

The viscosity coefficient values are given in centipoise (cP). The poise is an older unit of viscosity, equal to 1 g cm^{-1} s^{-1}, so that 1 poise = 0.1 kg m^{-1} s^{-1}. Find the values of η_0 and $E_{a\eta}$.

Solution

We linearize Eq. (10.4-6) by taking logarithms:

$$\ln(\eta/\eta_0) = \frac{E_{a\eta}}{RT}$$

A linear least squares fit of $\ln(\eta/1\mathrm{cP})$ to $1/T$ gives an intercept of -4.279 and a slope of 1245 K, with a correlation coefficient of 0.9998 (a good fit).

$$\begin{aligned} E_{a\eta} &= (\text{slope}) \times R = (1245\ \mathrm{K})\left(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}\right) \\ &= 1.035 \times 10^4\ \mathrm{J\ mol^{-1}} = 10.4\ \mathrm{kJ\ mol^{-1}} \\ \eta_0 &= (1\ \mathrm{cP})e^{-4.279} = 1.39 \times 10^{-2}\ \mathrm{cP} = 1.39 \times 10^{-5}\ \mathrm{kgm^{-1}\ s^{-1}} \end{aligned}$$

The value of this energy of activation is typical of liquids with small molecules. As might be expected, it is somewhat smaller than the energy of vaporization of $\mathrm{CCl_4}$, 33.9 kJ mol^{-1}, which corresponds to removing a molecule from all of its nearest neighbors.

EXAMPLE 10.18

The value of the self-diffusion coefficient of carbon tetrachloride at 25°C is equal to $1.4 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$. Estimate the value at 40°C, assuming the same value of the energy of activation as for the viscosity from the previous example.

Solution

$$\frac{D(313\ \mathrm{K})}{D(298\ \mathrm{K})} = \exp\left[-\left(10350\ \mathrm{J\ mol^{-1}}\right)\left(8.3145\ \mathrm{J\ K^{-1} mol^{-1}}\right)^{-1}\left(\frac{1}{313\ \mathrm{K}} - \frac{1}{298\ \mathrm{K}}\right)\right] = 1.22$$

$$D(313\ \mathrm{K}) = (1.4 \times 10^{-9}\ \mathrm{m^2\ s^{-1}})(1.22) = 1.7 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$$

Exercise 10.16

From data in the appendix, calculate the activation energy for the viscosity of glycerol.

Sedimentation

Macromolecules such as proteins can sediment though a solvent in an ultracentrifuge, which can turn at speeds of several thousand revolutions per second. An object of mass m that is at a distance r from the axis of rotation is maintained in a circular orbit by a centripetal force that is given by the formula

$$F_c = mr\omega^2 \tag{10.4-8}$$

where ω is the *angular speed* measured in radians per second. The rate of rotation measured in revolutions per second is equal to $\omega/2\pi$, since one revolution is equal to 2π radians.

The rotor of an ultracentrifuge has a sample cell with a transparent top and bottom so that a beam of light can pass through the cell each time it passes the location of the beam. The value of r, the distance of the molecules from the axis of rotation, can be measured by observing the position dependence of the index of refraction, which depends on composition. After the rotor has been spinning a short time, the *sedimentation speed* $v_{\text{sed}} = dr/dt$ will attain a steady value so that the frictional force provides the centripetal force given by Eq. (10.4-8).

Since a macromolecule is immersed in a solvent its centripetal force must be corrected for buoyancy, giving a net centripetal force:

$$F_c = (m_2 - m_1)r\omega^2 \tag{10.4-9}$$

where m_2 is the molecular mass of the macromolecular substance and m_1 is the mass of solvent displaced by the molecule. If ρ_1 is the density of the solvent and ρ_2 is the density of the macromolecular substance,

$$m_1 = \frac{\rho_1}{\rho_2}m_2 = \frac{\rho_1}{\rho_2}\frac{M_2}{N_{\text{Av}}} \tag{10.4-10}$$

where M_2 is the molar mass of the macromolecular substance and N_{Av} is Avogadro's constant. We assume that the frictional force given by Eq. (10.4-1) applies to the sedimenting molecules and equate the magnitude of the frictional force to the centripetal force:

$$fv_{\text{sed}} = \frac{M_2}{N_{\text{Av}}}\left(1 - \frac{\rho_1}{\rho_2}\right)r\omega^2 \tag{10.4-11}$$

The *sedimentation coefficient* S is defined as the ratio of v_{sed} to the centrifugal acceleration, $r\omega^2$:

The svedberg unit is named for Theodor Svedberg, 1884–1971, a Swedish biophysical chemist who received the 1926 Nobel Prize for his work on colloids and protein suspensions.

$$S = \frac{v_{\text{sed}}}{r\omega^2} = \frac{M_2}{N_{\text{Av}}}\frac{1 - \rho_1/\rho_2}{f} \tag{10.4-12}$$

The sedimentation coefficient has the units of seconds and is usually approximately equal to 10^{-13} s. The practical unit of sedimentation coefficients is the *svedberg*, defined so that 1 svedberg $= 10^{-13}$ s.

Equation (10.4-4) allows us to express f in terms of D_2, the diffusion coefficient of the macromolecular substance, giving

$$M_2 = \frac{RTS}{D_2(1 - \rho_1/\rho_2)} \tag{10.4-13}$$

where we have replaced $k_B N_{Av}$ by the ideal gas constant R. This equation has been widely used to obtain molar masses of proteins. It is possible to get values of both S and D_2 from the same experiment if a concentration profile similar to that of Figure 10.4 can be observed.

EXAMPLE 10.19

The sedimentation coefficient of a sample of human hemoglobin in water is equal to 4.48 svedberg at 20°C, and its density is 1.335 g $\mathrm{mL^{-1}}$. The density of water at this temperature is equal to 0.998 g $\mathrm{mL^{-1}}$. Use the value of the diffusion coefficient from Example 10.16 to determine the molar mass of hemoglobin.

Solution

$$M = \frac{\left(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}\right)(293.15\ \mathrm{K})\left(4.48 \times 10^{-13}\ \mathrm{s}\right)}{\left(6.9 \times 10^{-11}\ \mathrm{m^2\ s^{-1}}\right)\left(1 - \dfrac{0.998}{1.335}\right)}$$

$$= 63\ \mathrm{J\ m^{-2}\ s^2\ mol^{-1}} = 63\ \mathrm{kg\ mol^{-1}}$$

The actual molar mass is 68 kg $\mathrm{mol^{-1}}$.

Exercise 10.17

Assume that an ultracentrifuge rotor is rotating at 1.00×10^5 revolutions per second and that hemoglobin molecules in aqueous solution at 20°C are 12.0 cm from the axis of rotation.

a. Find the sedimentation speed. Find the mean distance sedimented by the molecules in 10.0 minutes.

b. Find the root-mean-square distance in one direction diffused by hemoglobin molecules in this temperature in 10.00 minutes.

PROBLEMS

Section 10.4: Transport Processes in Liquids

10.34 A lead BB (a spherical projectile) is falling at a steady speed in glycerol at 20°C. Find its speed. The diameter of the BB is 0.177 inch, and the density of lead is 11.35 g $\mathrm{cm^{-3}}$.

10.35 The following are data for the viscosity of benzene, with the viscosity in centipoise (1 poise = 1 g $\mathrm{cm^{-1}\ s^{-1}}$).

T/K	273.15	283.15	293.15	303.15	313.15
η/cP	0.912	0.758	0.652	0.564	0.503

T/K	323.15	333.15	343.15	353.15
η/cP	0.442	0.392	0.358	0.329

Fit the natural logarithm of the viscosity against $1/T$ and find the activation energy for the viscosity. Compare it with that of carbon tetrachloride from Example 10.17, and compare it with the enthalpy change of vaporization of benzene, 34.1 kJ mol^{-1}.

10.36 The diffusion coefficient of bovine serum albumin in water at 20.0°C equals $7 \times 10^{-11}\ \mathrm{m^2\ s^{-1}}$.

a. Assuming the molecule to be spherical, estimate its radius.

b. If the density of the protein molecule equals $1.25\ \mathrm{g\,cm^{-3}}$, estimate the molecular mass and the molar mass.

c. Estimate the sedimentation coefficient of the protein.

10.37 The diffusion coefficient of horse heart myoglobin in water at 20°C is equal to $1.13 \times 10^{-10}\ \mathrm{m^2 s^{-1}}$, and its sedimentation coefficient is equal to 2.04 svedberg. Assume that its density is equal to that of hemoglobin, $1.335\ \mathrm{g\,cm^{-3}}$, and find its molar mass.

10.38 Consider the buret described in Example 10.6. If the distance from the 50.00 mL mark to the constriction is 4.50 cm, find the time required for the meniscus to drain down to the 50.00 mL mark.

10.39 Many substances with fairly small molecules have liquid-state diffusion coefficients near $1 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$. What effective molecular radius corresponds to this value if water is the solvent and if the temperature is 25°C?

10.40 The value of the diffusion coefficient of hemoglobin in water is $6.9 \times 10^{-11}\ \mathrm{m^2\ s^{-1}}$ at 20°C. The viscosity of water at 20°C is $1.002 \times 10^{-3}\ \mathrm{kg\ m^{-1}\ s^{-1}}$. Find the time required for x_{rms} to equal 1.00 cm.

10.41 The Brownian motion of colloidal particles is observed for a length of time such that the root-mean-square displacement of the particles is 0.100 cm. How must the observation time be changed so that the root-mean-square displacement of the same set of particles is 0.200 cm at the same temperature?

10.42 Assume that a hemoglobin molecule is spherical with a radius of $27\ \text{Å} = 2.7 \times 10^{-9}\ \mathrm{m}$.

a. Assuming that the Brownian-motion result and Stokes' law can be applied, estimate the diffusion coefficient of hemoglobin in water at 298.15 K.

b. Estimate the time required for a hemoglobin molecule to diffuse 1.00 mm in one direction. (Use the root-mean-square displacement in one direction.)

10.43 Assume that a ship is towing an underwater SONAR antenna encased in a spherical shell 0.280 m in radius. Assume that the sea-water temperature is 15°C and that its viscosity is the same as that of pure water at this temperature, $0.001139\ \mathrm{kg\ m^{-1}\ s^{-1}}$.

a. Assuming that the Reynolds number can be applied with the diameter of the sphere used instead of the diameter of a tube, estimate the maximum speed at which the sphere can be towed and still have laminar flow around the sphere.

b. Using the maximum speed you calculated in part a, find the frictional force on the sphere.

10.44 Calculate the rms distance diffused in one direction in 30.0 minutes by hemoglobin molecules in water at 20°C. The value of the diffusion coefficient is $6.9 \times 10^{-11}\ \mathrm{m^2\ s^{-1}}$.

10.45 A certain bowling ball has a diameter equal to 7.0 inches and a density equal to $2.5\ \mathrm{g\ mL^{-1}}$. If the bowling ball is falling in a lake at 25°C and has achieved a steady speed, estimate its speed, assuming laminar flow. Do you think the flow is laminar?

10.46 Solve Newton's second law for a sphere initially moving upward in a fluid with velocity component given by $v_z(0)$ and initially at $z = 0$. Draw a sketch of its trajectory as a function of time. The equation of motion is an inhomogeneous equation.[9]

10.47 The molar mass of hemoglobin is $68\ \mathrm{kg\ mol^{-1}}$, and its average density is $1.335\ \mathrm{g\,cm^{-3}}$.

a. Estimate the radius of the molecule, assuming it to be spherical.

b. Estimate the diffusion coefficient of hemoglobin in water at 25°C.

c. Estimate the root-mean-square distance diffused in one direction by hemoglobin molecules in 30.00 seconds in water at 25°C.

d. Assume that hemoglobin molecules are sedimenting in water at 25°C in an ultracentrifuge rotor spinning at 100000 revolutions per minute (10472 radians per second) and with the sample at a distance $r = 5.00$ cm from the axis of rotation. Estimate the sedimentation speed of the hemoglobin molecules.

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[9] See Robert G. Mortimer, *Mathematics for Physical Chemistry*, 3rd ed., Academic Press, San Diego, CA, 2005, pp. 247–249, or any textbook of differential equations.

10.48 Poiseuille's equation for the flow of a gas through a tube is different from that of an incompressible liquid. If the gas is assumed to be ideal, the equation for the molar rate of flow is[10]

$$\frac{dn}{dt} = \frac{\pi r^4 \left(P_1^2 - P_2^2\right)}{16\eta LRT}$$

where we now use r for the radius of the tube and R for the ideal gas constant, and where n is the number of moles of the gas that has passed through the tube. Find the time required for 0.100 mol of carbon dioxide to flow through a tube of length 40.0 cm and diameter 0.850 mm at 20.0°C.

10.49 Liquid water at 20.0°C is flowing through a cylindrical tube of length 1.00 m and radius 0.00200 m. The average flow speed is 0.0500 m s^{-1}.

a. Find the volume rate of flow, dV/dt.

b. Find the difference in pressure at the ends of the tube.

c. Find the flow speed at the center of the tube.

d. Is the flow laminar?

10.5 Electrical Conduction in Electrolyte Solutions

Electric currents in metallic conductors and semiconductors are due to the motions of electrons, whereas electric currents in electrolyte solutions are due to the motions of ions. *Ohm's law* asserts that the current in a conducting system is proportional to the voltage imposed on the system:

$$I = \frac{V}{R} \tag{10.5-1}$$

where V is the voltage (the difference in electric potential between the ends of the system), I is the current (equal to the amount of charge passing a given location per second), and R is the resistance of the conductor. (Do not confuse this use of R with the ideal gas constant. There aren't enough letters in the alphabet for us to use a letter for only one variable.) The direction of an electric current is defined as the direction of apparent motion of positive charges. This convention was proposed by Benjamin Franklin. Ohm's law with a constant resistance is obeyed very nearly exactly by metallic conductors, to a good approximation by electrolyte solutions, and fairly accurately by semiconductors.

Benjamin Franklin, 1706–1790, was a self-trained physicist as well as a printer, inventor, politician, and diplomat. He also invented the designation of the two kinds of electric charge as positive and negative.

Ohm's law is named for Georg Simon Ohm, 1787–1854, a German physicist who was a high-school teacher when he discovered Ohm's law by carrying out experiments at home. He even made his own wires for his early experiments.

Ohm found by painstaking experiments with homemade equipment that the resistance of a conductor of uniform cross section is proportional to its length and inversely proportional to its cross-sectional area. We define the *resistivity* r of a conducting object shaped as in Figure 10.9 by

$$r = \frac{R\mathscr{A}}{d} \tag{10.5-2}$$

where $\mathscr{A}$ is the cross-sectional area and d is the length of the object. If Ohm's law is obeyed the resistivity is independent of d and $\mathscr{A}$, depending only on the composition of the object, the temperature, and (very slightly) on the pressure.

The SI unit of resistivity is the ohm meter (ohm m). The reciprocal of the resistivity is called the *conductivity* and denoted by σ:

$$\sigma = \frac{1}{r} \tag{10.5-3}$$

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[10] D. P. Shoemaker, C. W. Garland, and J. W. Nibler, *Experiments in Physical Chemistry*, 5th ed., McGraw-Hill, New York, 1989, p. 132ff.

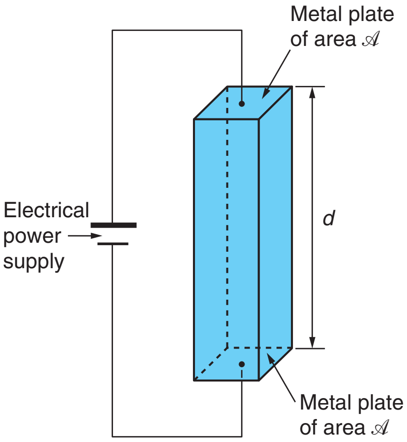

Figure 10.9 An Electrically Conducting System (Schematic).

The conductivity has the units $\text{ohm}^{-1}\ \text{m}^{-1}$. The ohm^{-1} has been called the *mho* (ohm spelled backwards) but the SI name for ohm^{-1} is the *siemens*, denoted by S, so that the conductivity has the units Siemens per meter (S m^{-1}).

We define the *current density* **j** as a vector with magnitude equal to the current per unit area and with the same direction as the current:

$$j = |\mathbf{j}| = \frac{I}{\mathscr{A}} \tag{10.5-4}$$

where $\mathscr{A}$ is the cross-sectional area of the conductor and I is the current. Ohm's law can be written

$$j = \frac{I}{\mathscr{A}} = \frac{V}{R\mathscr{A}} = \frac{\mathscr{E}\,d}{rd} = \frac{\mathscr{E}}{r} = \sigma\mathscr{E} \tag{10.5-5}$$

where $\mathscr{E}$ is the magnitude of the electric field, equal to V/d for an object like that of Figure 10.9.

Consider a solution of an electrolyte solute with one cation and one anion. Let the mean velocity of cations be denoted by $\mathbf{v}_+$ and the mean velocity of anions be denoted by $\mathbf{v}_-$. At equilibrium these mean velocities vanish because as many ions will be moving in a given direction as in the opposite direction. In the presence of an electric field $\mathbf{v}_+$ and $\mathbf{v}_-$ will be nonzero, in which case they are called *drift velocities*. The current density is the sum of a cation contribution and an anion contribution. On the average cations no farther from a fixed plane than a distance equal to v_+ times 1 second will pass in 1 second. For unit area, the number of cations passing the fixed plane per second is

$$\text{number of cations per unit area per second} = c_+ N_{\text{Av}} v_+ \tag{10.5-6}$$

where c_+ is the concentration of the cations in mol m^{-3} and N_{Av} is Avogadro's constant. The charge passing per second due to the cations is

$$\text{charge per unit area per second due to cations} = z_+ \mathscr{e} c_+ N_{\text{Av}} v_+ \tag{10.5-7}$$

where $\mathscr{e}$ is the charge on a proton, 1.6022×10^{-19} C, and z_+ is the valence of the cation (the number of proton charges on one ion). A similar expression can be written for the anions. The current density can be written

$$\mathbf{j} = z_+ N_{\text{Av}} e c_+ \mathbf{v}_+ + z_- N_{\text{Av}} e c_- \mathbf{v}_- = \mathbf{j}_+ + \mathbf{j}_- \tag{10.5-8}$$

Although $\mathbf{v}_+$ and $\mathbf{v}_-$ are in opposite directions, z_+ and z_- also have opposite signs so the two contributions have the same sign. The magnitude of the current density is

$$j = |\mathbf{j}| = F(z_+ c_+ v_+ + |z_-| c_- v_-) \tag{10.5-9}$$

where v_+ and v_- are the magnitudes of the drift velocities, and where F is Faraday's constant, equal to the charge on 1 mol of protons:

$$F = e N_{\text{Av}} = 96485\ \text{C mol}^{-1} \tag{10.5-10}$$

Exercise 10.18

Show that Eq. (10.5-8) is correct.

If dissociation or ionization of an electrolyte solute is complete and if c is its stoichiometric concentration (the concentration that the electrolyte would have if no dissociation or ionization occurred), then

$$c_+ = \nu_+ c \quad \text{and} \quad c_- = \nu_- c \tag{10.5-11}$$

where ν_+ is the number of cations in the formula of the solute and ν_- is the number of anions in the formula. (In some fonts the Greek "nu" and the English "vee" look quite similar. Please try to keep them straight.) If there is a single electrolyte solute these quantities must obey the electrical neutrality relation

$$\nu_+ z_+ + \nu_- z_- = 0 \tag{10.5-12}$$

For a single electrolyte we can write

$$j = F c z_+ \nu_+ (v_+ + v_-) \tag{10.5-13}$$

If the ions experience a frictional force according to Eq. (10.4-1), Ohm's law is obeyed by an electrolyte solution. The electrostatic force on an ion of charge ze in an electric field $\mathscr{E}$ is

$$\mathbf{F}_{\text{elec}} = z e \mathscr{E} \tag{10.5-14}$$

On the average, the ions are not accelerated if a steady current is flowing, so that the electrical force and the frictional force cancel:

$$\mathbf{F}_{\text{elec}} = -\mathbf{F}_{\text{friction}} = f\mathbf{v} \tag{10.5-15}$$

where f is the friction coefficient. For the case that $\nu_+ = \nu_- = 1$ (as with a uni-univalent electrolyte such as sodium chloride), we obtain

$$j = F c \mathscr{E} e \left(\frac{1}{f_+} + \frac{1}{f_-} \right) \quad (\text{if } \nu_+ = \nu_- = 1) \tag{10.5-16}$$

where f_+ is the friction coefficient for the cations and f_- is the friction coefficient for the anions. The conductivity is

$$\sigma = Fc\mathscr{e}\left(\frac{1}{f_+} + \frac{1}{f_-}\right) \quad (\text{if } \nu_+ = \nu_- = 1) \tag{10.5-17}$$

For a general binary electrolyte represented by $\mathrm{M}_{\nu_+}\mathrm{X}_{\nu_-}$, the analogue of Eq. (10.5-17) is

$$\sigma = F\mathscr{e}\left(\frac{c_+ z_+^2}{f_+} + \frac{c_- z_-^2}{f_-}\right) = Fc\mathscr{e}\left(\frac{\nu_+ z_+^2}{f_+} + \frac{\nu_- z_-^2}{f_-}\right) \tag{10.5-18}$$

Exercise 10.19

Show that Eq. (10.5-18) is correct.

Since the cations and anions in a given electrolyte will not generally have equal friction coefficients, the two kinds of ions will not necessarily carry the same amount of current. The fraction of the current that is carried by a given type of ion is called its *transference number*, t:

$$t_i = \frac{j_i}{j_{\text{total}}} \tag{10.5-19}$$

where j_i is the magnitude of the current density due to ions of type i and j_{total} is the magnitude of the total current density. If there is only one type of cation and one type of anion present, Eq. (10.5-18) implies that

$$t_+ = \frac{c_+ z_+^2/f_+}{c_+ z_+^2/f_+ + c_- z_-^2/f_-} = \frac{\nu_+ z_+^2/f_+}{\nu_+ z_+^2/f_+ + \nu_- z_-^2/f_-} \tag{10.5-20}$$

and

$$t_- = \frac{c_- z_-^2/f_-}{c_+ z_+^2/f_+ + c_- z_-^2/f_-} = \frac{\nu_- z_-^2/f_-}{\nu_+ z_+^2/f_+ + \nu_- z_-^2/f_-} \tag{10.5-21}$$

The *mobility* u_i of ions of type i is defined by

$$u_i = \frac{v_i}{\mathscr{E}} \tag{10.5-22}$$

where v_i is the magnitude of the mean drift velocity of this type of ion and where $\mathscr{E}$ is the magnitude of the electric field. If we apply Stokes' law,

$$u_i = \frac{|z_i|\mathscr{e}}{f_{\mathrm{i}}} = \frac{|z_i|\mathscr{e}}{6\pi\eta r_{\mathrm{eff},i}} \tag{10.5-23}$$

where $r_{\mathrm{eff},i}$ is the effective radius of the ions of type i. For a single electrolyte solute, the conductivity can be written in terms of the mobilities:

$$\sigma = F(c_+ z_+ u_+ + c_- |z_-| u_-) \tag{10.5-24}$$

Exercise 10.20

Write the transference numbers in terms of the ion mobilities.

The mobility and friction coefficient of a given ion depend on the concentrations of the other ions present. There are three important effects. The first effect is the *electrophoretic effect*, due to the fact that ions of the opposite charge are moving in the opposite direction from a given ion. Their attractive forces pull on a given ion in the direction of their motion, slowing that ion. The second effect is the *relaxation effect*. Every ion is surrounded by an "ion atmosphere" of excess charge of the opposite sign. If an ion moves, it is no longer at the center of its ion atmosphere, which must then relax to become centered on the new position of the ion. This effect also slows down the motion of the ion. The third effect is the *solvation effect*. In the limit of small concentration each ion can attract its full complement of solvent molecules, but at high concentrations ions compete with each other to attract solvent molecules. Since solvent molecules that are strongly attracted to it can move with an ion, any change in the solvation can affect the mobility of the ion. The electrophoretic effect and the relaxation effect vanish in the limit of small concentration and the solvation effect approaches a concentration-independent value. Therefore, ion mobilities and friction coefficients approach constant values in the limit of infinite dilution. Equation (10.5-23) is correct only in the limit of small concentrations. Table A.20 gives values of ion mobilities at infinite dilution in water at 25°C.

The ions with the largest mobilities in aqueous solutions are the hydrogen ion and the hydroxide ion. The reason is that hydrogen and hydroxide ions can "exchange" with water molecules. A hydrogen ion can attach itself to one or more water molecules, making the H_3O^+ ion or the $H_5O_2^+$ ion, and so on. A hydrogen ion on the other side of the H_3O^+ can be released and attach itself to a second water molecule, after which a different hydrogen ion is released, providing a rapid apparent motion of hydrogen ions. The exchange of hydroxide ions is similar, with a hydrogen ion moving from a water molecule to a hydroxide ion to form a "new" water molecule and a "new" hydroxide ion in a different location, corresponding to effective radii smaller than actual ionic radii.

EXAMPLE 10.20

Calculate the apparent radii of the hydrogen and hydroxide ions from the ion mobilities.

Solution

$$r_i(\text{eff}) = \frac{|z_i|e}{6\rho\eta u_i}$$

For H^+,

$$r_i(\text{eff}) = \frac{1.6022 \times 10^{-19}\ \text{C}}{6\pi(8.904 \times 10^{-4}\ \text{kg m}^{-1}\ \text{s}^{-1})(36.25 \times 10^{-8}\ \text{m}^2\ \text{s}^{-1}\ \text{V}^{-1})}$$

$$= 2.63 \times 10^{-11}\ \text{C V kg}^{-1}\ \text{m}^{-1}\ \text{s}^{-2} = 2.63 \times 10^{-11}\ \text{m} = 26.3\ \text{pm} = 0.263\ \text{A}$$

For OH^-:

$$r_i(\text{eff}) = \frac{1.6022 \times 10^{-19}\ \text{C}}{6\pi(8.904 \times 10^{-4}\ \text{kg m}^{-1}\ \text{s}^{-1})(20.5 \times 10^{-8}\ \text{m}^2\ \text{s}^{-1}\ \text{V}^{-1})}$$

$$= 4.66 \times 10^{-11}\ \text{C V kg}^{-1}\ \text{m}^{-1}\ \text{s}^{-2} = 4.66 \times 10^{-11}\ \text{m} = 46.6\ \text{pm} = 0.466\ \text{A}$$

Some cations with a small radius, such as the lithium ion, have somewhat lower mobilities and larger effective radii than might be expected. Small cations are more strongly hydrated (more strongly bound to water molecules) than larger cations, because water molecules can approach closely to the center of charge of the smaller ion. These strongly bound water molecules are likely to be carried along with the ions, increasing the apparent size of the ions.

Exercise 10.21

Calculate the effective radius of the lithium ion from its ion mobility.

The *molar conductivity* of an electrolyte solute is denoted by Λ and is defined by

$$\Lambda = \frac{\sigma}{c} \tag{10.5-25}$$

where c is the stoichiometric concentration of the electrolyte in mol m^{-3} or mol L^{-1}. For complete dissociation Eq. (10.5-24) gives

$$\Lambda = \frac{\sigma}{c} = F(\nu_+ z_+ u_+ + \nu_- |z_-| u_-) \tag{10.5-26}$$

At fairly small concentrations the molar conductivity of a strong electrolyte is found to depend linearly on the square root of the concentration:

$$\Lambda = \Lambda_0 - Ac^{1/2} \tag{10.5-27}$$

where A is a parameter depending on the temperature and identities of all ions present. This equation was discovered empirically by Kohlrausch in 1900. In the limit of infinite dilution, Λ approaches a constant limit, just as do the mobility and friction coefficient:

$$\Lambda_0 = \lim_{c \to 0} \Lambda \tag{10.5-28}$$

The value at infinite dilution, Λ_0, is called the *limiting molar conductivity*.

The conductivity contains a term for the cation and a term for the anion, so the molar conductivity can be written as a sum. For a uni-univalent electrolyte

$$\Lambda = \lambda_+ + \lambda_- \tag{10.5-29}$$

$$\Lambda_0 = (\lambda_+)_0 + (\lambda_-)_0 \tag{10.5-30}$$

Kohlrausch's laws are named for Friedrich Wilhelm Georg Kohlrausch, 1840–1910, who was probably the greatest experimental physicist of the 19th century. He studied many electric and magnetic phenomena as well as electrolyte conduction and the autoionization of water.

where $(\lambda_+)_0$ and $(\lambda_-)_0$ are the limiting molar conductivities of the ions. Equation (10.5-30) was established around 1875 by Kohlrausch. Equations (10.5-27) and (10.5-30) are known as *Kohlrausch's laws*. The limiting molar conductivities for the ions can be separately tabulated, making it possible to construct a shorter table than if values for neutral electrolytes were tabulated. Table A.20 contains values of limiting molar conductivities of several ions in water at 25°C.

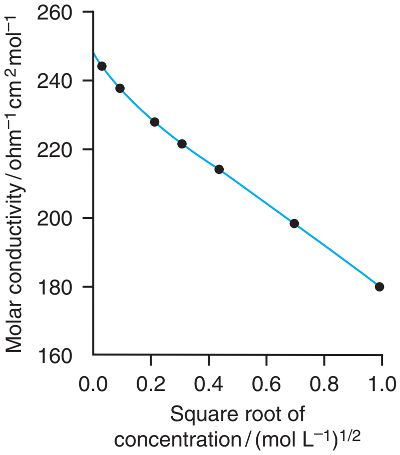

Figure 10.10 The Molar Conductivity of Sodium Hydroxide as a Function of the Square Root of the Concentration in mol L^{-1}.

EXAMPLE 10.21

Following are data on the molar conductivity of NaOH as a function of concentration at 25°C:

concentration/mol L^{-1}	Λ/ohm^{-1} cm^2 mol^{-1}
0.0010	244.5
0.0100	238.0
0.0500	227.6
0.1000	221.2
0.2000	213.0
0.5000	197.6
1.0000	178.8

Find the value of Λ_0 for NaOH. Compare the value obtained with the value from Table A.20.

Solution

As indicated in Eq. (10.6.19), a plot of Λ versus $c^{1/2}$ for a strong electrolyte should be nearly linear at small concentrations. Such a plot is shown in Figure 10.10.

The extrapolation to zero concentration was accomplished by fitting the data to a polynomial of degree 5, since the plot is not linear over the range of concentrations given. The formula for the polynomial is shown in the figure, and the intercept was found to be

$$\Lambda_0 = 247.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

From Table A.20,

$$\begin{aligned}\Lambda_0 &= \lambda(\text{Na}^+) + \lambda(\text{OH}^-)\\ &= 19.8 \times 10^{-3} \text{ ohm}^{-1} \text{ m}^2 \text{ mol}^{-1} + 5.011 \times 10^{-3} \text{ ohm}^{-1} \text{ m}^2 \text{ mol}^{-1}\\ &= 24.8 \times 10^{-3} \text{ ohm}^{-1} \text{ m}^2 \text{ mol}^{-1} = 248 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}\end{aligned}$$

in good agreement with the value from the extrapolation.

An extrapolation such as that in Example 10.21 is difficult for weak electrolytes, since the percent ionization and the ion mobilities are both changing with concentration. However, one can easily determine the limiting molar conductivity of a weak electrolyte such as acetic acid from the values for the ions.

Exercise 10.22

a. Find the value of the limiting molar conductivity for acetic acid from the values in Table A.20.

b. Following are data on the molar conductivity of acetic acid as a function of concentration at 25°C:

concentration/mol L^{-1}	Λ/ohm^{-1} cm^2 mol^{-1}
0.0001	134.6
0.0010	49.2
0.0100	16.18
0.0500	7.36
0.1000	5.20
0.2000	3.65

Can you carry out an extrapolation as in Example 10.21 to determine the limiting molar conductivity?

PROBLEMS

Section 10.5: Transport in Electrolyte Solutions

10.50 Calculate the transference numbers for H^+ and Cl^- ions in a dilute aqueous HCl solution at 25°C.

10.51 **a.** Calculate the force on 1.000 mol of sodium ions (assumed localized in a small volume) at a distance of 1.000 m in a vacuum from 1.000 mol of chloride ions.

b. Find the mass in kilograms and in pounds on which the gravitational force at the earth's surface would equal the force in part a.

10.52 Calculate the effective radii of K^+ and Cl^- ions in dilute aqueous solution at 25°C.

10.53 Calculate the transference numbers for K^+ and Cl^- ions in a dilute aqueous KCl solution at 25°C.

10.54 **a.** Calculate the conductivity of an aqueous solution of NaCl with molarity 0.100 mol L^{-1}. Assume that the infinite-dilution values of the mobilities can be used.

b. A cell with two electrodes of area 1.000 cm^2 and length between the electrodes of 10.00 cm is filled with the solution of part a. What is its resistance?

c. What is the transference number of each ion?

10.55 A conductance cell has two electrodes 1.00 cm by 1.00 cm, separated by a distance of 2.00 cm. Find the electrical resistance of this cell if it is filled with a 0.00100 mol L^{-1} solution of KCl at 25°C. Assume that infinite dilution values can be used at this concentration.

10.56 Calculate the transference numbers for each ion in an acetic acid solution, assuming that infinite-dilution values can be used. Does your answer depend on the extent of ionization? Explain your assertion.

10.57 **a.** Calculate the transference number of each ion in a solution with 0.00050 mol L^{-1} sodium acetate and 0.00100 mol L^{-1} sodium chloride, assuming that infinite-dilution values can be used. Neglect the hydrolysis of the acetate ions.

b. Calculate the conductivity of the solution of part a.

c. Find the resistance of a cube-shaped cell with side equal to 1.000 cm, containing the solution of part a and having electrodes on two opposite sides.

Summary of the Chapter

The three transport processes correspond to the transport of some quantity through space: Heat conduction is the transport of energy, diffusion is the transport of molecules, and viscous flow is the transport of momentum. These processes are described by empirical linear laws in which each rate is directly proportional to a single driving force. According to Fourier's law the flow of heat is proportional to the temperature gradient. According to Fick's law the diffusion flux is proportional to the concentration gradient. According to Newton's law of viscous flow the force per unit area to maintain a shearing flow is proportional to the rate of shear.

Transport processes in a hard-sphere gas can be analyzed theoretically. A formula for the self-diffusion coefficient was derived in this chapter, and similar formulas for thermal conductivities and viscosity coefficients were presented. Each transport coefficient is proportional to the mean free path and to the mean speed, and thus proportional to the square root of the temperature.

A molecule in a liquid was pictured as partially confined in a cage made up of its nearest neighbors. This model and an assumed frictional force were related to diffusion in liquid solutions, to viscosity in pure liquids, and to sedimentation in solutions of macromolecular substances.

We presented the consequences of assuming that an ion moving through a solution experiences a frictional force proportional to its speed with a proportionality constant called a friction coefficient. It was shown that this assumption leads to Ohm's law for an electrolyte solution, with a conductivity contribution for each type of ion that is inversely proportional to the friction coefficient.

ADDITIONAL PROBLEMS

10.58 The thermal conductivity, viscosity, and self-diffusion coefficient of argon gas are listed for one or more temperatures in Tables A.16, A.18, and A.19 of the appendix.

- **a.** Calculate the effective hard-sphere diameter of argon atoms at 0°C from the viscosity and self-diffusion coefficient values. Compare your two values with each other and with the value in Table A.15. Comment on any discrepancies.
- **b.** Calculate the effective hard-sphere diameter of argon atoms at 20°C from the thermal conductivity and viscosity values. Compare your two values with each other and with the value in Table A.15. Comment on any discrepancies.
- **c.** Calculate the value of the self-diffusion coefficient of argon at 20°C and 1.00 atm, using Eq. (10.3-9) and the value of the effective hard-sphere diameter from Table A.15.
- **d.** Calculate the self-diffusion coefficient of argon at 1.00 atm and 20°C by interpolation in Table A.19. To do the interpolation, divide each value in the table by $T^{3/2}$ and do a linear least-squares fit to the resulting values. Comment on the closeness of your fit. Why is $T^{3/2}$ the correct factor to use?
- **e.** Using your least-squares fit from part d, find the value of the self-diffusion coefficient of argon at 473 K and 1.00 atm.
- **f.** Using your value from part c, calculate the effective hard-sphere diameter of argon atoms at 473 K and compare it with the value in Table A.15.

10.59 The diffusion coefficient of urease (an enzyme) in water at 25°C is equal to $3.5 \times 10^{-11}\ \mathrm{m^2\ s^{-1}}$.

- **a.** Calculate the rms distance diffused in one direction in 1.000 hour by urease molecules in water at 20°C.
- **b.** Estimate the molecular radius, assuming spherical molecules.
- **c.** Assuming a density of $1.25\ \mathrm{g\ mL^{-1}}$ for the enzyme, estimate the molar mass.
- **d.** Estimate the sedimentation coefficient.
- **e.** A solution of urease is placed in an ultracentrifuge in which the same cell is 10.0 cm from the axis of rotation. If the ultracentrifuge is turning at 100000 revolutions per minute, calculate the time needed for urease molecules to sediment a distance of 2.00 mm.

10.60 Calculate the root-mean-square distance diffused in three dimensions in 30.0 minutes in a self-diffusion experiment at 273 K and 1.00 atm for each of the following gaseous substances:

- **a.** Argon
- **b.** Carbon dioxide
- **c.** Hydrogen
- **d.** Methane

10.61
- **a.** Derive an equation for the flow of heat that is analogous to Fick's second law of diffusion, Eq. (10.2-11). Assume a constant heat capacity and a constant thermal conductivity.
- **b.** Assume that two pieces of aluminum have been machined so that they fit together perfectly. Assume that one piece is initially at 30°C and the other is initially at 20°C and that they are suddenly placed in contact. Write a formula for the temperature profile as a function of time and of the perpendicular distance from the junction of the pieces.

10.62. Give verbal explanations for each of the following:

- **a.** Each of the formulas for the transport coefficients in a hard-sphere gas is proportional to λ and to $\langle v \rangle$.
- **b.** The viscosity of a gas increases with temperature.
- **c.** The diffusion coefficient is inversely proportional to $\mathcal{N}$.
- **d.** The thermal conductivity and viscosity of a hard-sphere gas are independent of $\mathcal{N}$.

10.63 Identify each statement as either true or false. If a statement is true only under certain circumstances, label it as false.

- **a.** An irreversible process always raises the entropy of the universe.
- **b.** An irreversible process always raises the entropy of the system.
- **c.** A temperature gradient can cause a diffusion flow to occur.
- **d.** Ohm's law is exactly obeyed by electrolyte solutions.

e. A smaller ion will always have a smaller effective radius in aqueous solution.

f. If the elapsed time of a diffusion experiment is quadrupled, the root-mean-square distance moved by diffusing molecules is increased by a factor of two.

g. If a mixture of two proteins of equal density is sedimenting in an ultracentrifuge, and if one protein has twice the molar mass of the other protein, its sedimentation velocity will be half as large as that of the other protein.

h. The viscosity of a gas increases with increasing temperature, whereas that of a liquid decreases with increasing temperature.

10.64 Show that if a metal bar with a uniform cross section is in a steady state with different temperatures at the two ends, the temperature must be a linear function of position if the thermal conductivity does not depend on temperature.

10.65 A sleeve bearing has an area of 26.6 cm^2. It is lubricated with an oil having a viscosity coefficient equal to 0.0237 $\mathrm{kg\ m^{-1}\ s^{-1}}$. If the film of oil has a thickness of 0.20 mm and the radius of the bearing is 2.00 cm, find the frictional torque on the shaft if it is turning at 600 revolutions per minute. Assume that the oil does not slip on the metal surfaces.

10.66 The diffusion coefficient of 1,1,1-trichloroethane (TCE) in carbon tetrachloride at 25°C is equal to $1.36 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$ and the viscosity of carbon tetrachloride at 25°C is equal to $9.1 \times 10^{-4}\ \mathrm{kg\ m^{-1}\ s^{-1}}$. Find the effective radius of TCE molecules.

11

The Rates of Chemical Reactions

PRINCIPAL FACTS AND IDEAS

1. The rate of a chemical reaction depends on the concentrations of the reactants and products and on the temperature.
2. The rate law of a chemical reaction is the differential equation for the rate of change of the concentration of a reactant or product as a function of concentrations of reactants and products.
3. Rate laws can be determined experimentally using the method of initial rates.
4. The rate laws for some reactions can be integrated to obtain integrated rate laws.
5. Experimental data on concentrations can be compared with integrated rate laws to determine the experimental rate law.
6. In a simple case it is possible to integrate the rate law for a reaction with a non-negligible reverse reaction.
7. Two consecutive reactions constitute a simple mechanism for a chemical reaction, and the rate law can be integrated for a simple case.
8. Specialized techniques exist for studying fast reactions.

11.1 The Macroscopic Description of Chemical Reaction Rates

In this chapter we discuss the rates of chemical reactions. We restrict our treatment to fluid systems and we will not attempt to treat systems in which the temperature and composition are not constant.[1] Consider a hypothetical chemical reaction:

$$aA + bB \longrightarrow dD + fF \tag{11.1-1}$$

where the capital letters stand for chemical formulas and the lower-case letters stand for stoichiometric coefficients. We want to define the rate of the reaction, denoted by r, in such a way that we can choose any of the substances to specify the rate:

$$\boxed{r = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = -\frac{1}{b}\frac{d[\mathrm{B}]}{dt} = \frac{1}{d}\frac{d[\mathrm{D}]}{dt}\frac{1}{f}\frac{d[\mathrm{F}]}{dt} \quad \text{(definition of } r\text{)}} \tag{11.1-2}$$

where [A] denotes the molar concentration (in $\mathrm{mol\,L^{-1}}$ or $\mathrm{mol\,m^{-3}}$) of substance A, and so on, and where t is the time.

We can write a chemical equation in the form used in Chapters 3 and 8,

$$0 = \sum_{i=1}^{s} v_i \mathscr{F}_i \tag{11.1-3}$$

where v_i stands for the stoichiometric coefficient and $\mathscr{F}_i$ stands for the chemical formula of substance number i. In this form the reaction of Eq. (11-1.1) is written as

$$0 = dD + fF - aA - bB$$

with negative stoichiometric coefficients for reactants and positive coefficients for products. The *rate of the reaction* can now be written as

$$\boxed{r = \frac{1}{v_i}\frac{d[\mathscr{F}_i]}{dt}} \tag{11.1-4}$$

This equation satisfies the inner urge of physical chemists to write one equation that holds for all cases.

On the molecular level, a chemical reaction can occur in both directions at the same time. While some reactant molecules are forming products at a rate called the *forward rate*, other product molecules are forming reactants at a rate called the *reverse rate*. The observable rate of a chemical reaction is a *net rate*:

$$r = r_{\mathrm{net}} = r_{\mathrm{f}} - r_{\mathrm{r}} \tag{11.1-5}$$

where r_{f} is the forward rate and where r_{r} is the reverse rate. Chemical reactions usually proceed smoothly toward a macroscopic equilibrium state in which the forward and reverse rates cancel each other and the net rate vanishes. However, some

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[1] See for example R. G. Mortimer, *J. Phys. Chem.*, **67**, 1938 (1963).

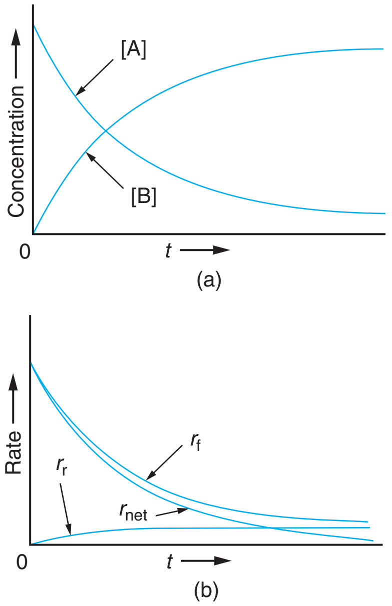

Figure 11.1 The Approach to Equilibrium of a Hypothetical Reaction. (a) The concentrations of the product B and the reactant A as a function of time. (b) The forward rate, the reverse rate, and the net rate as a function of time.

oscillatory reactions do exist.[2] Figure 11.1 shows schematically how a typical chemical reaction that produces B from A approaches equilibrium. Both of the concentrations eventually approach constant nonzero values and the net rate approaches zero. At equilibrium the forward and reverse rates do not vanish, but cancel each other.

The rate of a reaction can depend on temperature, pressure, and the concentrations or partial pressures of the substances in the system. In many reactions at constant temperature the forward rate depends only on the concentrations of the reactants. If A and B are the reactants,

$$r_{\mathrm{f}} = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = r_{\mathrm{f}}([\mathrm{A}], [\mathrm{B}]) \tag{11.1-6}$$

The functional relation expressed in this equation is called the *rate law* of the forward reaction. Similarly, the reverse reaction rate often depends only on the concentrations of the products. If D and F are the products, the rate law of the reverse reaction is

$$r_{\mathrm{r}} = \frac{1}{a}\frac{d[\mathrm{A}]}{dt} = r_{\mathrm{r}}([\mathrm{D}], [\mathrm{F}]) \tag{11.1-7}$$

There is a large class of chemical reactions in which the forward reaction rate is proportional to the concentration of each reactant raised to some power. If A and B are the reactants, the forward rate law would be

$$r_{\mathrm{f}} = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = k_{\mathrm{f}}[\mathrm{A}]^{\alpha}[\mathrm{B}]^{\beta} \tag{11.1-8}$$

This relation is called a *rate law with definite orders*. The exponent α is called the *order with respect to substance* A and the exponent β is called the *order with respect to substance* B. These orders are not necessarily equal to the stoichiometric coefficients a and b. The sum of the orders with respect to the different substances is called the *overall order*. If α and β both equal unity, the reaction is said to be first order with respect to substance A, first order with respect to substance B, and second order overall. Other orders are similarly assigned. The orders are usually small positive integers, but other cases do occur. Some reactions are not described by rate laws like Eq. (11.1-8). Such reactions are said not to have a definite order. The proportionality constant k_{f} in Eq. (11.1-8) is independent of the concentrations and is called the forward *rate constant*. Rate constants depend on temperature and pressure, although the pressure dependence is generally small.[3] We will discuss the temperature dependence of rate constants in Chapter 12.

One of the objectives of the study of a reaction is to determine what the rate law is. Knowledge of the rate law allows us to predict the rates of the reaction for new values of the concentrations without doing additional experiments. The form of the rate law can usually provide information about the sequence of molecular steps that constitute the reaction (the *mechanism of the reaction*).

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[2] R. J. Field and M. Burger, *Oscillations and Traveling Waves in Chemical Systems*, Wiley, New York, 1985.

[3] R. E. Weston and H. A. Schwarz, *Chemical Kinetics*, Prentice Hall, Englewood Cliffs, NJ, 1972, p. 181ff.

PROBLEMS

Section 11.1: The Macroscopic Description of Chemical Reaction Rates

11.1 Consider the chemical reaction balanced in two different ways:

$$2NO + Cl_2 \longrightarrow 2NOCl$$

and

$$NO + \frac{1}{2}Cl_2 \longrightarrow NOCl$$

a. If the rate of the reaction according to the first version is $7.1 \times 10^{-5}\ \mathrm{mol\,L^{-1}\,s^{-1}}$, what is the rate of the reaction according to the second version?

b. Write an expression for the rate of change of the concentration of each substance. Does this quantity differ for the two versions?

11.2 Consider the chemical reaction balanced two different ways:

$$2O_3 \longrightarrow 3O_2$$

and

$$O_3 \longrightarrow \frac{3}{2}O_2$$

a. If the rate of the reaction according to the first version is $5.0 \times 10^{-4}\ \mathrm{mol\,L^{-1}\,min^{-1}}$, what is the rate of the reaction according to the second version?

b. Write an expression for the rate of change of the concentration of each substance. Does this quantity differ for the two versions?

11.2 Forward Reactions with One Reactant

In this section we discuss reactions of a single reactant with a negligible reverse reaction. Inspection of Figure 11.1 shows that when a reaction approaches equilibrium, the reverse rate cannot be neglected. We must avoid applying the results of this section to reactions that are close to equilibrium. However, many reactions proceed essentially to completion and in that case we can neglect the reverse reaction for nearly the entire reaction.

The "classical" method for determining the rate law for a reaction is to mix the reactants and then to determine the concentration of one of the reactants or products as a function of time. A variety of methods have been used to determine concentrations, including measurement of the following:

1. The absorbance of radiation at some wavelength at which a given product or reactant absorbs.
2. The intensity of the emission spectrum of the system at a wavelength at which a given product or reactant emits.
3. The volume of a solution required to titrate an aliquot removed from the system.
4. The pressure of the system (for a reaction at constant volume).
5. The volume of the system (for a reaction at constant pressure).
6. The electrical conductance of the system.
7. The mass spectrum of the system.
8. The ESR or NMR spectrum of the system.
9. The dielectric constant or index of refraction of the system.
10. The mass loss if a gas is evolved.

Once we know from experiment how the concentration of a reactant or product depends on time we can determine the rate law. We now proceed to integrate the rate laws for a number of cases to obtain formulas with which to compare experimental data.

First-Order Reactions

Consider a reaction at constant temperature of a single reactant:

$$\mathrm{A} \longrightarrow \text{products} \tag{11.2-1}$$

If there is no significant reverse reaction and if the reaction is first order, the rate law is

$$r = -\frac{d[\mathrm{A}]}{dt} = k_{\mathrm{f}}[\mathrm{A}] \tag{11.2-2}$$

where the first-order rate constant k_{f} has units of reciprocal time (s^{-1}, min^{-1}, and so on). This is a differential equation that can be solved by separation of variables.

We multiply by dt, divide by [A], and recognize that $\frac{d[\mathrm{A}]}{dt}dt = d[\mathrm{A}]$:

$$\frac{1}{[\mathrm{A}]}\frac{d[\mathrm{A}]}{dt}dt = \frac{1}{[\mathrm{A}]}d[\mathrm{A}] = -k_{\mathrm{f}}dt \tag{11.2-3}$$

The variables have been separated. If the temperature is constant, k_{f} is constant and we can carry out a definite integration from $t = 0$ to $t = t'$:

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_{t'}} \frac{1}{[\mathrm{A}]}d[\mathrm{A}] = -\int_0^{t'} k_{\mathrm{f}}dt$$

$$\boxed{\ln([\mathrm{A}]_{t'}) - \ln([\mathrm{A}]_0) = \frac{\ln([\mathrm{A}]_{t'})}{\ln([\mathrm{A}]_0)} = -k_{\mathrm{f}}t' \quad \text{(first order, no reverse reaction)}} \tag{11.2-4}$$

where the subscript on [A] indicates the time at which it is measured. Taking antilogarithms of Eq. (11.2-4),

$$\boxed{[\mathrm{A}]_t = [\mathrm{A}]_0 e^{-k_{\mathrm{f}}t} \quad \text{(first order, no reverse reaction)}} \tag{11.2-5}$$

where we have written t instead of t' for the time.

Exercise 11.1

Carry out an indefinite integration of Eq. (11.2-3). Evaluate the constant of integration to obtain Eq. (11.2-5).

For a gas-phase reaction we can use partial pressures instead of concentrations in our rate law.

EXAMPLE 11.1

The gas-phase reaction

$$\mathrm{N_2O_5} \longrightarrow 2\mathrm{NO_2} + \frac{1}{2}\mathrm{O_2}$$

is found to be first order. The rate constant at 337.6 K is equal to $5.12 \times 10^{-3}\ \text{s}^{-1}$.[a] If the partial pressure of N_2O_5 is 0.500 atm at time $t = 0$, find the partial pressure of N_2O_5 at $t = 60.0$ s, neglecting any reverse reaction and assuming that the system is at constant volume.

Solution

Assuming the gas to be ideal, the partial pressure of a gas is proportional to the concentration. In the case of constant temperature Eq. (11.2-5) can be rewritten in terms of pressure:

$$
\begin{aligned}
P(\mathrm{N_2O_5})_t &= P(\mathrm{N_2O_5})_0 e^{-k_f t} \\
&= (0.500\ \text{atm})\exp\left[-(5.12 \times 10^{-3}\ \text{s}^{-1})(60.0\ \text{s})\right] = 0.368\ \text{atm}
\end{aligned}
$$

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[a] H. S. Johnston and Y. Tao, *J. Am. Chem. Soc.*, **73**, 2948 (1951).

The *half-life*, $t_{1/2}$, is defined as the time required for half of the original amount of the reactant to be consumed. Since $[\mathrm{A}]_{t_{1/2}} = [\mathrm{A}]_0/2$, we can write from Eq. (11.2-4)

$$k_f t_{1/2} = -\ln\left(\frac{[\mathrm{A}]_{t_{1/2}}}{[\mathrm{A}]_0}\right) = -\ln\left(\frac{1}{2}\right) = \ln(2)$$

or

$$t_{1/2} = \frac{\ln(2)}{k_f} \approx \frac{0.69315}{k_f} \quad \text{(first order, no reverse reaction)} \tag{11.2-6}$$

The *relaxation time* τ is the time for the amount of reactant to drop to a fraction $1/e$ (approximately 0.3679) of its original value. Substitution of this definition into Eq. (11.2-4) gives

$$\tau = \frac{1}{k_f} = \frac{t_{1/2}}{\ln(2)} \approx 1.4427 t_{1/2} \quad \text{(first order, no reverse reaction)} \tag{11.2-7}$$

Exercise 11.2

a. Verify Eq. (11.2-7).

b. Find the half-life and the relaxation time for the reaction of Example 11.1.

The decay of radioactive nuclides obeys first-order kinetics with rate constants that do not appear to depend on temperature. Half-lives, not rate constants, are tabulated for radioactive nuclides.

EXAMPLE 11.2

The half-life of $^{235}\mathrm{U}$ is equal to 7.1×10^8 years. Find the first-order rate constant and the relaxation time.

Solution

$$k = \frac{\ln(2)}{t_{1/2}} = \frac{\ln(2)}{7.1 \times 10^{8}\ \text{yr}} = 9.8 \times 10^{-10}\ \text{yr}^{-1}$$

$$\tau = \frac{1}{k} = \frac{1}{9.8 \times 10^{-10}\ \text{yr}^{-1}} = 1.02 \times 10^{9}\ \text{yr}$$

Exercise 11.3

Find the time required for a sample of ^{235}U to decay to 10.0% of its original amount.

Second-Order Reactions

The rate law for a second-order reaction with a single reactant and negligible reverse reaction is

$$r = r_{\text{f}} = -\frac{d[\text{A}]}{dt} = k_{\text{f}}[\text{A}]^2 \tag{11.2-8}$$

where the rate constant k_{f} has units of concentration^{-1} time^{-1} (L mol^{-1} s^{-1}, m^3 mol^{-1} min^{-1}, and so on) or pressure^{-1} time^{-1}(atm^{-1} s^{-1}, bar^{-1} min^{-1}, and so on). With the variables separated,

$$\frac{1}{[\text{A}]^2}\frac{d[\text{A}]}{dt}dt = \frac{d[\text{A}]}{[\text{A}]^2} = -k_{\text{f}}\,dt \tag{11.2-9}$$

If the temperature is constant, k_{f} is constant, and we can carry out a definite integration from time $t = 0$ to time $t = t'$.

$$\int_{[\text{A}]_0}^{[\text{A}]_{t'}} \frac{d[\text{A}]}{[\text{A}]^2} = -k_{\text{f}} \int_0^{t'} dt \tag{11.2-10}$$

The result is

$$\frac{1}{[\text{A}]_{t'}} - \frac{1}{[\text{A}]_0} = k_{\text{f}}t' \quad \text{(second order, no reverse reaction)} \tag{11.2-11}$$

where $[\text{A}]_{t'}$ denotes the concentration of substance A at time t.

Exercise 11.4

Carry out an indefinite integration and evaluate the constant of integration to obtain Eq. (11.2-11) in an alternative way.

EXAMPLE 11.3

The gas-phase reaction

$$\mathrm{NO_3} \longrightarrow \mathrm{NO_2} + \frac{1}{2}\mathrm{O_2}$$

obeys second-order kinetics. At a temperature of 20°C and an initial concentration of NO_3 equal to $0.0500\,\mathrm{mol\,L^{-1}}$, the concentration after 60.0 minutes is equal to $0.0358\,\mathrm{mol\,L^{-1}}$. Assuming the reverse reaction to be negligible, find the value of the forward rate constant.

Solution

$$k_\mathrm{f} = \frac{1}{t}\left(\frac{1}{[\mathrm{NO_3}]_t} - \frac{1}{[\mathrm{NO_3}]_0}\right) = \frac{1}{3600\,\mathrm{s}}\left[\frac{1}{0.0358\,\mathrm{mol\,L^{-1}}} - \frac{1}{0.0500\,\mathrm{mol\,L^{-1}}}\right]$$
$$= 2.2 \times 10^{-3}\,\mathrm{L\,mol^{-1}\,s^{-1}}$$

Exercise 11.5

a. Find the concentration of NO_3 in the experiment of the previous example after an elapsed time of 145 minutes. Assume the reverse reaction to be negligible.

b. Find the concentration after 145 minutes if the initial concentration is $0.100\,\mathrm{mol\,L^{-1}}$.

c. Assuming the gases to be ideal, find the value of the rate constant in $\mathrm{atm^{-1}\,min^{-1}}$. Assume the reverse reaction to be negligible.

d. Find the pressure of NO_3 after an elapsed time of 175 min with the initial concentration of $0.0500\,\mathrm{mol\,L^{-1}}$. Assume the reverse reaction to be negligible.

If the reverse reaction can be neglected, the half-life of a second-order reaction is given by

$$\frac{1}{[\mathrm{A}]_0/2} - \frac{1}{[\mathrm{A}]_0} = \frac{2}{[\mathrm{A}]_0} - \frac{1}{[\mathrm{A}]_0} = \frac{1}{[\mathrm{A}]_0} = k_\mathrm{f}t_{1/2} \tag{11.2-12}$$

$$\boxed{t_{1/2} = \frac{1}{k[\mathrm{A}]_0} \quad \text{(second order, no reverse reaction)}} \tag{11.2-13}$$

EXAMPLE 11.4

Find the half-life of the reaction of the previous example with the given initial concentration.

Solution

$$t_{1/2} = \frac{1}{k[\mathrm{NO_3}]_0} = \frac{1}{(2.2\times10^{-3}\,\mathrm{L\,mol^{-1}\,s^{-1}})(0.0500\,\mathrm{mol\,L^{-1}})(60\,\mathrm{s\,min^{-1}})} = 150\,\mathrm{min}$$

Exercise 11.6

a. Find the half-life of the reaction of the previous example if the initial concentration is equal to $0.0200\,\mathrm{mol\,L^{-1}}$.

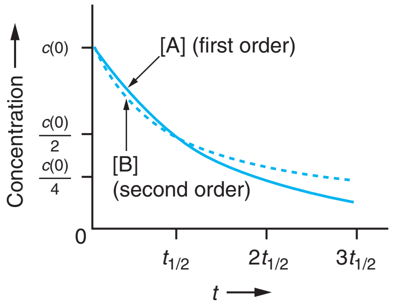

Figure 11.2 Comparison of the Concentrations of the Reactants of a First-Order Reaction and a Second-Order Reaction.

b. Find the half-life of the reaction of the previous example if the initial concentration is equal to 0.1000 mol L^{-1}.

If there is considerable experimental error it might be difficult to tell a first-order reaction from a second-order reaction by inspection of a graph of the concentration versus time if the graph extends over only one half-life. Figure 11.2 shows two hypothetical reactions with the same initial concentration: Substance A undergoes a first-order reaction and substance B undergoes a second-order reaction with the same half-life. The concentrations in the two cases differ only slightly for times up to $t_{1/2}$. For longer times the difference is greater.

Exercise 11.7

Find expressions for the time required for the concentration of the reactant in each of the reactions of Figure 11.2 to drop to one-sixteenth of its original value, assuming that the reverse reaction is negligible. Express these times in terms of $t_{1/2}$.

---

*n*th-Order Reactions

The rate law for an nth order reaction with a single reactant and negligible reverse reaction is

$$r = -\frac{d[\mathrm{A}]}{dt} = k_{\mathrm{f}}[\mathrm{A}]^n \tag{11.2-14}$$

Consider the case that the order n is not necessarily an integer but is not equal to unity or zero. The variables can be separated by division by $[\mathrm{A}]^n$ and multiplication by dt, giving

$$-\frac{d[\mathrm{A}]}{[\mathrm{A}]^n} = k_{\mathrm{f}}\,dt \tag{11.2-15}$$

Assuming constant temperature, we perform a definite integration from $t = 0$ to $t = t'$:

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_{t'}} \frac{d[\mathrm{A}]}{[\mathrm{A}]^n} = -k_{\mathrm{f}} \int_0^{t'} dt \tag{11.2-16}$$

The result is:

$$\frac{1}{n-1}\left[\frac{1}{[\mathrm{A}]_t^{n-1}} - \frac{1}{[\mathrm{A}]_0^{n-1}}\right] = k_{\mathrm{f}}t \quad (n\text{th order, no reverse reaction}) \tag{11.2-17}$$

where we omit the prime symbol on t. The half-life is found by substituting $[\mathrm{A}]_{t_{1/2}} = [\mathrm{A}]_0/2$ into Eq. (11.2-17). The result is

$$t_{1/2} = \frac{2^{n-1}-1}{(n-1)k_{\mathrm{f}}[\mathrm{A}]_0^{n-1}} \quad (n\text{th order, no reverse reaction}) \tag{11.2-18}$$

These formulas are not valid if $n = 1$ or $n = 0$.

Exercise 11.8

a. Verify Eq. (11.2-18).

b. Find the units of the rate constant k_{f} for an nth-order reaction.

c. For a third-order reaction with a single reactant and negligible reverse reaction, find an expression for the time required for 80% of the reactant to react.

d. In terms of $t_{1/2}$, how long will it take for 7/8 (87.5%) of the reactant of part c to react?

Zero-Order Reactions

In the rare case that a reaction of a single reactant is zero order (the rate is independent of the concentration of the reactant), the rate law for the forward reaction is

$$r = -\frac{d[\mathrm{A}]}{dt} = k_{\mathrm{f}}[\mathrm{A}]^0 = k_{\mathrm{f}} \tag{11.2-19}$$

If there is no reverse reaction and if the temperature is constant, the solution of this equation is

$$[\mathrm{A}]_t = \begin{cases} [\mathrm{A}]_0 - k_{\mathrm{f}}t & \text{if } 0 < t < [\mathrm{A}]_0/k_{\mathrm{f}} \\ 0 & \text{if } [\mathrm{A}]_0/k_{\mathrm{f}} < t \end{cases} \tag{11.2-20}$$

where the first line of the solution is obtained from Eq. (11.2-19). The second line of the solution is obtained from the fact that the reaction stops when no reactant remains.

EXAMPLE 11.5

A hypothetical zero-order reaction has a rate constant equal to $0.0150\ \mathrm{mol\,L^{-1}\,s^{-1}}$ at a certain temperature. If the initial concentration of the single reactant is $1.000\ \mathrm{mol\,L^{-1}}$, find the concentration after a reaction time of 5.00 s at this temperature.

Solution

$$[\mathrm{A}]_t = [\mathrm{A}]_0 - k_{\mathrm{f}}t = 1.000\ \mathrm{mol\,L^{-1}} - (0.0150\ \mathrm{mol\,L^{-1}\,s^{-1}})(5.00\ \ \mathrm{s}) = 0.925\ \mathrm{mol\,L^{-1}}$$

Exercise 11.9

a. Find the time required for all of the reactant of the previous example to react at this temperature.

b. Find an expression for the half-life of a zero-order reaction and the value of the half-life of the reaction of the previous example.

Determination of Reaction Order Using Integrated Rate Laws

For a reaction of a single substance with a negligible reverse reaction, we can compare the integrated rate law with experimental data on the concentration of the reactant. Since graphs of linear functions are easy to recognize, for each order one can plot the appropriate function of the reactant's concentration that will give a linear graph. Denote the reactant by A. To test for zero order, one makes a graph of $[\mathrm{A}]_t$ as a function of t. To test for first order, one makes a graph of $\ln([\mathrm{A}])$ as a function of t. To test for second order, one makes a graph of $1/[\mathrm{A}]$ as a function of t. To test for third order, one makes a graph of $1/(2\,[\mathrm{A}]^2)$ as a function of t. Graphs of $1/\left((n-1)\,[\mathrm{A}]^{n-1}\right)$ for various nonintegral values of n can also be made. The graph that is most nearly linear corresponds to the correct order. Figure 11.3 shows schematic graphs for zero, first, second, and third order. Using commercially available software packages such as Excel, MathCad, or Mathematica, one can construct the graphs and carry out least-squares (regression) fits to the data. These software packages automatically calculate the *correlation coefficient* (or its square), which is a measure of the closeness of the fit of the function to the data. A perfect fit corresponds to a value of the correlation coefficient equal to unity. Some packages will print out a list of *residuals*, which are the set of differences between the data points and the least-squares line. The Excel spreadsheet can also print out the expected errors in the slope and intercept.

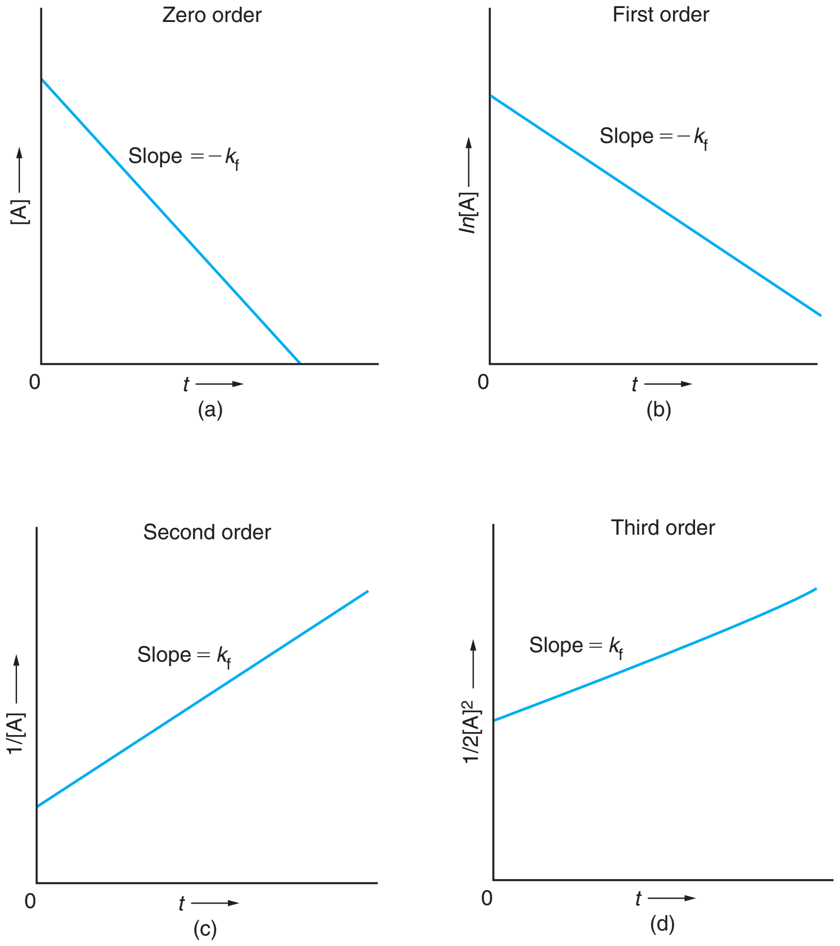

Figure 11.3 Linear Graphs for Zero-, First-, Second-, and Third-Order Reactions. (a) Zero order. (b) First order. (c) Second order. (d) Third order.

Determination of Reaction Order Using the Half-Life

You can carry out several experiments with different initial concentrations at the same temperature. If the half-life of the reaction is independent of concentration the reaction is first order. To test for other orders we take the natural logarithm of both sides of Eq. (11.2-18) to obtain

$$\ln(t_{1/2}) = \ln\left(\frac{2^{n-1}-1}{(n-1)k_{\mathrm{f}}}\right) - (n-1)\ln([\mathrm{A}]_0) \quad (n \neq 1, n \neq 0) \qquad (11.2\text{-}21)$$

To use Eq. (11.2-21), one could construct a plot of $\ln(t_{1/2})$ versus $\ln([\mathrm{A}]_0)$. A straight line should result, with slope equal to $-(n-1)$ and with intercept equal to the first term on the right-hand side of Eq. (11.2-21). Instead of carrying out different experiments, one can also take the data for a single experiment and regard different times during the experiment as "initial" times. The reverse reaction must be negligible for the entire experiment.

EXAMPLE 11.6

For the gas-phase reaction at 300°C:

$$\mathrm{C_2F_4} \longrightarrow \frac{1}{2}\text{cyclo-}\mathrm{C_4F_8}$$

the following data on the concentration of $\mathrm{C_2F_4}$ were taken. Determine the order of the reaction and the rate constant at this temperature. Assume that the reverse reaction is negligible.

Time/min	Concentration /mol $\mathrm{L^{-1}}$
0	0.0500
250	0.0250
750	0.0125
1750	0.00625
3750	0.00312

Solution

This example can be solved by inspection. Each concentration is half of the previous concentration, so that the time interval from a given data point to the next is the half-life for the reaction using the given data point as an "initial state." We have

Half-life/min	Initial concentration/mol $\mathrm{L^{-1}}$
250	0.0500
500	0.0250
1000	0.0125
2000	0.00625

The half-life doubles each time the "initial" concentration is reduced to half its previous value. This behavior indicates a second-order reaction. A linear least-squares fit of $\ln(t_{1/2})$ versus $\ln([\mathrm{A}]_0)$ confirms this result with order = 2.00 and $k_{\mathrm{f}} = 0.080\ \mathrm{L\,mol^{-1}\,min^{-1}} = 1.3 \times 10^{-3}\ \mathrm{L\,mol^{-1}\,s^{-1}}$.

The Method of Initial Rates

In this method we compare data directly with the rate law instead of with an integrated rate law. The reaction is followed for a short time Δt during which there is a change $\Delta[\mathrm{A}]$ in the concentration of a reactant, A:

$$\Delta[\mathrm{A}] = [\mathrm{A}]_{\Delta t} - [\mathrm{A}]_0 \tag{11.2-22}$$

The time Δt must be short enough that $\Delta[\mathrm{A}]$ is much smaller than [A]. The method has the advantage that the reverse reaction is almost certain to be negligible. The initial rate is approximated by a quotient of finite differences:

$$r_{\mathrm{initial}} = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} \approx -\frac{1}{a}\frac{\Delta[\mathrm{A}]}{\Delta t} \tag{11.2-23}$$

where a is the stoichiometric coefficient of the reactant A. If there is only one reactant and if the rate law corresponds to order α, the initial rate corresponds to Eq. (11.1-8):

$$r_{\mathrm{initial}} = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = k_{\mathrm{f}}[\mathrm{A}]_0^{\alpha} \tag{11.2-24}$$

where $[\mathrm{A}]_0$ is the initial concentration of the reactant A. We take the natural logarithm of both sides of this equation

$$\ln(r_{\mathrm{initial}}) = \ln(k_{\mathrm{f}}) + \alpha\ln([\mathrm{A}]_0) \tag{11.2-25}$$

To determine the order and the rate constant, one carries out several experiments at the same temperature but with different values of $[\mathrm{A}]_0$. A plot of the logarithm of the initial rate as a function of the logarithm of the initial concentration is constructed and a linear least-squares fit is performed. The slope of the line fitting the data points is the order of the reaction, and the intercept is the logarithm of the rate constant. A modification to the foregoing method would be to run the experiment over a longer period of time and then to determine the value of $\Delta[\mathrm{A}]/\Delta t$ and the value of [A] at different times and to use these values in a fit to Eq. (11.2-25).

EXAMPLE 11.7

Following are data for the decomposition of ethyl chloride, C_2H_5Cl, at 500°C. Find the order of the reaction and the rate constant at this temperature.

Initial concentration /mol L^{-1}	Initial rate /mol L^{-1} hour^{-1}
0.0500	0.00130
0.0400	0.00104
0.0300	0.00080
0.0200	0.00052
0.0100	0.00026

Solution

A linear least-squares fit of $\ln(r_{\mathrm{initial}})$ against $\ln([C_2H_5Cl]_0)$ gives

$$\alpha = 1.00, \quad \ln(k_{\mathrm{f}}) = -3.64, \quad k_{\mathrm{f}} = 0.026\ \mathrm{hour}^{-1}$$

Figure 11.4 shows the graph of the data points and the least-squares line. The correlation coefficient squared was equal to 1.000.

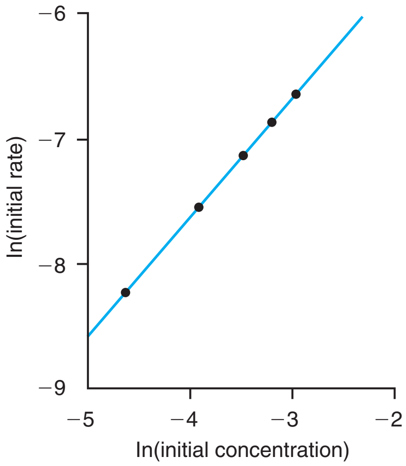

Figure 11.4 The Linear Plot for Example 11.7.

PROBLEMS

Section 11.2: Forward Reactions with One Reactant

11.3 A hypothetical chemical reaction with a single reactant and negligible back reaction is 40.0% complete after 185 s at some fixed temperature if the initial concentration is $0.100\ \mathrm{mol\ L^{-1}}$.

a. If the reaction is first order, find the rate constant and the half-life.

b. If the reaction is second order, find the rate constant and the half-life.

11.4 Write the reaction equation of Example 11.1 in the form

$$2\ \mathrm{N_2O_5} \longrightarrow 4\ \mathrm{NO_2} + \mathrm{O_2}$$

with the rate equation

$$-\frac{1}{2}\frac{d[\mathrm{N_2O_5}]}{dt} = k_f''\,[\mathrm{N_2O_5}]$$

a. How does k_f'' relate to the coefficient k_f given in the example?

b. How does the change in the writing of the reaction equation affect the half-life of the reaction? Write the equation relating $t_{1/2}$ to k_f''. Find the value of the half-life of the reaction at the temperature of Example 11.1.

c. How does the change in the writing of the reaction equation affect the concentration or partial pressure of the reactant at a given reaction time? Find the partial pressure of $\mathrm{N_2O_5}$ after a reaction time of 100.0 s.

11.5 The gas-phase thermal decomposition of bromoethane follows first-order kinetics. At 500°C, the rate constant is equal to $0.1068\ \mathrm{s^{-1}}$. If the initial pressure of bromoethane is equal to 1.000 bar, find the partial pressure of bromoethane at 10.00 s and at 100.0 s if the bromoethane is decomposed at a constant volume and at a constant temperature of 500°C.

11.6 For the gas-phase decomposition of $\mathrm{N_2O_3}$, the following data were taken:

time/s:	0	1109	2218
concentration/mol $\mathrm{L^{-1}}$:	0.500	0.250	0.125

a. What is the order of the reaction?

b. What is the value of the rate constant?

11.7 The gas-phase reaction

$$\mathrm{SO_2Cl_2} \longrightarrow \mathrm{SO_2} + \mathrm{Cl_2}$$

obeys first-order kinetics, with $k_f = 2.2 \times 10^{-5}\ \mathrm{s^{-1}}$ at 320°C.

a. Find the half-life of the reaction at 320°C.

b. What length of time is required for 90.0% of the reactant to be consumed at 320°C?

11.8 The gas-phase reaction

$$\mathrm{N_2O_5} \longrightarrow 2\mathrm{NO_2} + \frac{1}{2}\mathrm{O_2}$$

is found to be first order. The reaction was carried out at constant temperature of 337.6 K in a constant-volume container. The initial pressure is equal to 0.100 bar and no substance is initially present except for $\mathrm{N_2O_5}$. The total pressure after 100.0 s of reaction is found to be 0.160 bar.

a. Find the value of the rate constant at this temperature.

b. Find the partial pressure of $\mathrm{N_2O_5}$ after 100.0 s of reaction. Neglect the reverse reaction.

c. Find the half-life of the reaction and find the total pressure at this time.

11.9 The following data were taken for the decomposition of dinitrogen trioxide at some fixed temperature:

t/s:	0	184	526	867	1877
$[\mathrm{N_2O_3}]$ /mol $\mathrm{L^{-1}}$:	2.33	2.08	1.67	1.36	0.72

Assuming that the reverse reaction is negligible, determine whether the reaction is first, second, or third order, and find the value of the rate constant at this temperature. Proceed by graphing $\ln(c)$, $1/c$, and $1/c^2$, or by making linear least-squares fits to these functions. Express the rate constant in terms of partial pressure instead of concentration.

11.10 A certain reaction was studied at a fixed temperature. It was found that if the initial concentration of the single reactant were equal to $4.86 \times 10^{-3}\ \mathrm{mol\ L^{-1}}$, the half-life of the reaction were equal to 399 s. When the initial concentration was $2.28 \times 10^{-3}\ \mathrm{mol\ L^{-1}}$, the half-life was equal to 696 s. Find the order of the reaction and the value of the rate constant.

11.11 A certain reaction with a single reactant is found to be fourth order and to have at a certain temperature a half-life of 10.00 s with an initial concentration of 0.100 mol L^{-1}.

a. Find the concentration of the reactant after a reaction time of 15.00 s for the same initial concentration and temperature.

b. Find the concentration after a reaction time of 30.00 s.

11.12 The following data were taken for the gas-phase dimerization of butadiene at some fixed temperature.

Time/min	P/atm	Time/min	P/atm
0	0.8315	55.08	0.6450
3.25	0.8138	68.05	0.6244
8.02	0.7886	90.05	0.5954
12.18	0.7686	119.00	0.5694
17.30	0.7464	176.67	0.5332
24.55	0.7194	259.50	0.5013
33.00	0.6944	373.00	0.4698
42.50	0.6701		

a. Assuming ideal gas behavior, show that

$$P_B = 2P - P_B(0)$$

where P_B is the partial pressure of butadiene and P is the observed pressure.

b. Find the order of the reaction and the value of the rate constant at this temperature.

11.13 For a reaction of a single reactant at a certain fixed temperature, the following data were presented:

Time/s	[A]/mol L^{-1}
0	1.000
30	0.7912
60	0.6415
90	0.5306
120	0.4462
150	0.3804
180	0.3283
210	0.2860

Assume that the reverse reaction can be neglected. Show that the order of the reaction is 3/2 and find the value of the rate constant at this temperature.

11.14 The gas-phase dimerization of butadiene,

$$2C_4H_6 \longrightarrow C_8H_{12}$$

follows second-order kinetics. At time $t = 0$, pure butadiene is introduced into a vessel at 599 K and 0.832 atm. At time $t = 60.9$ minutes, the total pressure is 0.635 atm. Assume that both gases are ideal and that no back reaction occurs.

a. Find the partial pressure of butadiene at this time.

b. Find the value of the second-order rate constant at this temperature.

c. Find the half-life of the reaction under these conditions.

d. Find the partial pressure of butadiene and the total pressure at $t = 100.0$ minutes.

11.3 Forward Reactions with More Than One Reactant

Reactions with more than one reactant are somewhat more complicated than reactions with a single reactant.

Integration of the Rate Law

Consider a reaction that is first order in each of two reactants:

$$aA + bB \longrightarrow \text{products} \tag{11.3-1}$$

where a and b represent stoichiometric coefficients and where A and B represent chemical formulas. The rate law is

$$r = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = k_{\mathrm{f}}[\mathrm{A}][\mathrm{B}] \tag{11.3-2}$$

We first consider the case that the reactants' concentrations are initially in the stoichiometric ratio:

$$\frac{[\mathrm{A}]_0}{[\mathrm{B}]_0} = \frac{a}{b} \tag{11.3-3}$$

The concentrations will remain in this ratio during the reaction.

Exercise 11.10

Show that if Eq. (11.3-3) holds then

$$\frac{[\mathrm{A}]_t}{[\mathrm{B}]_t} = \frac{a}{b} \tag{11.3-4}$$

for all values of t greater than 0.

We define a single dependent variable $x(t)$:

$$x(t) = \frac{[\mathrm{A}]_0 - [\mathrm{A}]_t}{a} = \frac{[\mathrm{B}]_0 - [\mathrm{B}]_t}{b} \tag{11.3-5}$$

Exercise 11.11

Show that both versions of Eq. (11.3-5) correspond to the same value of x.

We can now write Eq. (11.3-2) in the form

$$\frac{dx}{dt} = k_{\mathrm{f}}([\mathrm{A}]_0 - ax)([\mathrm{B}]_0 - bx) \tag{11.3-6a}$$

$$= k_{\mathrm{f}}ab\left(\frac{[\mathrm{A}]_0}{a} - x\right)\left(\frac{[\mathrm{B}]_0}{b} - x\right) = k_{\mathrm{f}}ab\left(\frac{[\mathrm{A}]_0}{a} - x\right)^2 \tag{11.3-6b}$$

where we have used the fact that $[\mathrm{B}]_0/b = [\mathrm{A}]_0/a$.

The variables can be separated in Eq. (11.3-6b) by dividing by $[[\mathrm{A}]_0/a - x]^2$ and multiplying by dt:

$$\frac{dx}{\left(\frac{[\mathrm{A}]_0}{a} - x\right)^2} = k_{\mathrm{f}}ab\,dt \tag{11.3-7}$$

We integrate both sides of Eq. (11.3-7) from $t = 0$ to $t = t'$:

$$\frac{1}{\frac{[\mathrm{A}]_0}{a} - x(t')} - \frac{1}{\frac{[\mathrm{A}]_0}{a}} = k_{\mathrm{f}}abt'$$

This is the same as

$$\frac{1}{[\mathrm{A}]_t} - \frac{1}{[\mathrm{A}]_0} = k_{\mathrm{f}} bt \tag{11.3-8}$$

where we drop the prime symbol (′) on t. Equation (11.3-8) is the same as Eq. (11.2-11) except for the appearance of the factor b in the right-hand side.

EXAMPLE 11.8

Some of the damage to the ozone layer of the upper atmosphere might involve the reaction

$$\mathrm{NO} + \mathrm{O_3} \longrightarrow \mathrm{NO_2} + \mathrm{O_2}$$

The reaction is first order in each reactant and the rate constant is equal to 1.3×10^6 L mol^{-1} s^{-1} at 298 K. If the initial concentrations of NO and O_3 are both equal to 1.00×10^{-6} mol L^{-1}, find the concentrations of NO and O_3 at time $t = 2.00$ s.

Solution

$$\frac{1}{[\mathrm{NO}]} = \frac{1}{\mathrm{NO}_0} + k_{\mathrm{f}} t = \frac{1}{1.00 \times 10^{-6}\ \mathrm{mol\,L^{-1}}} + (1.3 \times 10^6\ \mathrm{L\,mol^{-1}\,s^{-1}})(2.00\ \mathrm{s})$$

$$= 3.6 \times 10^6\ \mathrm{L\,mol^{-1}}$$

$$[\mathrm{NO}] = [\mathrm{O_3}] = \frac{1}{3.6 \times 10^6\ \mathrm{L\,mol^{-1}}} = 2.8 \times 10^{-7}\ \mathrm{mol\,L^{-1}}$$

Exercise 11.12

a. Find the half-life of the reaction in the previous example with the given initial concentrations.

b. Find the half-life of the reaction in the previous example with initial concentrations both equal to 5.00×10^{-5} mol L^{-1}.

In the case that the reactants are not mixed in the stoichiometric ratio we separate the variables in Eq. (11.3-6a):

$$\frac{1}{([\mathrm{A}]_0 - ax)([\mathrm{B}]_0 - bx)} dx = k_{\mathrm{f}}\, dt \tag{11.3-9}$$

This equation can be integrated by the method of *partial fractions*. If we write

$$\frac{1}{([\mathrm{A}]_0 - ax)([\mathrm{B}]_0 - bx)} = \frac{G}{[\mathrm{A}]_0 - ax} + \frac{H}{[\mathrm{B}]_0 - bx} \tag{11.3-10}$$

then G and H are guaranteed by a theorem of algebra to be constants. These constants are found to be

$$G = \frac{1}{[\mathrm{B}]_0 - b[\mathrm{A}]_0/a} \quad \text{and} \quad H = \frac{1}{[\mathrm{A}]_0 - a[\mathrm{B}]_0/b}$$

Exercise 11.13

Verify the expressions for G and H.

When the expressions for G and H are substituted into Eq. (11.3-10) and the resulting expression is substituted into Eq. (11.3-9), a definite integration gives

$$\frac{1}{a[\mathrm{B}]_0 - b[\mathrm{A}]_0} \ln\left(\frac{[\mathrm{B}]_t[\mathrm{A}]_0}{[\mathrm{A}]_t[\mathrm{B}]_0}\right) = k_\mathrm{f} t \qquad (11.3\text{-}11)$$

This integrated rate law can now be compared with experimental data.

Exercise 11.14

Verify Eq. (11.3-11) by carrying out the integration.

EXAMPLE 11.9

Assume that for the reaction

$$\mathrm{NO} + \mathrm{O_3} \longrightarrow \mathrm{NO_2} + \mathrm{O_2}$$

$[\mathrm{NO}]_0 = 1.00 \times 10^{-6}\ \mathrm{mol\,L^{-1}}$ and $[\mathrm{O_3}]_0 = 5.00 \times 10^{-7}\ \mathrm{mol\,L^{-1}}$. Find the concentration of $\mathrm{O_3}$ after 3.50 s.

Solution

Let $\mathrm{O_3}$ be denoted by A and NO be denoted by B. Use of Eq. (11.3-11) with $a = b = 1$ gives, with some manipulation:

$$\frac{[\mathrm{B}]_0 - x}{[\mathrm{A}]_0 - x} = \frac{[\mathrm{B}]_0}{[\mathrm{A}]_0} \exp[kt([\mathrm{B}]_0 - [\mathrm{A}]_0)]$$

Using the values given, solution of the equation gives $x = 4.73 \times 10^{-7}$ and $[\mathrm{O_3}] = 0.27 \times 10^{-7}\ \mathrm{mol\,L^{-1}}$.

Exercise 11.15

Carry out the mathematical steps to verify the solution of the preceding example.

The Method of Initial Rates

Consider the hypothetical reaction

$$a\mathrm{A} + b\mathrm{B} + f\mathrm{F} \longrightarrow \text{products} \qquad (11.3\text{-}12)$$

We assume the reaction has definite orders so that the initial rate is

$$r_\mathrm{initial} = k_\mathrm{f}[\mathrm{A}]_0^\alpha[\mathrm{B}]_0^\beta[\mathrm{F}]_0^\phi \approx -\frac{1}{a}\frac{\Delta[\mathrm{A}]}{\Delta t} \qquad (11.3\text{-}13)$$

Several experiments are carried out with the same values of $[\mathrm{B}]_0$ and $[\mathrm{F}]_0$ but with different values of $[\mathrm{A}]_0$. The initial rate is determined for each experiment. We write

$$\ln(r_\mathrm{initial}) = \ln(k_\mathrm{f}[\mathrm{B}]_0^\beta[\mathrm{F}]_0^\phi) + \alpha\ln([\mathrm{A}]_0) \qquad (11.3\text{-}14)$$

The first term on the right-hand side of this equation has the same value in all of these experiments. A plot of $\ln(r_{\text{initial}})$ as a function of $\ln([\text{A}]_0)$ should give a straight line with slope equal to α.

Additional sets of experiments are carried out in which $[\text{B}]_0$ is varied while keeping $[\text{A}]_0$ and $[\text{F}]_0$ fixed. An equation analogous to Eq. (11.3-14) allows the order with respect to B to be determined. A third set of experiments is carried out in which $[\text{F}]_0$ is varied while keeping $[\text{A}]_0$ and $[\text{B}]_0$ fixed. If there are only a few experiments, an algebraic method can be used, as in the following example. After all of the orders are determined, everything in the right-hand side of Eq. (11.3-13) is known except for k_{f}, so k_{f} can be computed from any one of the experiments. Since there is always some experimental error, a reasonable policy is to calculate the rate constant separately for each experiment and then average the values.

EXAMPLE 11.10

The following data were taken at 298 K for the gas-phase reaction

$$2\,\text{NO} + \text{Cl}_2 \longrightarrow 2\,\text{NOCl}$$

$[\text{NO}]/\text{mol L}^{-1}$	$[\text{Cl}_2]/\text{mol L}^{-1}$	initial rate/$\text{mol L}^{-1}\text{ s}^{-1}$
0.0200	0.0200	7.1×10^{-5}
0.0400	0.0200	2.8×10^{-4}
0.0200	0.0400	1.4×10^{-4}

Find the order with respect to each reactant and find the rate constant.

Solution

In this case we proceed algebraically since there are only three experiments. Let the initial rate in the first experiment be r_1 and that of the second experiment be r_2. We write

$$\begin{aligned}\frac{r_2}{r_1} &= \frac{2.8 \times 10^{-4}\text{ mol L}^{-1}\text{ s}^{-1}}{7.1 \times 10^{-5}\text{ mol L}^{-1}\text{ s}^{-1}} = 4.0\\ &= \frac{k[\text{NO}]_2^{\alpha}[\text{Cl}_2]_2^{\beta}}{k[\text{NO}]_1^{\alpha}[\text{Cl}_2]_1^{\beta}} = \frac{[\text{NO}]_2^{\alpha}}{[\text{NO}]_1^{\alpha}} = \left(\frac{0.0400\text{ mol L}^{-1}}{0.0200\text{ mol L}^{-1}}\right)^{\alpha} = 2.00^{\alpha}\\ \alpha &= \frac{\ln(4.0)}{\ln(2.00)} = 2.0\end{aligned}$$

The reaction is second order with respect to NO. The order with respect to Cl_2 is obtained from the first and the third experiments:

$$\begin{aligned}\frac{r_3}{r_1} &= \frac{1.4 \times 10^{-4}\text{ mol L}^{-1}\text{ s}^{-1}}{7.1 \times 10^{-5}\text{ mol L}^{-1}\text{ s}^{-1}} = 2.0\\ &= \frac{k[\text{NO}]_3^{\alpha}[\text{Cl}_2]_3^{\beta}}{k[\text{NO}]_1^{\alpha}[\text{Cl}_2]_1^{\beta}} = \frac{[\text{Cl}_2]_3^{\beta}}{[\text{Cl}_2]_1^{\beta}} = \left(\frac{0.0400\text{ mol L}^{-1}}{0.0200\text{ mol L}^{-1}}\right)^{\beta} = 2.00^{\beta}\\ \beta &= \frac{\ln(2.0)}{\ln(2.00)} = 1.0\end{aligned}$$

The reaction is first order with respect to Cl_2. We compute the rate constant from the data of the first experiment.

$$k_f = \frac{r_{\text{initial}}}{[\text{NO}]^2\,[\text{Cl}_2]} = \frac{(7.1 \times 10^{-5}\ \text{mol L}^{-1}\ \text{s}^{-1})}{(0.0200\ \text{mol L}^{-1})^2\,(0.0200\ \text{mol L}^{-1})} = 8.9\ \text{L}^2\ \text{mol}^{-2}\ \text{s}^{-1}$$

The average value calculated from all three experiments is $8.8\ \text{L}^2\ \text{mol}^{-2}\ \text{s}^{-1}$. This example could have been solved by inspection, noticing that the rate quadrupled when [NO] was doubled and doubled when $[\text{Cl}_2]$ was doubled.

The Method of Isolation

In this method an experiment is carried in which the initial concentration of one reactant is chosen to be much smaller than the concentrations of the other reactants. During the reaction the fractional changes in the large concentrations are small, and these concentrations are treated as constants. The species having the small concentration is monitored as in the case of a single reactant. For example, in the reaction of Eq. (11.3-12), if [A] is much smaller than [B] and [F], the relative changes in [B] and [F] will be small. We write

$$-\frac{1}{a}\frac{d[\text{A}]}{dt} = \left(k_f\,[\text{B}]^{\beta}[\text{F}]^{\phi}\right)[\text{A}]^{\alpha} \qquad (11.3\text{-}15)$$

where the quantity in parentheses is approximately constant. Data from this kind of experiment can be treated like data from reactions with a single reactant. For example, if $\alpha = 2$, Eq. (11.2-11) can be transcribed to obtain

$$\frac{1}{[\text{A}]_t} = \frac{1}{[\text{A}]_0} + (k_f[\text{B}]^{\beta}[\text{F}]^{\phi})t \qquad (11.3\text{-}16)$$

Sets of experiments can also be carried out in which [B] is made much smaller than [A] and [F], and then in which [F] is made much smaller than [A] and [B], in order to determine β, ϕ, and k_f.

If a reaction in a solution includes the solvent as a reactant, the concentration of the solvent is usually much larger than the concentrations of other reactants and is almost constant. Assume that the solvent S is involved in the reaction

$$\text{A} + \text{S} \longrightarrow \text{products} \qquad (11.3\text{-}17)$$

and that the forward rate law is

$$r = -\frac{d[\text{A}]}{dt} = k_f[\text{S}]^{\sigma}\,[\text{A}]^{\alpha} = k_{\text{app}}[\text{A}]^{\alpha} \qquad (11.3\text{-}18)$$

where σ is the order with respect to the solvent. The quantity k_{app} is equal to $k_f[\text{s}]^{\sigma}$ is called an *apparent rate constant*. The order with respect to substance A and the apparent rate constant can be determined by any of the methods that apply to a single reactant. If the reaction is first-order with respect to substance A and of unknown order with respect to the solvent, the reaction is called a *pseudo first-order reaction*. If the reaction is second order with respect to substance A, the reaction is called a *pseudo second-order reaction*, and so on. The actual rate constant k_f and the order with respect to the solvent cannot be determined unless the concentration of the solvent can somehow be varied to determine the order with respect to the solvent.

The method of isolation applies automatically to a reaction that is catalyzed by a substance in the same phase as the reactants. For example, the hydrolysis of methyl acetate is catalyzed by KI. The reaction equation is

$$\text{CH}_3\text{CO}_2\text{CH}_3 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CO}_2\text{H} + \text{CH}_3\text{OH} \qquad (11.3\text{-}19)$$

Not only is the concentration of H_2O nearly constant, but the concentration of KI is also constant, since it is not consumed. We can find the pseudo order with respect to methyl acetate and the apparent rate constant as though there were only one reactant. See Problem 11.25.

PROBLEMS

Section 11.3: Forward Reactions with More Than One Reactant

11.15 The following forward reaction is first order in each reactant, second order overall:

$$NO + O_3 \longrightarrow NO_2 + O_2$$

At 600 K, the rate constant for the reaction is equal to $8.68 \times 10^{-6}\,\mathrm{L\,mol^{-1}\,s^{-1}}$.

a. If the initial concentration of each reactant is equal to $0.100\,\mathrm{mol\,L^{-1}}$ and the initial concentration of HI is zero, find the concentration of HI after a reaction time of 1.00×10^{6} s (11.6 days) at 600 K.

b. What is the half-life of the reaction at this temperature for these initial concentrations?

11.16 The rate constant for the forward reaction

$$H_3O^+ + OH^- \longrightarrow 2H_2O$$

is equal to $1.4 \times 10^{11}\,\mathrm{L\,mol^{-1}\,s^{-1}}$.

a. Assuming instantaneous mixing, find the half-life of the neutralization reaction between a strong acid and a strong base if both the acid and the base have initial concentrations (after mixing) of $0.150\,\mathrm{mol\,L^{-1}}$.

b. Repeat the calculation for initial concentrations of $1.00 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$.

11.17 The following reaction is first order in each reactant:

$$C_6H_5N(CH_3)_2 + CH_3I \longrightarrow C_6H_5N(CH_3)_3^+ + I^-$$

Assume that the reverse reaction is negligible.

a. At 24.8°C with nitrobenzene as the solvent, the rate constant is $8.39 \times 10^{-5}\,\mathrm{L\,mol^{-1}\,s^{-1}}$. Assuming that both reactants have initial concentrations of $0.100\,\mathrm{mol\,L^{-1}}$, find the half-life of the reaction at this temperature.

b. Find the time required for 75% of the reactants to react at 24.8°C.

c. Find the time required for 95% of the reactants to react at 24.8°C.

11.18 For the reaction of the previous problem, find the time required at 24.8°C for half of the methyl iodide to react if its initial concentration is $0.100\,\mathrm{mol\,L^{-1}}$ and the initial concentration of the dimethyl phenylamine is equal to $0.0600\,\mathrm{mol\,L^{-1}}$. Assume that the reverse reaction can be neglected.

11.19 Assume that the following initial-rate data were taken for a hypothetical reaction at some temperature:

$$A + 2B + C \longrightarrow \text{products}$$

Find the order with respect to each reactant and find the value of the rate constant.

[A]/mol $\mathrm{L^{-1}}$	[B]/mol $\mathrm{L^{-1}}$	[C]/mol $\mathrm{L^{-1}}$	initial rate/mol $\mathrm{L^{-1}\,min^{-1}}$
0.100	0.100	0.100	0.120
0.200	0.100	0.100	0.170
0.300	0.100	0.100	0.207
0.400	0.100	0.100	0.241
0.100	0.200	0.100	0.239
0.100	0.300	0.100	0.360
0.100	0.400	0.100	0.481
0.100	0.100	0.200	0.480
0.100	0.100	0.300	1.079
0.100	0.100	0.400	1.93

11.20 The gas-phase reaction

$$2NO_2 + F_2 \longrightarrow 2NO_2F$$

is first order in each reactant, second order overall. Assume that at some temperature, $k = 4.98 \times 10^{-3}\,\mathrm{L\,mol^{-1}\,s^{-1}}$.

a. If at the start of the reaction $[NO_2] = 0.200\,\mathrm{mol\,L^{-1}}$ and $[F_2] = 0.100\,\mathrm{mol\,L^{-1}}$, find the value of $[F_2]$ for a reaction time of 30.0 minutes.

b. For the case of part a, find the half-life of the reaction.

11.21 Assume that the reaction $A + B \longrightarrow$ products is second order with respect to A and first order with respect to B. Integrate the rate differential equation

$$-d[A]/dt = k[A]^2[B]$$

to obtain the result

$$kt = \left(\frac{1}{[\mathrm{B}]_0 - [\mathrm{A}]_0}\right)\left(\frac{1}{[\mathrm{A}]} - \frac{1}{[\mathrm{A}]_0}\right) + \frac{1}{([\mathrm{B}]_0 - [\mathrm{A}]_0)^2}\ln\left(\frac{[\mathrm{B}]_0[\mathrm{A}]}{[\mathrm{A}]_0[\mathrm{B}]}\right)$$

11.22 For the reaction

$$\mathrm{aA + bB + cC \longrightarrow products}$$

assume that the rate law is third order overall:

$$\text{rate} = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = k_{\mathrm{f}}[\mathrm{A}][\mathrm{B}][\mathrm{C}]$$

Integrate the rate law for the case of a stoichiometric mixture, such that

$$[\mathrm{A}] : [\mathrm{B}] : [\mathrm{C}] = a : b : c$$

11.23 For the reaction of the previous problem, integrate the rate law for the case of a nonstoichiometric mixture, using the method of partial fractions.

11.24 For the hypothetical reaction

$$\mathrm{A + 2B + 2C \longrightarrow products}$$

assume that the following initial-rate data were obtained:

Run	$[\mathrm{A}]_0/\mathrm{mol\,L^{-1}}$	$[\mathrm{B}]_0/\mathrm{mol\,L^{-1}}$	$[\mathrm{C}]_0/\mathrm{mol\,L^{-1}}$	$-d[\mathrm{A}]/dt/$ $\mathrm{mol\,L^{-1}\,min^{-1}}$
1	0.635	0.985	0.985	1.23×10^{-5}
2	0.635	0.985	0.635	7.93×10^{-6}
3	0.635	0.438	0.635	1.57×10^{-6}
4	0.438	0.438	0.635	1.08×10^{-6}

Find the order with respect to each reactant and find the value of the rate constant.

11.25 Methyl acetate was hydrolyzed using HC1 as a catalyst. The reaction is monitored by titrating aliquots of the reaction solution with base.

Time/s	(Volume of base − volume of base at end of reaction)/mL
339	13.47
1242	12.01
2745	10.11
4546	8.00

Find the pseudo order of the reaction, the apparent rate constant, and the volume of base that would have been required at $t = 0$. Remember that the apparent rate constant depends on the concentration of the catalyst.

11.26 The reaction

$$2\mathrm{H_2O_2} \longrightarrow 2\mathrm{H_2O} + \mathrm{O_2}$$

is catalyzed by iodide ions. Since the iodide ions are not consumed, we can determine the order with respect to $\mathrm{H_2O_2}$ in the same way as for a reaction with a single reactant. The following data were obtained for the decomposition of hydrogen peroxide in 0.02 mol $\mathrm{L^{-1}}$ KI at 25°C:

Time/minutes	Volume of $\mathrm{O_2}$ evolved/mL
0	0
5.00	7.50
10.00	14.00
25.00	28.80
45.00	41.20
65.00	48.30
∞	57.90

a. Determine the order with respect to $\mathrm{H_2O_2}$ and find the value of the apparent rate constant at this temperature. Assume that the reverse reaction can be neglected.

b. Find the volume of $\mathrm{O_2}$ evolved at a time of 35.00 s.

11.27 The decomposition of benzenediazonium chloride in water is given by the reaction equation

$$\mathrm{C_6H_5N_2^+ + 2H_2O \longrightarrow C_6H_5OH + N_2 + H_3O^+}$$

Since the concentration of water is nearly fixed, we can determine the pseudo order with respect to the diazonium ion as with a reaction having a single reactant.

Moelwyn-Hughes and Johnson followed the reaction at 40°C by monitoring the pressure of the nitrogen evolved by the reaction. The following data were taken, with the pressure in arbitrary units:

Time/s	$P_\infty - P$	Time/s	$P_\infty - P$
0	22.62	900	15.49
60	22.08	1200	13.62
120	21.55	1800	10.54
240	20.47	2400	8.15
360	19.45	3000	6.34
480	18.48	3600	4.88
600	17.60	4800	2.98

a. Determine the pseudo order with respect to the diazonium ion and find the value of the apparent rate constant for this temperature.

b. Find the pressure of the evolved nitrogen gas at 1500 s.

11.4 Inclusion of a Reverse Reaction. Chemical Equilibrium

If the reverse reaction cannot be neglected we must extend our previous discussion. We consider the simplest case, an isomerization reaction that is first order in both directions:

$$\mathrm{A} \underset{k_{\mathrm{r}}}{\overset{k_{\mathrm{f}}}{\rightleftharpoons}} \mathrm{B} \tag{11.4-1}$$

We denote the rate constant for the forward reaction by k_{f} and the rate constant for the reverse reaction by k_{r}. The observable rate of the reaction is a *net rate* given by the difference between the forward rate and the reverse rate:

$$r_{\mathrm{net}} = -\frac{d[\mathrm{A}]}{dt} = k_{\mathrm{f}}[\mathrm{A}] - k_{\mathrm{r}}[\mathrm{B}] \tag{11.4-2}$$

At equilibrium,

$$r_{\mathrm{net,eq}} = k_{\mathrm{f}}[\mathrm{A}]_{\mathrm{eq}} - k_{\mathrm{r}}[\mathrm{B}]_{\mathrm{eq}} = 0 \tag{11.4-3}$$

If we can ignore activity coefficients, the equilibrium constant for this reaction is

$$\boxed{K = \frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{k_{\mathrm{f}}}{k_{\mathrm{r}}}} \tag{11.4-4}$$

A large value for the equilibrium constant means that the rate constant for the forward reaction is large compared with the rate constant for the reverse reaction. A small value means that the rate constant for the forward reaction is small compared with the rate constant for the reverse reaction. Equation (11.4-4) can apply to a more general case if orders are equal to stoichiometric coefficients, as shown in the following exercise:

Exercise 11.16

For the reaction

$$a\mathrm{A} + b\mathrm{B} \underset{k_{\mathrm{r}}}{\overset{k_{\mathrm{f}}}{\rightleftharpoons}} d\mathrm{D} + f\mathrm{F} \tag{11.4-5}$$

assume that the order with respect to each substance is equal to its stoichiometric coefficient:

$$r_{\mathrm{f}} = k_{\mathrm{f}}[\mathrm{A}]^a[\mathrm{B}]^b \quad \text{and} \quad r_{\mathrm{r}} = k_{\mathrm{r}}[D]^d[F]^{\mathrm{f}} \tag{11.4-6}$$

Show that

$$K = \frac{k_{\mathrm{f}}}{k_{\mathrm{r}}} \tag{11.4-7}$$

We subtract Eq. (11.4-3) for the equilibrium case from Eq. (11.4-2) to obtain

$$-\frac{d[\mathrm{A}]}{dt} = k_{\mathrm{f}}([\mathrm{A}] - [\mathrm{A}]_{\mathrm{eq}}) - k_{\mathrm{r}}([\mathrm{B}] - [\mathrm{B}]_{\mathrm{eq}}) \tag{11.4-8}$$

We can express [B] in terms of [A]. Assume that initially only substance A is present so that $[A]_0 \neq 0$ and $[\mathrm{B}]_0 = 0$:

$$[\mathrm{B}] = [\mathrm{A}]_0 - [\mathrm{A}] \quad \text{and} \quad [\mathrm{B}]_{\mathrm{eq}} = [\mathrm{A}]_0 - [\mathrm{A}]_{\mathrm{eq}}$$

so that

$$[\mathrm{B}] - [\mathrm{B}]_{\mathrm{eq}} = [\mathrm{A}]_0 - [\mathrm{A}] - ([\mathrm{A}]_0 - [\mathrm{A}]_{\mathrm{eq}}) = -[\mathrm{A}] + [\mathrm{A}]_{\mathrm{eq}} \tag{11.4-9}$$

When this relation is substituted into Eq. (11.4-8), we obtain

$$-\frac{d[\mathrm{A}]}{dt} = (k_{\mathrm{f}} + k_{\mathrm{r}})([\mathrm{A}] - [\mathrm{A}]_{\mathrm{eq}}) \tag{11.4-10a}$$

Since $[\mathrm{A}]_{\mathrm{eq}}$ is a constant for any particular initial condition, we can replace $d[\mathrm{A}]/dt$ by $d([\mathrm{A}] - [\mathrm{A}]_{\mathrm{eq}})/dt$.

$$-\frac{d\left([\mathrm{A}] - [\mathrm{A}]_{\mathrm{eq}}\right)}{dt} = (k_{\mathrm{f}} + k_{\mathrm{r}})([\mathrm{A}] - [\mathrm{A}]_{\mathrm{eq}}) \tag{11.4-10b}$$

Equation (11.4-10b) is the same as Eq. (11.2-2) except for the symbols used, and the solution is obtained by transcribing Eq. (11.2-5) with appropriate changes in symbols:

$$[\mathrm{A}]_{t'} - [\mathrm{A}]_{\mathrm{eq}} = ([\mathrm{A}]_0 - [\mathrm{A}]_{\mathrm{eq}})e^{-(k_{\mathrm{f}}+k_{\mathrm{r}})t'} \tag{11.4-11}$$

The difference $[\mathrm{A}] - [\mathrm{A}]_{\mathrm{eq}}$ decays exponentially, as did [A] in the case of Figure 11.2.

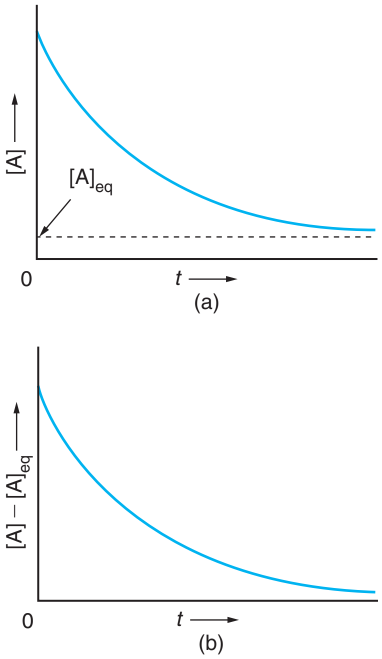

Figure 11.5 Concentration of the Reactant in a Hypothetical Reaction with Forward and Reverse Reactions. (a) [A] as a function of time. (b) $[\mathrm{A}] - [\mathrm{A}]_{\mathrm{eq}}$ as a function of time.

Exercise 11.17

Carry out the separation of variables to obtain Eq. (11.4-11).

Figure 11.5 shows the concentration of a hypothetical reactant as a function of time.

We define the half-life of the reversible reaction to be the time required for $[\mathrm{A}] - [\mathrm{A}]_{\mathrm{eq}}$ to drop to half of its initial value. We find that

$$t_{1/2} = \frac{\ln(2)}{k_{\mathrm{f}} + k_{\mathrm{r}}} \tag{11.4-12}$$

Exercise 11.18

Verify Eq. (11.4-12).

We define the *relaxation time* τ as the time required for $[\mathrm{A}] - [\mathrm{A}]_{\mathrm{eq}}$ to drop to $1/e$ of its original value:

$$\tau = \frac{1}{k_{\mathrm{f}} + k_{\mathrm{r}}} \tag{11.4-13}$$

A large value of the reverse rate constant is as effective in giving a rapid relaxation to equilibrium as is a large value of the forward rate constant, even if there is no product initially present.

EXAMPLE 11.11

For a hypothetical isomerization that is first order in both directions with $k_f = 17.7\,\text{min}^{-1}$ and $k_r = 32.2\,\text{min}^{-1}$, find the equilibrium composition if the initial concentration of A is equal to $0.175\,\text{mol L}^{-1}$ and the initial concentration of B is equal to zero. Find the half-life and the relaxation time.

Solution

$$K = \frac{k_f}{k_r} = \frac{17.7\ \text{min}^{-1}}{32.2\ \text{min}^{-1}} = 0.528$$

We let

$$x = \frac{[\text{B}]_{eq}}{1\ \text{mol L}^{-1}} = \frac{[\text{A}]_0 - [\text{A}]_{eq}}{1\ \text{mol L}^{-1}}$$

$$0.528 = \frac{x}{0.150 - x}$$

$$x = (0.528)(0.150 - x) = 0.0792 - 0.528x$$

$$x = \frac{0.0792}{1.528} = 0.0518$$

$$[\text{B}]_{eq} = 0.0518\ \text{mol L}^{-1}$$

$$[\text{A}]_{eq} = 0.0982\ \text{mol L}^{-1}$$

$$t_{1/2} = \frac{\ln(2)}{k_f + k_r} = \frac{\ln(2)}{17.7\ \text{min}^{-1} + 32.2\ \text{min}^{-1}} = 0.0139\ \text{min}$$

$$\tau = \frac{1}{k_f + k_r} = \frac{1}{17.7\ \text{min}^{-1} + 32.2\ \text{min}^{-1}} = 0.0200\ \text{min}$$

Exercise 11.19

Find the composition for the reaction of the previous example at time $t = 0.100\,\text{min}$.

PROBLEMS

Section 11.4: Inclusion of a Reverse Reaction. Chemical Equilibrium

11.28 Assume that the reaction

$$\text{A} \rightleftharpoons \text{B}$$

is first order in both directions. The initial concentration of A is $1.000\,\text{mol L}^{-1}$ and that of B is 0.

a. Construct a graph of [A] and [B] as a function of time for the case that $k_f = 10.0\ \text{s}^{-1}$ and $k_r = 1.00\ \text{s}^{-1}$.

b. Repeat part a for $k_f = k_r = 10.0\,\text{s}^{-1}$.

c. Calculate the half-life of the reaction for both part a and part b.

11.29 Calculate the concentration of each substance after a reaction time of 0.35 s for the reaction of part a of the previous problem.

11.30 Assume that the reaction

$$\text{A} \rightleftharpoons \text{B}$$

is first order in both directions.

a. Integrate the rate differential equation for the case that the initial concentrations of both A and B are nonzero.

b. Construct a graph of the concentrations of A and B as a function of time for the case that $[\mathrm{A}] = [\mathrm{B}] = 1.00\,\mathrm{mol\,L^{-1}}$, $k_\mathrm{f} = 10.0\ \mathrm{s^{-1}}$ and $k_\mathrm{r} = 1.00\,\mathrm{s^{-1}}$.

c. For the reaction of part b, find each concentration after a reaction time of 0.35 s.

11.31 Consider the reaction

$$2\mathrm{A} \rightleftharpoons \mathrm{B} + \mathrm{C}$$

The forward reaction is second order, and the reverse reaction is first order with respect to B and first order with respect to C. Write a computer program using Euler's method to integrate the rate differential equations for the case that the initial concentration of A is nonzero and those of B and C are zero.[4]

11.5 A Simple Reaction Mechanism: Two Consecutive Steps

Almost every chemical reaction takes place through a set of steps, called the *reaction mechanism*. We now consider the simplest possible mechanism, a two-step mechanism in which the product of the first step is the reactant of the second step. We assume that both steps are first order and that the reverse reactions are negligible:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{F} \tag{11.5-1a}$$

where k_1 is the rate constant for the first step and k_2 is the rate constant for the second step. The substance B is called a *reactive intermediate*. We will usually number the steps of a mechanism:

$$(1) \quad \mathrm{A} \longrightarrow \mathrm{B} \tag{11.5-1b}$$

$$(2) \quad \mathrm{B} \longrightarrow \mathrm{F} \tag{11.5-1c}$$

We assign a subscript to the rate constant equal to the number of the step.

Since there is no reverse reaction, step (1) has the same rate law as Eq. (11.2-2),

$$\frac{d[\mathrm{A}]}{dt} = -k_1 dt \tag{11.5-2}$$

Since B is produced by the first step and consumed by the second step,

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_2[\mathrm{B}] \tag{11.5-3}$$

Equations (11.5-2) and (11.5-3) are a set of simultaneous differential equations. The solution to the first equation has already been obtained:

$$[\mathrm{A}]_t = [\mathrm{A}]_0 e^{-k_1 t} \tag{11.5-4}$$

This solution can be substituted into Eq. (11.5-3) to obtain a single differential equation for [B]:

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}]_0 e^{-k_1 t} - k_2[\mathrm{B}] \tag{11.5-5}$$

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[4] R. G. Mortimer, *Mathematics for Physical Chemistry*, 3rd ed., Elsevier/Academic Press, San Diego, CA, 2005, p. 260. The method is also found in books on numerical analysis and in some calculus textbooks.

The solution of this equation is carried out in Appendix B for the case that no B or F is present at time $t = 0$. The solution is

$$[\mathrm{B}]_t = \frac{k_1[\mathrm{A}]_0}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \tag{11.5-6}$$

If $k_1 = k_2$, the solution in Eq. (11.5-6) cannot be used. See Problem 11.34 for the solution in this case.

Exercise 11.20

Substitute the function of Eq. (11.5-6) into the original differential equation of Eq. (11.5-5) and show that it satisfies this equation.

The concentration of F is obtained from

$$[\mathrm{F}] = [\mathrm{A}]_0 - [\mathrm{A}] - [\mathrm{B}] \tag{11.5-7}$$

Figure 11.6a shows the concentrations of all three substances for the case that $k_1 = 0.100\ \mathrm{s}^{-1}$ and $k_2 = 0.500\ \mathrm{s}^{-1}$, and Figure 11.6b shows the concentrations for the case

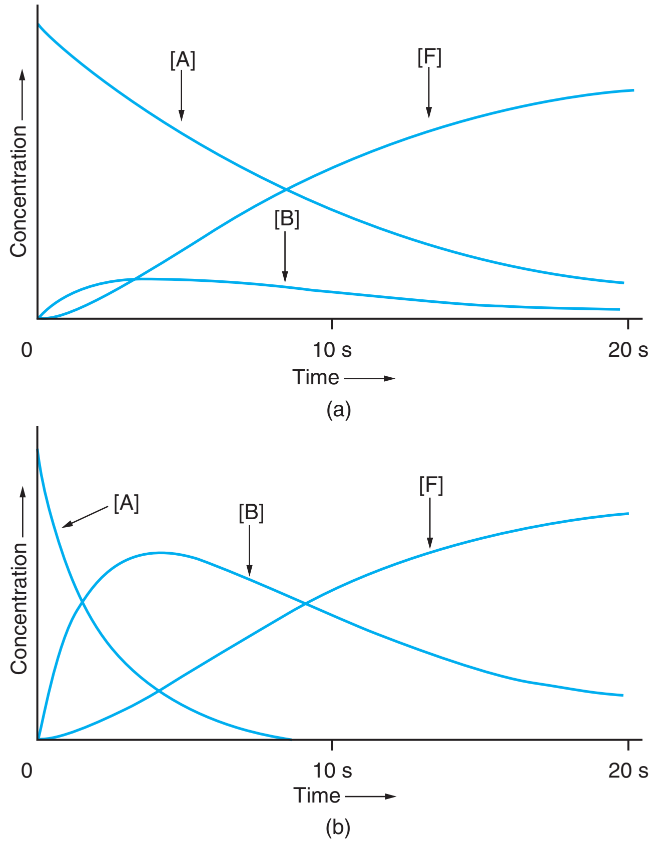

Figure 11.6 The Concentrations of Substances A, B, and F for Consecutive Reactions. (a) The case that $k_1 = 0.10\ \mathrm{s}^{-1}$ and that $k_2 = 0.50\ \mathrm{s}^{-1}$. (b) The case that $k_1 = 0.50\ \mathrm{s}^{-1}$ and that $k_2 = 0.10\ \mathrm{s}^{-1}$.

that $k_1 = 0.500\,\mathrm{s}^{-1}$ and $k_2 = 0.100\,\mathrm{s}^{-1}$. If $k_1 < k_2$, the amount of B remains relatively small, but if $k_1 > k_2$, the amount of B becomes fairly large before dropping eventually to zero. Since the reverse reactions are assumed to be negligible, the final state corresponds to complete conversion to the product F in both cases.

If steps 1 and 2 have reverse reactions that cannot be neglected, the mechanism becomes

$$(1)\quad \mathrm{A} \rightleftharpoons \mathrm{B} \tag{11.5-8a}$$

$$(2)\quad \mathrm{B} \rightleftharpoons \mathrm{F} \tag{11.5-8b}$$

the differential equations giving the rates are

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_1'[\mathrm{B}] \tag{11.5-9a}$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] + k_1'[\mathrm{B}] - k_2[\mathrm{B}] + k_2'[\mathrm{F}] \tag{11.5-9b}$$

$$\frac{d[\mathrm{F}]}{dt} = k_2[\mathrm{B}] - k_2'[\mathrm{F}] \tag{11.5-9c}$$

where we use a prime ($'$) to label the reverse rate constants. This set of simultaneous differential equations can be solved, but we do not present the solution.[5]

Both steps are at equilibrium when the entire reaction is at equilibrium:

$$\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{k_1}{k_1'} = K_1 \tag{11.5-10}$$

and

$$\frac{[\mathrm{F}]_{\mathrm{eq}}}{[\mathrm{B}]_{\mathrm{eq}}} = \frac{k_2}{k_2'} = K_2 \tag{11.5-11}$$

The equilibrium constant K for the overall reaction is equal to

$$K = \frac{[\mathrm{F}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{[\mathrm{F}]_{\mathrm{eq}}}{[\mathrm{B}]_{\mathrm{eq}}}\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = K_1K_2 = \frac{k_1}{k_1'}\frac{k_2}{k_2'} \tag{11.5-12}$$

Relationships analogous to that shown in Eq. (11.5-12) are valid for any sequence of steps: *If the orders in all steps are equal to the stoichiometric coefficients, the equilibrium constant is equal to the product of all of the rate constants for the forward reactions divided by the product of all of the rate constants for the reverse reactions if activity coefficients can be ignored.*

Exercise 11.21

Consider the sequence of reactions:

$$(1)\quad a\mathrm{A} + b\mathrm{B} \rightleftharpoons c\mathrm{C}$$

$$(2)\quad \mathrm{C} + d\mathrm{D} \rightleftharpoons f\mathrm{F} + g\mathrm{G}$$

Assume that the orders are equal to the stoichiometric coefficients and show that the above assertion is correct in this case.

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[5] T. M. Lowry and W. T. John, *J. Chem. Soc.*, **97**, 2634 (1910).

PROBLEMS

Section 11.5: A Simple Reaction Mechanism: Two Consecutive Steps

11.32 For the consecutive first-order reaction without reverse reactions, assume that $k_1 = 0.01000\ \mathrm{s^{-1}}$ and $k_2 = 0.1000\ \mathrm{s^{-1}}$. If $[\mathrm{A}]_0 = 0.100\ \mathrm{mo\ L^{-1}}$, find the value of each concentration at $t = 10.00$ s and at $t = 100.0$ s.

11.33 **a.** For the consecutive first-order reactions without reverse reactions, make a graph of [A], [B], and [F] in the case that $k_1 = 0.0100\ \mathrm{s^{-1}}$ and $k_2 = 0.100\ \mathrm{s^{-1}}$. Assume that $[\mathrm{A}]_0 = 1.00\ \mathrm{mol\ L^{-1}}$ and that B and F are initially absent.

b. For the values of part a, make a graph of $d[\mathrm{A}]/dt$, $d[\mathrm{B}]/dt$, and $d\,[\mathrm{F}]/dt$.

11.34 **a.** For the consecutive first-order reactions without reverse reactions $\mathrm{A} \longrightarrow \mathrm{B} \longrightarrow \mathrm{F}$, obtain the expression for [B] in the case that $k_1 = k_2$, assuming that no B or F is present at the beginning of the reaction. Proceed by taking the limit of the expression of Eq. (11.5-6) as $k_1 \longrightarrow k_2$, using l'Hôpital's rule.[6]

b. Construct a graph showing [A], [B], and [F] as functions of time for the case that $k_1 = k_2 = 0.100\ \mathrm{s^{-1}}$ and $[\mathrm{A}]_0 = 1.00\ \mathrm{mol\ L^{-1}}$.

c. Draw a graph showing [A], [B], and [F] as functions of time for the case that $k_1 = 0.099\ \mathrm{s^{-1}}$ and $k_2 = 0.101\ \mathrm{s^{-1}}$ and $[\mathrm{A}]_0 = 1.00\ \mathrm{mol\ L^{-1}}$. Compare it with your graph from part b.

11.35 For the case of two consecutive reactions in which the reverse reaction of the first reaction cannot be neglected, sketch a rough graph showing the three concentrations as functions of time. Compare your graph with those in Figure 11.6.

11.6 Competing Reactions

In many syntheses a side reaction consumes part of the reactants but gives undesired products. We consider the simplest case: that two competing reactions are first order with negligible reverse reaction.

$$\mathrm{A} \xrightarrow{k_1} \mathrm{F} \tag{11.6-1a}$$

$$\mathrm{A} \xrightarrow{k_2} \mathrm{G} \tag{11.6-1b}$$

The rates of the two reactions combine to give

$$-\frac{d[\mathrm{A}]}{dt} = (k_1 + k_2)[\mathrm{A}] \tag{11.6-2}$$

This equation is the same as Eq. (11.2-2) except that k_f is replaced by $k_1 + k_2$, and its solution is

$$[\mathrm{A}]_t = [\mathrm{A}]_0 e^{-(k_1+k_2)t} \tag{11.6-3}$$

The half-life for the disappearance of A is

$$t_{1/2} = \frac{\ln(2)}{k_1 + k_2} \tag{11.6-4}$$

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[6] See Robert G. Mortimer, *Mathematics for Physical Chemistry*, 3rd ed., Elsevier/Academic Press, San Diego, CA, 2005, p. 113ff, or any calculus textbook.

We have

$$\frac{d[\mathrm{F}]}{dt} = k_1[\mathrm{A}] = k_1[\mathrm{A}]_0 e^{-(k_1+k_2)t} \tag{11.6-5}$$

The right-hand side of this equation does not contain [F], so we can multiply by dt and integrate to obtain

$$[\mathrm{F}]_{t'} - [\mathrm{F}]_0 = [\mathrm{F}]_{t'} = \frac{-k_1[\mathrm{A}]_0}{k_1 + k_2}(e^{-(k_1+k_2)t'} - 1) \tag{11.6-6}$$

where we assume that $[\mathrm{F}]_0 = 0$. A similar treatment for [G] gives the same result except that k_1 is replaced by k_2 in the numerator:

$$[\mathrm{G}]_{t'} - [\mathrm{G}]_0 = [\mathrm{G}]_{t'} = \frac{-k_2[\mathrm{A}]_0}{k_1 + k_2}(e^{-(k_1+k_2)t'} - 1) \tag{11.6-7}$$

where we also assume that $[\mathrm{G}]_0 = 0$. The ratio [F]/[G] has the same value at any time:

$$\frac{[\mathrm{F}]}{[\mathrm{G}]} = \frac{k_1}{k_2} \quad \text{(reverse reactions negligible)} \tag{11.6-8}$$

Exercise 11.22

For the reactions shown in Eq. (11.6-1) assume that $[\mathrm{A}]_0 = 0.500\ \mathrm{mol\ L^{-1}}$, that $k_1 = 0.100\ \mathrm{s^{-1}}$ and that $k_2 = 0.0100\ \mathrm{s^{-1}}$. Construct a graph showing [A], [F], and [G] for t ranging from 0 to 20 s.

If the reverse reactions cannot be neglected, the situation can be different. If the system comes to equilibrium,

$$\frac{[\mathrm{F}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{k_1}{k_1'} = K_1 \tag{11.6-9a}$$

$$\frac{[\mathrm{G}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{k_2}{k_2'} = K_2 \tag{11.6-9b}$$

so that

$$\frac{[\mathrm{F}]_{\mathrm{eq}}}{[\mathrm{G}]_{\mathrm{eq}}} = \frac{k_1}{k_1'}\frac{k_2'}{k_2} = \frac{k_1}{k_2}\frac{k_2'}{k_1'} = \frac{K_1}{K_2} \quad \text{(at equilibrium)} \tag{11.6-10}$$

Depending on the values of the four rate constants, this ratio might differ significantly from the ratio in Eq. (11.6-8). If F is a desired product and G is an undesired product, the ratio of [F] to [G] might be optimized by allowing the system to come to equilibrium (using *thermodynamic control*) or by stopping the reaction before it comes to equilibrium (using *kinetic control*).

PROBLEMS

Section 11.6: Competing Reactions

11.36 Consider the competing reactions with significant reverse reactions:

$$(1)\ \mathrm{A} \rightleftharpoons \mathrm{F}$$
$$(2)\ \mathrm{A} \rightleftharpoons \mathrm{G}$$

Assume that all of the reactions are first order.

a. Write a computer program using Euler's method to integrate the rate differential equations for the case that the initial concentration of A is nonzero and those of F and G are zero.

b. Run the program for several sets of rate constants.

11.7 The Experimental Study of Fast Reactions

The "classical" method of studying reaction rates is to mix the reactants and then to determine the concentration of some reactant or product as a function of time. This method is clearly inadequate if the reaction time is comparable to or shorter than the time required to mix the reactants.

Flow Techniques

There are two common flow methods that can be used to speed up the mixing of liquids or gases. In the *continuous-flow method*, two fluids are forcibly pumped into a chamber where they are rapidly mixed. The newly mixed fluid passes into a transparent tube of uniform diameter. The flow rates into the mixing chamber are kept constant so that the distance along the tube is proportional to the elapsed time after mixing. The concentration of a reactant or product is determined spectrophotometrically as a function of position along the tube, using the tube as a spectrophotometer cell.

In the *stopped-flow method*, two fluids are forced into a mixing chamber as in the continuous-flow method. After a steady state is attained the flow of solutions into the chamber is suddenly stopped and the concentration of a product or reactant is determined spectrophotometrically as a function of time as the system approaches equilibrium. The mixing chamber is used as a spectrophotometer cell. Figure 11.7 schematically shows a stopped-flow apparatus. Flow systems have been designed that can mix two liquids in a tenth of a millisecond, so that reactions with half-lives ranging from 1 millisecond to 1 second can be studied by either of the two flow methods. Spectrophotometers can be built that record concentrations very quickly, so the response of the spectrophotometer does not limit this method.

Relaxation Techniques

Relaxation techniques do not rely on mixing, but use the fact that equilibrium compositions can depend on temperature and pressure. The experiment begins with a system at equilibrium. The temperature or the pressure of the system is suddenly changed so that it is no longer at equilibrium and the relaxation of the system to its new equilibrium state is then monitored.

The Shock-Tube Method

In the *shock-tube method* a reaction vessel is constructed with two chambers separated by a diaphragm that can be ruptured suddenly. On one side is a mixture of gaseous

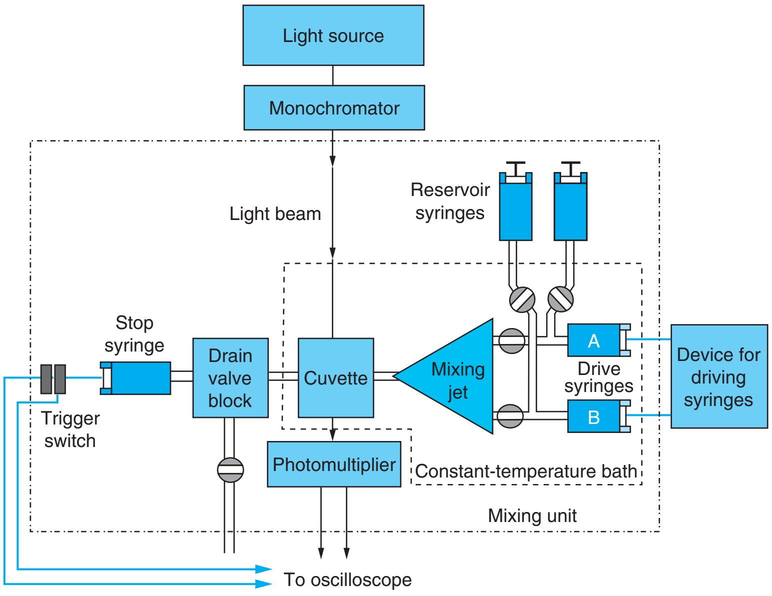

Figure 11.7 A Stopped-Flow Apparatus (Schematic).

reactants and products at equilibrium at a fairly low pressure. On the other side is a "driver" gas at a higher pressure. When the diaphragm is ruptured the driver gas moves quickly into the low-pressure chamber. Collisions of the driver gas molecules with the other molecules produce a shock wave that propagates through the low-pressure gas and heats it. The reacting system will then relax to the equilibrium state for the new temperature. The concentration of a reactant or product is monitored spectrophotometrically during this relaxation. This method is applied to reactions that have half-lives in the range from 1 millisecond to 1 microsecond, but it is limited to gas-phase reactions.

The Flash Photolysis Method

In the *flash photolysis method*[7] a brief burst of light irradiates the system. If this light is absorbed it can quickly change the temperature of the system and possibly its composition. The concentration of a reactant or product is measured spectrophotometrically as a function of time as the system relaxes to its new equilibrium. Figure 11.8 shows schematically an apparatus for flash photolysis. Flash photolysis differs from the shock-wave technique in that the radiation can produce new species as well as change the temperature of the system.

The Temperature-Jump and Pressure-Jump Methods

In the *temperature-jump* ("T-jump") and the *pressure-jump* ("P-jump") methods a gaseous or liquid system is subjected to a rapid heating or a rapid change in pressure. A heating pulse can be delivered by a burst of microwave radiation or by the passage of a brief pulse of electric current if the system is electrically conductive. A rapid change

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[7] See G. Porter, *J. Chem. Soc., Faraday Trans.*, 2, **82**, 2445 (1986) for a historical survey.

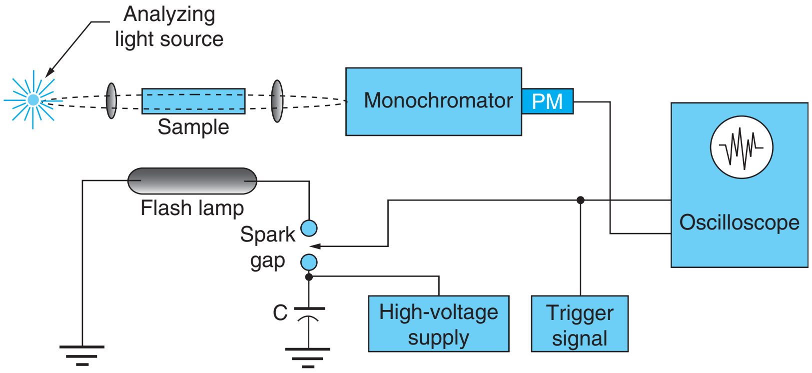

Figure 11.8 **A Flash Photolysis Apparatus (Schematic).**

in pressure can be achieved by rupturing a diaphragm. After the temperature or pressure change the system relaxes to its new equilibrium state. The concentration of a reactant or product is monitored spectroscopically or by some other rapid means.

Consider the reaction:

$$(1) \quad A + B \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} C \tag{11.7-1}$$

Assume that this reaction is second order overall in the forward direction and first order in the reverse direction. A temperature jump is suddenly imposed on the system at time $t = 0$. Figure 11.9 shows schematically the concentrations of A, B, and C before and after a T-jump. The initial concentration $[A]_0$ was the equilibrium concentration at the temperature prior to the temperature jump, but because the equilibrium constant of the reaction depends on temperature, $[A]_0$ is not equal to the new equilibrium concentration, denoted by $[A]_{eq}$. The same is true of [B] and [C]. We now let

$$\Delta[A] = [A] - [A]_{eq} \tag{11.7-2a}$$

$$\Delta[B] = [B] - [B]_{eq} \tag{11.7-2b}$$

$$\Delta[C] = [C] - [C]_{eq} \tag{11.7-2c}$$

From the stoichiometry of the reaction shown in Eq. (11.7-1),

$$\Delta[A] = \Delta[B] = -\Delta[C] \tag{11.7-3}$$

so that we can express the concentrations in terms of Δ[C]:

$$[C] = [C]_{eq} + \Delta[C] \tag{11.7-4a}$$

$$[A] = [A]_{eq} - \Delta[C] \tag{11.7-4b}$$

$$[B] = [B]_{eq} - \Delta[C] \tag{11.7-4c}$$

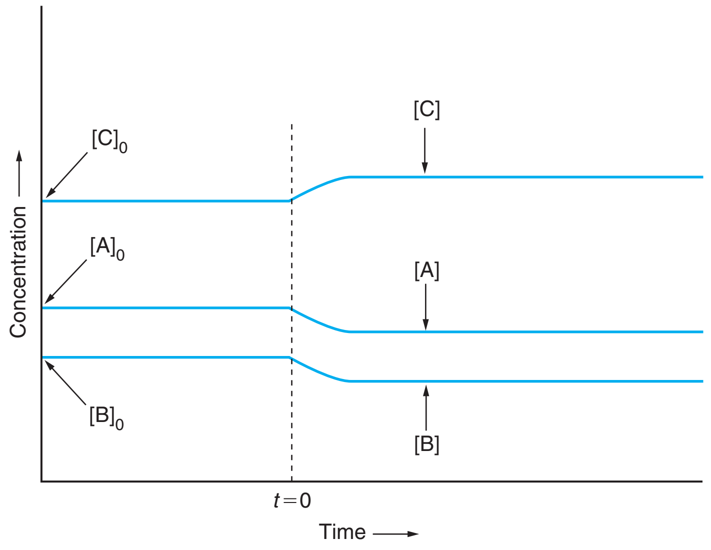

Figure 11.9 The Behavior of a System in a T-Jump Experiment.

The differential equation for the net rate is

$$\text{rate} = \frac{d\Delta[\mathrm{C}]}{dt} = k_1[\mathrm{A}][\mathrm{B}] - k_1'[\mathrm{C}] \tag{11.7-5}$$

Using Eq. (11.7-4),

$$\begin{aligned}\frac{d\Delta[\mathrm{C}]}{dt} &= k_1([\mathrm{A}]_{\mathrm{eq}} - \Delta[\mathrm{C}])([\mathrm{B}]_{\mathrm{eq}} - \Delta[\mathrm{C}]) - k_1'([\mathrm{C}]_{\mathrm{eq}} + \Delta\,[\mathrm{C}])\\ &= k_1[\mathrm{A}]_{\mathrm{eq}}[\mathrm{B}]_{\mathrm{eq}} - k_1'[\mathrm{C}]_{\mathrm{eq}} - k_1([\mathrm{A}]_{\mathrm{eq}} + [\mathrm{B}]_{\mathrm{eq}})\Delta[\mathrm{C}]\\ &\quad - k_1'\Delta[\mathrm{C}] + k_1(\Delta[\mathrm{C}])^2\end{aligned} \tag{11.7-6}$$

The first two terms on the right-hand side of the final version of Eq. (11.7-6) cancel because the first term is the forward rate at equilibrium and the second term is the reverse rate at equilibrium. We assume that $|\Delta[\mathrm{C}]|$ is small, since it is not possible to change the equilibrium composition very much with a temperature jump. We neglect the final term on the right-hand side since if $|\Delta[\mathrm{C}]|$ is small $(\Delta[\mathrm{C}])^2$ will be even smaller.

$$\frac{d\Delta[\mathrm{C}]}{dt} = -(k_1([\mathrm{A}]_{\mathrm{eq}} + [\mathrm{B}]_{\mathrm{eq}}) + k_1')\Delta[\mathrm{C}] \tag{11.7-7}$$

Equation (11.7-7) is exactly like Eq. (11.2-2) except for the symbols used, so we can transcribe its solution and write

$$\Delta[\mathrm{C}] = \Delta[\mathrm{C}]_0 e^{-t/\tau} \tag{11.7-8}$$

where

$$\frac{1}{\tau} = k_1([\mathrm{A}]_{\mathrm{eq}} + [\mathrm{B}]_{\mathrm{eq}}) + k_1' \tag{11.7-9}$$

The quantity τ is the *relaxation time* for $\Delta[\mathrm{C}]$. Although the reaction is not first order in both directions, $\Delta[\mathrm{C}]$ decays exponentially. This is because we linearized Eq. (11.7-6) by neglecting the $(\Delta[\mathrm{C}])^2$ term.

Exercise 11.23

a. Verify the steps of algebra leading to Eq. (11.7-7).
b. Verify that Eq. (11.7-8), with Eq. (11.7-9), is a solution to Eq. (11.7-7).
c. Write the expressions for Δ[A] and Δ[B].

If we assume that hydrogen ions in water primarily occur as hydronium ions, the reaction of hydrogen ions and hydroxide ions can be written

$$\mathrm{H_3O^+ + OH^- \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} 2H_2O} \tag{11.7-10}$$

which has the general form

$$\mathrm{A + B \underset{k_1'}{\overset{k_1}{\rightleftharpoons}} 2C} \tag{11.7-11}$$

Assume that the reaction is second order in both directions. We write

$$[\mathrm{C}] = [\mathrm{C}]_{\mathrm{eq}} + \Delta[\mathrm{C}] \tag{11.7-12a}$$

$$[\mathrm{A}] = [\mathrm{A}]_{\mathrm{eq}} - \frac{1}{2}\Delta[\mathrm{C}] \tag{11.7-12b}$$

$$[\mathrm{B}] = [\mathrm{B}]_{\mathrm{eq}} - \frac{1}{2}\Delta[\mathrm{C}] \tag{11.7-12c}$$

When Eqs. (11.7-12) are substituted into the differential equation for the rate of the reaction and the necessary steps of algebra are carried out with neglect of terms proportional to $(\Delta[\mathrm{C}])^2$, we obtain

$$\Delta[\mathrm{C}] = \Delta[\mathrm{C}]_0 e^{-t/\tau} \tag{11.7-13}$$

where

$$\frac{1}{\tau} = k_1 \frac{[\mathrm{A}]_{\mathrm{eq}} + [\mathrm{B}]_{\mathrm{eq}}}{2} + 2k_1'[\mathrm{C}]_{\mathrm{eq}} \tag{11.7-14}$$

EXAMPLE 11.12

At 25°C, the forward rate constant of Eq. (11.7-10) is equal to $1.4 \times 10^{11}\ \mathrm{L\,mol^{-1}\,s^{-1}}$. At this temperature, the dissociation equilibrium constant K_w equals $1.008 \times 10^{-14}\ \mathrm{mol^2\,L^{-2}}$.

a. Using Eq. (11.5-3), find the value of k_1'.
b. For pure water, find the relaxation time if a T-jump experiment has a final temperature of 25°C.

Solution

a. We convert K_w, for which the $\mathrm{H_2O}$ activity is expressed in terms of the mole fraction, to the equilibrium constant for the reaction of Eq. (11.7-10) with all concentrations in terms of molarities:

$$K_1 = \frac{k_1}{k_1'} = \frac{[H_2O]^2}{[H^+][OH^-]} = \frac{(55.35\ \text{mol L}^{-1})^2}{1.008 \times 10^{-14}\ \text{mol}^2\ \text{L}^{-2}} = 3.039 \times 10^{17}$$

$$k_1' = \frac{k_1}{K_1} = \frac{1.4 \times 10^{11}\ \text{L mol}^{-1}\ \text{s}^{-1}}{3.039 \times 10^{17}} = 4.6 \times 10^{-7}\ \text{L mol}^{-1}\ \text{s}^{-1}$$

b. From Eq. (11.7-14):

$$\begin{aligned}\frac{1}{\tau} &= \frac{(1.4 \times 10^{11}\ \text{L mol}^{-1}\ \text{s}^{-1})(2 \times 1.004 \times 10^{-7}\ \text{mol L}^{-1})}{2} \\ &\quad + 2(4.6 \times 10^{-7}\ \text{L mol}^{-1}\ \text{s}^{-1})(55.35\ \text{mol L}^{-1}) \\ &= 1.4 \times 10^{4}\ \text{s}^{-1} \\ \tau &= 7.1 \times 10^{-5}\ \text{s}\end{aligned}$$

Similar expressions for the relaxation time can be derived for other rate laws.[a]

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[a] K. J. Laidler, *Chemical Kinetics*, 3rd ed., Harper and Row, New York, 1987, p. 38.

Exercise 11.24

a. Verify Eq. (11.7-14).

b. For the reaction equation

$$A + B \rightleftharpoons X + Y$$

assume second order in both directions, show that the relaxation time is given by

$$\frac{1}{\tau} = k_1([A]_{eq} + [B]_{eq}) + k_1'([X]_{eq} + [Y]_{eq}) \qquad (11.7\text{-}15)$$

We have discussed temperature-jump experiments. Pressure-jump experiments are analyzed in the same way, with sudden changes in pressure that produce partial pressures that deviate from equilibrium partial pressures at the new total pressure.

PROBLEMS

Section 11.7: The Experimental Study of Fast Reactions

11.37 Find the expression for the relaxation time for the reaction $A \rightleftharpoons C$ when the system is subjected to a small perturbation from equilibrium. Assume both the forward reaction and the reverse reaction to be second order.

11.38 **a.** Find the expression for the relaxation time for the reaction

$$A \rightleftharpoons 2X$$

when the system is subjected to a small perturbation from equilibrium. Assume the forward reaction to be first order and the reverse reaction to be second order.

b. Find the expression for the relaxation time for the reaction

$$2A \rightleftharpoons X$$

when the system is subjected to a small perturbation from equilibrium. Assume the forward reaction to be second order and the reverse reaction to be first order.

c. Find the expression for the relaxation time for the reaction

$$A \rightleftharpoons X$$

when the system is subjected to a small perturbation from equilibrium. Assume both the forward reaction and the reverse reaction to be first order.

11.39 Find the expression for the relaxation time for the reaction

$$A + B + C \rightleftharpoons X$$

when the system is subjected to a small perturbation from equilibrium. Assume the forward reaction to be third order overall, first order with respect to each reactant, and the reverse reaction to be first order.

11.40 For the reaction at 298 K

$$CH_3CO_2^- + H^+ \rightleftharpoons CH_3CO_2H$$

$k_f = 4.5 \times 10^{10}\ \mathrm{L\,mol^{-1}\,s^{-1}}$ and $k_r = 8.0 \times 10^5\ \mathrm{s^{-1}}$. A solution is made from 0.100 mol of acetic acid and enough water to make 1.000 L.

a. Find the value of the equilibrium constant for the reaction at 298 K, using the concentration description.

b. Find the equilibrium concentrations of all three solutes at 298 K.

c. Find the relaxation time if a small perturbation is imposed on the solution such that the final temperature is 298 K.

11.41 For the reaction at 298.15 K in aqueous solution

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

the equilibrium constant at 25.00°C is equal to 1.75×10^{-5}, and the reverse rate constant k' is equal to $4.0 \times 10^{11}\ \mathrm{L\,mol^{-1}\,s^{-1}}$.

a. Find the molalities of OH^- and NH_4^+ in a solution made from 0.0100 mol of NH_3 and 1.000 kg of water. Assume that all activity coefficients are equal to unity.

b. Find the value of the forward rate constant at this temperature.

c. If the solution is originally at 15°C and is suddenly brought to a temperature of 25.00°C, find the relaxation time for the reaction.

Summary of the Chapter

A rate law of the form

$$\text{rate} = k\,[A]^{\alpha}[B]^{\beta}$$

is said to have definite orders, with order α with respect to A and with order β with respect to B. The proportionality constant k is called the rate constant although it depends on temperature. We solved several such differential rate laws to obtain the integrated rate laws.

Some techniques for determination of the rate law involve comparison of the integrated rate equation with experimental data on the concentration of a reactant. The method of initial rates allows direct comparison of the differential rate law with the experimental data. In the method of isolation, the concentration of one reactant is made much smaller than the concentrations of the other reactants. During the reaction, the fractional changes in the larger concentrations are negligible, and the small concentration behaves like the concentration in a reaction with one reactant.

For a reversible reaction that is first order in each direction the difference between the concentration of the reactant and its equilibrium value relaxes exponentially, and it was found that the relaxation time and the half-life are both inversely proportional to the sum of the two rate constants.

A reaction mechanism consisting of two consecutive first-order reactions without reverse reactions was considered. It was found that the concentration of the reactive intermediate rose and then fell as the reaction proceeds.

Some techniques were presented for studying fast reactions that cannot be studied by classical experimental techniques. These techniques included continuous flow and stopped-flow techniques, which are rapid mixing methods, as well as relaxation techniques. The relaxation techniques included shock-tube methods, flash photolysis, and T-jump and P-jump methods. Equations were derived for the relaxation of a reaction after a small perturbation, giving an exponential relaxation for a variety of rate laws.

ADDITIONAL PROBLEMS

11.42 The reaction

$$\mathrm{NO} + \mathrm{H_2} \longrightarrow \mathrm{H_2O} + \frac{1}{2}\mathrm{N_2}$$

has been studied in the gas phase at 826°C by the method of initial rates. The initial rate was monitored by measuring the total pressure of the system, and the data were obtained:

$P(\mathrm{H_2})_{\mathrm{initial}}$/kPa	$P(\mathrm{NO})_{\mathrm{initial}}$/kPa	$-\frac{dP}{dt}$/kPa $\mathrm{s^{-1}}$
53.3	40.0	0.137
53.3	20.3	0.033
38.5	53.3	0.213
19.6	53.3	0.105

a. Find the order with respect to each reactant and find the value of the rate constant. Use the partial pressures in the same way as concentrations are used, since concentrations are proportional to partial pressures in an ideal gas mixture.

b. For $P(\mathrm{H_2})_{\mathrm{initial}} = 100$ kPa and $P(\mathrm{NO})_{\mathrm{initial}} = 100$ kPa, find the initial rate.

c. For the initial pressures of part b, find the pressure of each substance 1.00 s after the start of the reaction.

d. For $P(\mathrm{NO})_{\mathrm{initial}} = 200$ kPa and $P(\mathrm{H_2})_{\mathrm{initial}} =$ 5.00 kPa, find the time for half of the H_2 to react.

e. For $P(\mathrm{NO})_{\mathrm{initial}} = 5.00$ kPa and $P(\mathrm{H_2})_{\mathrm{initial}} =$ 200 kPa, find the time for half of the NO to react.

11.43 Label each of the following statements as either true or false. If a statement is true only under special circumstances, label it false.

a. The rate of a forward reaction can depend on the concentrations of substances other than the substances in the stoichiometric equation.

b. The order of a reaction with respect to a substance is not necessarily equal to the stoichiometric coefficient of that substance in the reaction equation.

c. The reverse reaction is unimportant during the first half-life of any chemical reaction.

d. The method of initial rates cannot be used in conjunction with the method of isolation.

e. At the equilibrium of a chemical reaction, the rate of the forward reaction and the rate of the reverse reaction cancel.

f. A rate constant is not a true constant, since it depends on temperature and pressure.

g. In the method of initial rates, one must worry about the effect of the reverse reaction.

h. In the case of two consecutive reactions without reverse reactions, the final state corresponds to zero concentration of the reactant and of the intermediate.

i. In the case of two consecutive reactions without reverse reactions, the concentration of the intermediate always remains small compared with the initial concentration of the reactant.

j. The linearization of the rate equation that is done in the study of the temperature-jump method is usually a good approximation, because the state immediately after the temperature jump does not deviate very much from the final equilibrium state.

k. First-order processes occur only in chemical processes.

l. All rate laws can be written in a form with definite orders.

12

Chemical Reaction Mechanisms I: Rate Laws and Mechanisms

PRINCIPAL FACTS AND IDEAS

1. Nearly every chemical reaction proceeds by a mechanism consisting of several steps.
2. An elementary step is a chemical process that cannot be broken down into simpler steps.
3. The molecularity of an elementary step is the number of atoms, molecules, ions, or radicals involved in the step.
4. For elementary processes, the overall order of the rate law equals the molecularity.
5. The temperature dependence of gas-phase reaction rates can be understood through collision theory.
6. An approximate rate law for a given mechanism can often be deduced by use of the rate-limiting step approximation or the steady-state approximation.
7. Chain reactions have mechanisms that involve reactive intermediates called chain carriers, which are produced as well as being consumed in steps of the mechanism.
8. A photochemical chain reaction is initiated by the absorption of a photon.

12.1 Reaction Mechanisms and Elementary Processes in Gases

Most chemical reactions occur through mechanisms that involve at least two steps. In many cases we have a *sequential mechanism*, with one step being completed before the next step occurs. There are also *concerted mechanisms*, in which two steps occur simultaneously. The steps in a mechanism are assumed to be *elementary processes*. An elementary process is one that cannot be broken down into simpler steps. We classify an elementary process by its *molecularity*, which is the number of reactant particles (molecules, atoms, ions, or radicals) that are involved in it. If more than one substance is involved in an elementary process, we define the molecularity of each substance as the number of particles of that substances involved in the step and the overall molecularity as the sum of these molecularities.

One of the gas-phase reactions that endanger the ozone layer in the earth's upper atmosphere is

$$2NO_2 + O_3 \longrightarrow N_2O_5 + O_2 \tag{12.1-1}$$

The reaction mechanism of the forward reaction is thought to consist of the following steps:[1]

$$\begin{array}{ll} (1) & NO_2 + O_3 \longrightarrow NO_3 + O_2 \\ (2) & NO_3 + NO_2 \longrightarrow N_2O_5 \end{array} \tag{12.1-2}$$

There is one *reactive intermediate*, NO_3, which is produced in one step and consumed in the other step. Addition of the steps of this mechanism gives the stoichiometric equation, with cancellation of NO_3. Both steps in the mechanism of Eq. (12.1-2) are *bimolecular*. That is, they involve two reactant particles. *Unimolecular* steps involve a single particle. *Termolecular* steps involve three particles. Termolecular processes are relatively slow because of the small probability that three molecules will collide or diffuse together at once, and these processes occur less frequently in mechanics than do bimolecular processes. Elementary processes involving four or more reactant particles probably do not occur in chemical reaction mechanisms. We now make an important assertion concerning the rate law of any elementary process: *In an elementary process, the order of any substance is equal to the molecularity of that substance.* We now justify this assertion for bimolecular elementary processes in the gas phase.

The Collision Theory of Bimolecular Elementary Processes in Gases

Bimolecular elementary processes involve the collisions of two molecules, which we discussed in Chapter 9. We now show that such a process obeys a second-order rate law. The collision rate in a gas is very large, typically several billion collisions per second for each molecule. If every collision in a reactive mixture led to chemical reaction, gas-phase reactions would be complete in nanoseconds. Since gas-phase reactions are almost never this rapid, it is apparent that only a small fraction of all collisions lead to chemical reaction. We make the important assumption: *The fraction of binary collisions*

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[1] H. S. Johnston and D. M. Yost, *J. Chem. Phys.*, **17**, 386 (1949).

that lead to chemical reaction in a gas-phase bimolecular elementary process depends only on the temperature. We will discuss the validity of this assumption in Section 12.3.

Consider first a gaseous bimolecular elementary process involving two molecules of substance number 1:

$$\mathscr{F}_1 + \mathscr{F}_1 \longrightarrow \text{products} \tag{12.1-3}$$

where we abbreviate its formula by $\mathscr{F}_1$. Eq. (9.8-22) gives the rate of two-body collisions of a single substance, which is proportional to the square of the number density of the substance. If we assume that at a fixed temperature a fixed fraction f of the collisions leads to reaction, the reaction is second order:

$$\begin{aligned} \text{rate} &= -\frac{1}{2}\frac{d[\mathscr{F}_1]}{dt} = \frac{fZ_{11}}{N_{\text{Av}}} = \frac{1}{N_{\text{Av}}} f\pi d_1^2\left(\frac{4k_{\text{B}}T}{\pi m_1}\right)^{1/2} \mathscr{N}_1^2 \\ &= N_{\text{Av}} f\pi d_1^2\left(\frac{4k_{\text{B}}T}{\pi m_1}\right)^{1/2} [\mathscr{F}_1]^2 \end{aligned} \tag{12.1-4}$$

where m_1 is the mass of a molecule of the reacting substance, d_1 is its effective hard-sphere diameter, $\mathscr{N}_1$ is its number density (equal to N_1/V), and $[\mathscr{F}_1]$ is its molar concentration. The quantity πd_1^2 is the *collision cross section* that we defined in Section 9.8. The quantity $f\pi d_1^2$ is an effective cross-sectional area, or the effective area of the "target" that actually leads to reaction. It is called the *reaction cross section*. The divisor N_{Av} in the first line of Eq. (12.1-4) is included to express the rate in moles rather than molecules.

By comparison with Eq. (11.2-8) we can write an expression for the forward rate constant:

$$k = f\pi d_1^2\left(\frac{4k_{\text{B}}T}{\pi m_1}\right)^{1/2} N_{\text{Av}} \qquad \begin{array}{l}\text{(bimolecular gas-phase}\\ \text{reaction, one reactant)}\end{array} \tag{12.1-5}$$

The units of this second-order rate constant are m^3 mol^{-1} s^{-1}. If concentrations and rates are to be measured in mol L^{-1}, an additional conversion factor of 1000 L m^{-3} is needed, giving k the units L mol^{-1} s^{-1}.

Exercise 12.1

Show that Eq. (12.1-5) is correct. Remember that a factor of 1/2 occurs in the definition of the rate as in Eq. (11.1-6), that each reactive collision uses up two molecules of substance number 1, and that a factor of 1/2 was introduced into Eq. (9.8-22) to avoid overcounting of collisions.

In the case of a bimolecular elementary process involving one molecule of substance 1 and one molecule of substance 2, the elementary bimolecular process is first order in each substance and second order overall. The rate constant is given by

$$k = f\pi d_{12}^2\left(\frac{8k_{\text{B}}T}{\pi \mu_{12}}\right)^{1/2} N_{\text{Av}} \qquad \begin{array}{l}\text{(bimolecular gas-phase}\\ \text{reaction, two reactants)}\end{array} \tag{12.1-6}$$

where d_{12} is the collision diameter for substance 1 and substance 2, and where μ_{12} is the reduced mass of molecules of mass m_1 and m_2, defined in Eq. (9.8-27) and in Appendix B:

$$\mu_{12} = \frac{m_1 m_2}{m_1 + m_2} \quad \text{or} \quad \frac{1}{\mu_{12}} = \frac{1}{m_1} + \frac{1}{m_2} \tag{12.1-7}$$

We can now summarize our results for both types of bimolecular processes in gaseous reactions: *A gaseous bimolecular elementary process is second order overall, and for a two-substance reaction it is first order in each substance.*

Exercise 12.2

Show that Eq. (12.1-6) is correct.

EXAMPLE 12.1

For the gas-phase reaction

$$H_2 + I_2 \longrightarrow 2\,HI$$

at 373.15 K, the rate constant is equal to $8.74 \times 10^{-15}\,\mathrm{L\,mol^{-1}\,s^{-1}}$. Assume that the reaction is elementary and estimate the fraction of collisions that leads to reaction.

Solution

From Table A.15,

$$d_{12} = \frac{1}{2}(2.72 \times 10^{-10}\,\mathrm{m} + 6.53 \times 10^{-10}\,\mathrm{m}) = 4.54 \times 10^{-10}\,\mathrm{m}$$

$$\mu = \frac{(0.002016\,\mathrm{kg\,mol^{-1}})(0.2538\,\mathrm{kg\,mol^{-1}})}{(0.002016\,\mathrm{kg\,mol^{-1}} + 0.2538\,\mathrm{kg\,mol^{-1}})(6.022 \times 10^{23}\,\mathrm{mol^{-1}})} = 3.321 \times 10^{-27}\,\mathrm{kg}$$

$$f = \frac{k}{\pi d_{12}^2 \left(\dfrac{8 k_B T}{\pi \mu_{12}}\right)^{1/2} N_{Av}}$$

$$f = \frac{(8.74 \times 10^{-15}\,\mathrm{L\,mol^{-1}\,s^{-1}})(0.001\,\mathrm{m^3\,L^{-1}})}{\pi(4.54 \times 10^{-10}\,\mathrm{m})^2 \left(\dfrac{8(1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}})(373.15\,\mathrm{K})}{\pi(3.321 \times 10^{-27}\,\mathrm{kg})}\right)^{1/2} (6.022 \times 10^{23}\,\mathrm{mol^{-1}})}$$

$$= 1.1 \times 10^{-26}$$

Exercise 12.3

At 473.15 K the rate constant for the reaction of the previous example is equal to $9.53 \times 10^{-10}\,\mathrm{L\,mol^{-1}\,s^{-1}}$. Estimate the fraction of collisions that leads to reaction at this temperature.

Termolecular Gas-Phase Reactions

A termolecular elementary process in the gas phase involves a three-body collision, which we picture as a collision of a third particle with a pair of molecules that is undergoing a two-body collision. The number of three-body collisions is proportional to the number of such pairs and is also proportional to the number of "third" particles. The rate of three-body collisions of a single substance is therefore proportional to the third power of the number density. The rate of three-body collisions of two particles of type 1 and a particle of type 2 is proportional to $\mathcal{N}_1^2\mathcal{N}_2$, and so on. If we again assume that the fraction of three-body collisions that lead to reaction depends only on temperature, we obtain a second important result: *Gaseous termolecular elementary processes are third order overall, and the order with respect to any substance is equal to the number of molecules of that substance involved in the three-body collision.*

Unimolecular Elementary Processes

These processes involve a single reactant molecule. We assert that *gaseous unimolecular elementary processes are first order.* We will discuss unimolecular processes in Section 12.4 and will find that this assertion applies to gaseous unimolecular processes only under certain conditions.

General Statement

Our results for gas-phase elementary reactions are summarized as follows: *For a gaseous elementary process, the order with respect to any substance is equal to the molecularity of that substance, and the overall order is equal to the sum of the molecularities of all substances.* This equality of order and molecularity holds only for elementary processes. The order of a reaction does not imply anything about its molecularity unless it is an elementary process.

12.2 Elementary Processes in Liquid Solutions

There are at least three steps involved in a chemical reaction in a liquid solution: The reactants diffuse together, they react chemically, and the products diffuse apart. We will speak of a process that has an elementary chemical part as an elementary process in spite of the occurrence of the diffusion processes.

If the chemical part of a reaction is rapid, the rate of the reaction is controlled by the diffusion of the reactants. If so, a reaction in solution can occur very rapidly. For example, the reaction between hydrogen ions and hydroxide ions in aqueous solution is a second-order process with a rate constant at 25°C equal to $1.4 \times 10^{11}\ \mathrm{L\,mol^{-1}\,s^{-1}}$. If solutions could be mixed instantaneously to give a solution containing hydrogen ions at $0.10\ \mathrm{mol\,L^{-1}}$ and hydroxide ions at $0.10\ \mathrm{mol\,L^{-1}}$, the reaction would have a half-life of 7×10^{-11} s.

Exercise 12.4

Verify the half-life value just given.

The rapidity of some liquid-state reactions at first seems surprising since ordinary diffusion processes in liquids take hours or days to occur. The difference is that in an ordinary diffusion process the root-mean-square distance traveled by molecules might be several centimeters, whereas the mean distance between reacting molecules in a solution reaction might be a few nanometers.

EXAMPLE 12.2

a. Estimate the mean distance between a molecule of substance 2 and the nearest-neighbor molecule of substance 3 in a well-mixed solution with a concentration of each substance equal to 0.10 mol L^{-1}.

b. For a substance with a diffusion coefficient equal to $1.0 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$, find the time for which the root-mean-square distance diffused in one direction is equal to the mean distance in part a.

Solution

a. We estimate the mean distance as the side of a cube in the solution that contains on the average one molecule of each solute.

$$V_{\mathrm{cube}} = \frac{1\ \mathrm{L}}{0.10\ \mathrm{mol}}\,\frac{1\ \mathrm{mol}}{6.0 \times 10^{23}}\,\frac{1\ \mathrm{m^3}}{1000\ \mathrm{L}} = 1.7 \times 10^{-26}\ \mathrm{m^3}$$

$$\text{Side of cube} = d = \left(1.7 \times 10^{-26}\ \mathrm{m^3}\right)^{1/3} = 2.6 \times 10^{-9}\ \mathrm{m} = 2.6\ \mathrm{nm}$$

b. From Eq. (10.2-19),

$$\left\langle x^2 \right\rangle^{1/2} = \sqrt{2Dt}$$

$$t = \frac{d^2}{2D} = \frac{(2.6 \times 10^{-9}\ \mathrm{m})^2}{2\left(1.0 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}\right)} = 3.4 \times 10^{-9}\ \mathrm{s} = 3.4\ \mathrm{ns}$$

Bimolecular Liquid-Phase Reactions

As in Chapter 9, we picture a molecule in a liquid as being confined in a “cage” of other molecules, but occasionally moving past its nearest neighbors into an adjacent cage. Assume that substances 2 and 3 are dissolved in a solvent, substance 1. In a dilute solution, most cages surrounding a solute molecule are made up entirely of solvent molecules, but a few will also have one molecule of type 2 or type 3. The motion of a type-2 molecule into a cage with a type-3 molecule is called an *encounter* of the two molecules. In a *diffusion-limited* or *diffusion-controlled* bimolecular elementary process, the chemical part of the process is so rapid that every encounter of the reacting molecules immediately leads to reaction. The rate is therefore controlled (limited) by the rate at which the reactant molecules diffuse together.

A theory for the rate of a bimolecular elementary diffusion-limited process was developed by Smoluchowski.[2] The first version of the theory was based on the assumption that molecules of type 2 are diffusing toward stationary molecules of type 3. On the average, the motion of type 2 molecules toward the fixed molecules of type 3

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[2] M. V. Smoluchowski, *Z. Phys. Chem.*, **92**, 129 (1917). See K. J. Laidler, *Chemical Kinetics*, Harper and Row, New York, 1987, p. 212ff.

constitutes a diffusion flux that obeys Fick's law of diffusion. It is assumed that the reaction occurs as soon as the center of the type 2 molecule reaches a critical distance d_{23} from the center of the type 3 molecule. The distance d_{23} is called the *reaction diameter*. The concentration of type 2 molecules at distances smaller than d_{23} vanishes because of the immediate reaction. A concentration gradient is set up, with the value of the concentration ranging from its "bulk" value at large distances down to zero at a distance d_{23}. A solution to Fick's law of diffusion was sought that matched these conditions. The diffusion flux gives the rate of reaction, since all molecules that diffuse up to the sphere of radius d_{23} react immediately. We do not discuss the theory, but the result is that the reaction is second order overall, first order with respect to 2, and first order with respect to 3. The second-order rate constant is found to be

$$k = 4\pi N_{\mathrm{Av}} D_2 d_{23} \quad \text{(approximate equation)} \tag{12.2-1}$$

where N_{Av} is Avogadro's constant and D_2 is the diffusion coefficient of substance 2. When the fact that the type 3 molecules are also moving is included, the result is[3]

$$k = 4\pi N_{\mathrm{Av}}(D_2 + D_3)d_{23} \quad \begin{array}{l}\text{(diffusion-limited second-order}\\ \text{reaction with two reactants)}\end{array} \tag{12.2-2}$$

where D_3 is the diffusion coefficient of substance 3. Equation (12.2-2) is used in preference to Eq. (12.2-1) for calculations.

If two molecules of substance 2 react in a diffusion-limited reaction, the reaction is second order in that substance. By an analysis that is analogous to that leading to Eq. (12.2-2),

$$k = \frac{1}{2}4\pi N_{\mathrm{Av}}(2D_2)d_{22} = 4\pi N_{\mathrm{Av}} D_2 d_{22} \quad \begin{array}{l}\text{(diffusion-limited second-order}\\ \text{reaction with one reactant)}\end{array} \tag{12.2-3}$$

where d_{22} is the reaction diameter for two type 2 molecules. The factor 1/2 in Eq. (12.2-3) is included because of the factor of 1/2 in the definition of the rate in Eq. (11.1-6) for a substance with stoichiometric coefficient equal to 2.

EXAMPLE 12.3

Assume that the following reaction in carbon tetrachloride is elementary and diffusion-controlled:

$$2\mathrm{I} \longrightarrow \mathrm{I}_2$$

Calculate the rate constant at 298 K. Assume that the reaction diameter is 4.0×10^{-10} m. The diffusion coefficient of iodine atoms in CCl_4 at this temperature is equal to $4.2 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$.

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[3] K. J. Laidler, *Chemical Kinetics*, Harper and Row, New York, 1987, p. 212ff.

Solution

$$k = 4\pi(6.02 \times 10^{23}\ \text{mol}^{-1})(4.2 \times 10^{-9}\ \text{m}^2\ \text{s}^{-1})(4.0 \times 10^{-10}\ \text{m})$$
$$= 1.3 \times 10^{7}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1} = 1.3 \times 10^{10}\ \text{L mol}^{-1}\ \text{s}^{-1}$$

According to a theory of Debye,[4] the formula for the rate constant shown in Eq. (12.2-2) must be multiplied by the *electrostatic factor* f if the particles are ions:

$$f = \frac{y}{e^{y} - 1} \tag{12.2-4}$$

where

$$y = \frac{z_2 z_3 e^2}{4\pi\varepsilon d_{23} k_B T} \tag{12.2-5}$$

The valences (number of proton charges) of the two ions are represented by z_2 and z_3. The symbol e stands for the charge on a proton and ε stands for the permittivity of the solvent, which was introduced in Eq. (6.4-19).

The electrostatic factor f is greater than unity if z_2 and z_3 have opposite signs, corresponding to an enhancement of the rate due to electrostatic attraction of the ion pair. If z_2 and z_3 have the same sign, the electrostatic factor is smaller than unity, corresponding to a decrease in the rate due to electrostatic repulsion.

EXAMPLE 12.4

The diffusion coefficient of H^+ in water at 25°C is equal to $9.31 \times 10^{-9}\ \text{m}^2\ \text{s}^{-1}$, and that of OH^- is equal to $5.26 \times 10^{-9}\ \text{m}^2\ \text{s}^{-1}$. Estimate the reaction diameter d. The value of the dielectric constant for water is equal to 78.4 at 25°C and the permittivity of the vacuum is equal to $8.85 \times 10^{-12}\ \text{C}^2\ \text{N}^{-1}\ \text{m}^{-2}$. The dielectric constant is the ratio of the permittivity of the medium to that of a vacuum. At this temperature $k = 1.4 \times 10^{11}\ \text{L mol}^{-1}\ \text{s}^{-1}$.

Solution

From Eq. (12.2-5), we first obtain the relation between y and d:

$$y = \frac{(-1)(1.6022 \times 10^{-19}\ \text{C})^2}{4\pi(78.4)\left(8.85 \times 10^{-12}\ \text{C}^2\ \text{N}^{-1}\ \text{m}^{-2}\right)\left(1.38 \times 10^{-23}\ \text{J K}^{-1}\right)(298\ \text{K})d}$$
$$= -\frac{7.15 \times 10^{-10}\ \text{m}}{d}$$

Since the reaction diameter d occurs both in the expression for k in Eq. (12.2-2) and in the expression for y in Eq. (12.2-5), we solve by successive approximation. We guess a value for d and calculate the value of k for that value, then guess another value of d and calculate k again, and so forth, until an adequate approximation for k is obtained. By this procedure the correct value of k is obtained with a value of d equal to 8.64×10^{-10} m = 0.864 nm = 8.64 Å.

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[4] P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).

The reaction diameter for the reaction between hydrogen ions and hydroxide ions in aqueous solution is larger than the sum of the radii of these ions. The explanation for this fact is that water molecules can exchange hydrogen and hydroxide ions as described in Chapter 10.

Exercise 12.5

Calculate the values of the electrostatic factor f for z_2z_3 equal to 2, 1, 0, -1, and -2 at 298.15 K, assuming a dielectric constant equal to 78.4 and a reaction diameter equal to 0.50 nm. Comment on your results.

Equation (10.4-4) relates a diffusion coefficient to the effective radius of a diffusing particle of substance 2 and the viscosity of the solvent:

$$D_2 = \frac{k_B T}{6\pi\eta r_{\mathrm{eff},2}}$$

where $r_{\mathrm{eff},2}$ is the effective radius of the particle of substance 2, η is the viscosity of the solvent, k_B is Boltzmann's constant, and T is the absolute temperature. If we use this relation in Eq. (12.2-2) and assume that $d_{23} = r_{\mathrm{eff},2} + r_{\mathrm{eff},3}$, we obtain the relation for uncharged molecules

$$k = \frac{4N_{\mathrm{Av}}k_B T}{6\eta}\left(\frac{1}{r_{\mathrm{eff},2}} + \frac{1}{r_{\mathrm{eff},3}}\right)\left(r_{\mathrm{eff},2} + r_{\mathrm{eff},3}\right) = \frac{2RT}{3\eta}\left(2 + \frac{r_{\mathrm{eff},2}}{r_{\mathrm{eff},3}} + \frac{r_{\mathrm{eff},3}}{r_{\mathrm{eff},2}}\right) \tag{12.2-6}$$

where R is the ideal gas constant. If $r_{\mathrm{eff},2}$ and $r_{\mathrm{eff},3}$ are nearly equal, Eq. (12.2-6) becomes

$$k \approx \frac{8RT}{3\eta} \quad \text{(two reacting substances)} \tag{12.2-7}$$

so that the rate constant k depends only on the viscosity of the solvent and the temperature. If the two reacting molecules are of the same substance, we must divide by 2 in order to avoid counting the same encounter twice:

$$k \approx \frac{4RT}{3\eta} \quad \text{(single reacting substance)} \tag{12.2-8}$$

EXAMPLE 12.5

Use the value of the viscosity of water at 25°C to estimate the value of the rate constant for any bimolecular diffusion-controlled reaction of uncharged molecules in water at that temperature.

Solution

Use Eq. (12.2-7) as an approximation:

$$k = \frac{8(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298\ \mathrm{K})}{3\left(8.904 \times 10^{-4}\ \mathrm{kg\ m^{-1}\ s^{-1}}\right)}$$
$$= 7.4 \times 10^{6}\ \mathrm{m^3\ mol^{-1}\ s^{-1}} = 7.4 \times 10^{9}\ \mathrm{L\ mol^{-1}\ s^{-1}}$$

Solution reactions that are much slower than diffusion-limited reactions are called *activation-limited reactions*. After an encounter occurs, the molecules undergo numerous collisions inside a "cage" of other molecules before finally reacting. The rate of collisions is very large (see Example 9.12), but only a small fraction of them will lead to reaction. If this fraction depends only on the temperature, the rate will be proportional to the number of encounters as well as to the fraction of collisions that lead to reaction. Since the number of 2–3 encounters is proportional to the number of type 2 molecules and the number of type 3 molecules, an activation-limited bimolecular elementary reaction is first order with respect to each reactant and second order overall, just as with a diffusion-limited reaction and a gas-phase reaction. The rate of a reaction between molecules of the same substance is second order with respect to that substance, and its temperature dependence should be similar to that of a gas-phase reaction.

Termolecular and Unimolecular Liquid-Phase Reactions

The rates of diffusion-limited termolecular elementary processes in liquid phases are proportional to the number of encounter pairs (pairs of molecules in the midst of an encounter) and also to the number of "third" molecules present to diffuse into the same cage as the encounter pair. Therefore, diffusion-limited termolecular elementary processes are third order, just as in the gas phase. Activation-limited termolecular elementary reactions in liquids are also third order if the fraction of collisions that lead to reaction is independent of the concentration. We assume further that unimolecular elementary processes in liquids exhibit first-order kinetics, as in the gas phase. We can now summarize the facts for elementary processes in both liquids and gases: *The molecularity of a substance in an elementary process is equal to its order, and the overall order is equal to the sum of the orders of the individual substances.*

PROBLEMS

Section 12.2: Elementary Processes in Liquid Solutions

12.1 The reaction

$$2\mathrm{I} \longrightarrow \mathrm{I}_2$$

is diffusion-controlled in carbon tetrachloride and also in water. Estimate the rate constant of the reaction in water at 20°C from data in Example 12.3 and from viscosities in Table A.18 of Appendix A.

12.2 The reaction in aqueous solution

$$\mathrm{NH_4^+ + OH^- \longrightarrow NH_3 + H_2O}$$

is diffusion-controlled with rate constant equal to $1.0 \times 10^{10}\ \mathrm{L\,mol^{-1}\,s^{-1}}$ at some temperature. Estimate the sum of the diffusion coefficients of $\mathrm{NH_4^+}$ and $\mathrm{OH^-}$ at this temperature.

12.3 Compute the reaction diameter d_{12} for the reaction

$$\mathrm{CH_3CO_2^- + H^+ \longrightarrow CH_3CO_2H}$$

for which $k = 4.5 \times 10^{10}\ \mathrm{L\,mol^{-1}\,s^{-1}}$. Use the values of the ion mobilities from Table A.20 of Appendix A.

12.4 **a.** The reaction

$$\mathrm{2CH_3 \longrightarrow C_2H_6}$$

in toluene is diffusion-controlled. The viscosity of toluene at 30°C is equal to $5.236 \times 10^{-4}\ \mathrm{kg\,m^{-1}\,s^{-1}}$. Estimate the rate constant of the reaction. State any assumptions.

b. The viscosity of toluene at 20°C is equal to $5.9 \times 10^{-4}\ \mathrm{kg\ m^{-1}\ s^{-1}}$. Estimate the activation energy of the reaction of part a and the value of the rate constant at 40°C. State any assumptions.

12.5 For the reaction of C_2H_5Br and $(C_2H_5)_2S$ at 20.00°C in benzyl alcohol, the rate constant is equal to $1.44 \times 10^{-8}\ \mathrm{L\ mol^{-1}\ s^{-1}}$. The viscosity of benzyl alcohol at this temperature is $5.8 \times 10^{-3}\ \mathrm{kg\ m^{-1}\ s^{-1}}$.

a. Find the value that the rate constant would have if the reaction were diffusion-controlled. Assume a diameter of 500 pm = 5.0 Å for each reactant.

b. What fraction of the encounters leads to reaction?

12.6 For the reaction at 25.00°C in methanol

$$\mathrm{CH_3Br + I^- \longrightarrow CH_3I + Br^-}$$

the rate constant is equal to $9.48 \times 10^{-4}\ \mathrm{L\ mol^{-1}\ s^{-1}}$. The viscosity of methanol at this temperature is $5.47 \times 10^{-4}\ \mathrm{kg\ m^{-1}\ s^{-1}}$.

a. Find the value that the rate constant would have if the reaction were diffusion-controlled. Assume a diameter of 400 pm = 4.0 Å for each reactant.

b. What fraction of the encounters leads to reaction?

12.3 The Temperature Dependence of Rate Constants

The Arrhenius Relation

Reaction rates depend strongly on temperature, nearly always increasing when the temperature is raised. The first quantitative studies of the temperature dependence of rate constants were published in the last half of the 19th century, and various empirical formulas were proposed.[5] The *Arrhenius relation*, which was proposed in 1889, is widely used because it is based on a physical picture of elementary processes and because it usually fits experimental data quite well.

Svante Arrhenius, 1859–1927, was a Swedish chemist who won the 1905 Nobel Prize in chemistry for his theory of dissociation and ionization of electrolytes in solution.

Arrhenius postulated that only "activated" molecules (those with high energy) can react and that the numbers of such activated molecules would be governed by the Boltzmann probability distribution of Eq. (9.3-41). This assumption leads to the Arrhenius relation:

$$\boxed{k = Ae^{-\varepsilon_a/k_BT}} \qquad (12.3\text{-}1)$$

The quantity ε_a is the energy that the molecules must have in order to react and is called the *activation energy*. The temperature-independent factor A is called the *preexponential factor*. We can express Eq. (12.3-1) in the form

$$\boxed{k = Ae^{-E_a/RT}} \qquad (12.3\text{-}2)$$

where $E_a = N_{Av}\varepsilon_a$ is the *molar activation energy* and where $R = k_BN_{Av}$ is the ideal gas constant. Experimental molar activation energy values are usually in the range from 50 to 200 kJ mol^{-1}, somewhat smaller than energies required to break chemical bonds. These magnitudes seem reasonable if we picture the activation process as partially breaking one bond while partially forming another.

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[5] K. J. Laidler, *op. cit.*, p. 40ff. (note 3).

EXAMPLE 12.6

For the gas-phase reaction

$$H_2 + I_2 \longrightarrow 2\,HI$$

at 373.15 K, the rate constant is equal to $8.74 \times 10^{-15}\,\mathrm{L\,mol^{-1}\,s^{-1}}$. At 473.15 K it is equal to $9.53 \times 10^{-10}\,\mathrm{L\,mol^{-1}\,s^{-1}}$. Find the value of the activation energy and of the preexponential factor.

Solution

For any two temperatures T_1 and T_2, Eq. (12.3-2) gives

$$E_a = \frac{R\ln\left(\dfrac{k(T_2)}{k(T_1)}\right)}{\dfrac{1}{T_1} - \dfrac{1}{T_2}} \tag{12.3-3}$$

Substitution of the values gives

$$\begin{aligned} E_a &= \frac{(8.3145\ \mathrm{J\,K\,mol^{-1}})\ln\left(\dfrac{9.53 \times 10^{-10}}{8.74 \times 10^{-15}}\right)}{\dfrac{1}{373.15\ \mathrm{K}} - \dfrac{1}{473.15\ \mathrm{K}}} \\ &= 1.70 \times 10^5\ \mathrm{J\,mol^{-1}} \end{aligned}$$

$$\begin{aligned} A &= ke^{E_a/RT} \\ &= (8.74 \times 10^{-15}\ \mathrm{L\,mol^{-1}\,s^{-1}})\exp\left(\frac{1.70 \times 10^5\ \mathrm{J\,mol^{-1}}}{\left(8.3145\ \mathrm{J\,K\,mol^{-1}}\right)(373.15\ \mathrm{K})}\right) \\ &= 5.47 \times 10^9\ \mathrm{L\,mol^{-1}\,s^{-1}} \end{aligned}$$

Exercise 12.6

A common rule of thumb is that the rate of a reaction doubles if the temperature is raised by 10°C.

a. Find the value of the activation energy if a rate constant doubles in value between 20°C and 30° C.

b. Find the value of the activation energy if a rate constant doubles in value between 90°C and 100°C.

c. A common definition of the activation energy of a reaction is

$$E_a = RT^2\left(\frac{d\ln(k)}{dT}\right) \quad \text{(common definition of } E_a\text{)} \tag{12.3-4}$$

Show that if k is given by Eq. (12.3-2), Eq. (12.3-4) gives the same E_a as in Eq. (12.3-2) if A is temperature-independent.

The Collision Theory of Bimolecular Elementary Gas-Phase Reactions

The principal assumption of the theory is that the initiation of the reaction requires an inelastic collision in which at least a certain amount of energy is transferred from translational motion to internal motions (rotations, vibrations, or electronic motion) that can lead to reaction. We first assume that the probability of reaction equals zero if the relative speed of two colliding particles is smaller than a certain critical value and equals unity for relative speeds larger than this value. This probability is represented in Figure 12.1a.

Consider a gas-phase bimolecular elementary reaction between molecules of substance 1 and substance 2. Equation (2.8-31) gives the total rate of collisions per unit volume between molecules of type 1 and type 2:

$$Z_{12} = \sqrt{\frac{8k_{\mathrm{B}}T}{\pi\mu_{12}}}\pi d_{12}^2\mathcal{N}_1\mathcal{N}_2 = \langle v_{12}\rangle\pi d_{12}^2\mathcal{N}_1\mathcal{N}_2 \tag{12.3-5}$$

where $\langle v_{12}\rangle$ is the mean relative speed, $\mathcal{N}_1$ is the number density of molecules of type 1, $\mathcal{N}_2$ is the number density of molecules of type 2, and d_{12} is the collision diameter of the molecule pair. We now want to include only molecules of type 1 whose velocities lie in the infinitesimal range $d^3\mathbf{v}_1$ and molecules of type 2 whose velocities lie in the infinitesimal range $d^3\mathbf{v}_2$. We replace the mean relative speed by our particular relative speed, v, the magnitude of the difference between the two velocities:

$$v = |\mathbf{v}| = |\mathbf{v}_2 - \mathbf{v}_1| \tag{12.3-6}$$

We multiply by the probability that the first molecule has its velocity $\mathbf{v}_1$ in the infinitesimal range $d^3\mathbf{v}_1$ and that the second molecule has its velocity $\mathbf{v}_2$ in the infinitesimal range $d^3\mathbf{v}_2$. We call this collision rate dZ_{12}:

$$dZ_{12} = |\mathbf{v}|\pi d_{12}^2\mathcal{N}_1\mathcal{N}_2 g(\mathbf{v}_1)d^3\mathbf{v}_1 g(\mathbf{v}_2)d^3\mathbf{v}_2 \tag{12.3-7}$$

where g is the probability distribution of Eq. (2.3-40).

In order to obtain the total rate of collisions that leads to reaction, we integrate over all velocities that satisfy the condition that the relative speed exceeds v_c, the *critical*

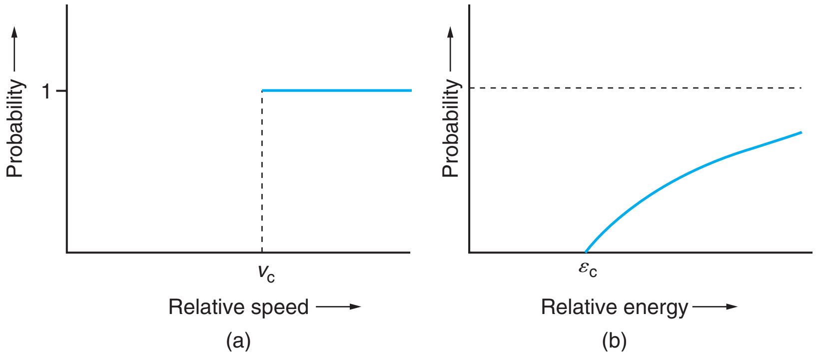

Figure 12.1 Probability of Reaction as a Function of Relative Speed. (a) First assumption. (b) Assumed probability of reaction as a function of relative kinetic energy according to Eq. (12.3-16).

speed, the minimum relative speed that can lead to reaction:

$$v > v_c \tag{12.3-8}$$

This integration is carried out in Appendix D. The result is

$$\begin{aligned} Z_{12}(\text{reactive}) &= \pi d_{12}^2 \mathcal{N}_1 \mathcal{N}_2 (8k_\text{B}T/\pi\mu_{12})^{1/2} \left(1 + \frac{\mu v_c^2}{2k_\text{B}T}\right) e^{-\mu_{12} v_c^2/2k_\text{B}T} \\ &= \langle v_{12} \rangle \pi d_{12}^2 \mathcal{N}_1 \mathcal{N}_2 \left(1 + \frac{\mu_{12} v_c^2}{2k_\text{B}T}\right) e^{-\mu_{12} v_c^2/2k_\text{B}T} \end{aligned} \tag{12.3-9}$$

where $\langle v_{12} \rangle$ is the mean relative speed. Comparison of this equation with Eq. (12.1-4) shows that we have an expression for the fraction of collisions that leads to reaction in a bimolecular elementary process:

$$f = \left(1 + \frac{\mu_{12} v_c^2}{2k_\text{B}T}\right) e^{-\mu_{12} v_c^2/2k_\text{B}T} \tag{12.3-10}$$

The *critical energy* is given by

$$\varepsilon_\text{c} = \frac{1}{2} \mu_{12} v_c^2 \tag{12.3-11}$$

so that Eq. (12.3-9) can be written

$$Z_{12}(\text{reactive}) = \langle v_{12} \rangle \pi d_{12}^2 \mathcal{N}_1 \mathcal{N}_2 \left(1 + \frac{\varepsilon_\text{c}}{k_\text{B}T}\right) e^{-\varepsilon_\text{c}/k_\text{B}T} \tag{12.3-12}$$

which corresponds to

$$\begin{aligned} \text{rate} &= -\frac{d[\mathcal{F}_1]}{dt} = -\frac{d\mathcal{N}_1}{dt} = \frac{Z_{12}(\text{reactive})}{N_\text{Av}} \\ &= \frac{1}{N_\text{Av}} \langle v_{12} \rangle \pi d_{12}^2 \left(1 + \frac{\varepsilon_\text{c}}{k_\text{B}T}\right) e^{-\varepsilon_\text{c}/k_\text{B}T} \mathcal{N}_1 \mathcal{N}_2 \\ &= N_\text{Av} \langle v_{12} \rangle \pi d_{12}^2 \left(1 + \frac{\varepsilon_\text{c}}{k_\text{B}T}\right) e^{-\varepsilon_\text{c}/k_\text{B}T} [\mathcal{F}_1][\mathcal{F}_2] \end{aligned} \tag{12.3-13}$$

where we have used the fact that

$$\mathcal{N}_1 = N_\text{Av}[\mathcal{F}_1] \quad \text{and} \quad \mathcal{N}_2 = N_\text{Av}[\mathcal{F}_2]$$

The reaction is second order with a rate constant given by

$$k = N_\text{Av} \pi d_{12}^2 \left(\frac{8k_\text{B}T}{\pi\mu_{12}}\right)^{1/2} \left(1 + \frac{E_\text{c}}{RT}\right) e^{-E_\text{c}/RT} \tag{12.3-14}$$

where we define a *molar critical energy*

$$E_\text{c} = N_\text{Av} \varepsilon_\text{c} \tag{12.3-15}$$

EXAMPLE 12.7

For the reaction of Example 12.6, calculate the fractional change in the exponential factor and in the preexponential factor in Eq. (12.3-14) if T is changed from 20°C to 30°C.

Solution

The value of E_c/R is 2.045×10^4 K. The ratio of the exponential factors is

$$\frac{\exp(-2.045 \times 10^4\ \mathrm{K}/303.15\ \mathrm{K})}{\exp(-2.045 \times 10^4\ \mathrm{K}/293.15\ \mathrm{K})} = 10.0$$

The ratio of the preexponential factors is

$$\frac{(303.15\ \mathrm{K})^{1/2}(1 + 2.045 \times 10^4\ \mathrm{K}/303.15\ \mathrm{K})}{(293.15\ \mathrm{K})^{1/2}\big(1 + 2.045 \times 10^4\ \mathrm{K}/293.15\ \mathrm{K}\big)} = 0.984$$

The change in the preexponential factor is negligible compared with the change in the exponential factor.

Equation (12.3-14) corresponds to the probability of reaction shown in Figure 12.1a. A more realistic assumption is that the probability of reaction is given by

$$\text{probability} = \begin{cases} 0 & \text{if } \varepsilon_r < \varepsilon_c \\ 1 - \varepsilon_c/\varepsilon_r & \text{if } \varepsilon_r > \varepsilon_c \end{cases} \tag{12.3-16}$$

where ε_r is the relative kinetic energy of the pair of molecules,

$$\varepsilon_r = \frac{1}{2}\mu v^2$$

and where ε_c is the minimum relative kinetic energy that can lead to reaction. This probability function is represented in Figure 12.1b. The dependence shown in this figure is more reasonable than that of Figure 12.1a because a collision with a relative kinetic energy barely great enough to initiate a reaction should have a lower probability of producing a reaction than collisions with a much larger relative kinetic energy.

We do not present the mathematics, but when the probability of Eq. (12.3-16) is introduced into the integration of Eq. (12.3-11), the result is[6]

$$k = N_{\mathrm{Av}}\langle v_{12}\rangle \pi d_{12}^2 e^{-E_c/RT} = N_{\mathrm{Av}}\pi d_{12}^2\left(\frac{8k_{\mathrm{B}}T}{\pi\mu}\right)^{1/2} e^{-E_c/RT} \tag{12.3-17}$$

We will use this equation in preference over Eq. (12.3-14). It does not exactly agree with the Arrhenius formula since the preexponential factor in this formula depends on temperature. However, the exponential factor depends much more strongly on temperature than does the preexponential factor. The difference between the two equations is numerically small over a limited range of temperature, and E_c can be approximately identified with E_a, the Arrhenius activation energy.

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[6] K. J. Laidler, *op. cit.*, p. 85ff. (note 3).

EXAMPLE 12.8

Assuming the activation energy and the value of the rate constant at 373 K from Example 12.6, find the effective collision diameter of a hydrogen molecule and an iodine molecule.

Solution

Using Eq. (12.3-17)

$$\pi d^2 = \left(\frac{\pi\mu}{8k_BT}\right)^{1/2}\frac{k}{N_{Av}}e^{E_a/RT} = \frac{k}{\langle v_{rel}\rangle N_{Av}}e^{E_a/RT}$$

The value of $\langle v_{rel}\rangle$ is 1988 m s^{-1}, so that

$$d^2 = \frac{8.74\times10^{-18}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}}{\pi\left(1988\ \text{m}^{-1}\ \text{s}^{-1}\right)\left(6.022\times10^{23}\ \text{mol}^{-1}\right)}e^{54.794} = 1.45\times10^{-21}\ \text{m}^2$$

$$d = 3.8\times10^{-11}\ \text{m} = 38\ \text{pm} = 0.38\ \text{Å}$$

The value of the collision diameter in Example 12.8 is too small by a factor of about 1/10, which is typical of the collision theory. The explanation for the smallness of the apparent collision diameter is that the molecules not only have to collide with at least a minimum relative energy, but in many reactions must also be oriented properly in order to react. Even two small molecules like H_2 and I_2 would presumably have to be oriented correctly for the reaction to occur.

To account for the orientation dependence, a factor called the *steric factor* is introduced into the collision theory. The steric factor is defined to be the fraction of collisions in which the orientation of the molecules is appropriate for reaction. If this factor is denoted by φ, Eq. (12.3-17) becomes

$$k = \varphi N_{Av}\pi d_{12}^2\left(\frac{8k_BT}{\pi\mu}\right)^{1/2}e^{-E_c/RT} \qquad (12.3\text{-}18)$$

Exercise 12.7

Find the value of the steric factor for the reaction of Example 12.8 that will give a value for the collision diameter equal to the mean of the hard-sphere diameters of H_2 and I_2 in Table A.15 of Appendix A.

Liquid-State Reactions

The temperature dependence of rate constants for both gaseous and liquid-state reactions is usually well described by the Arrhenius formula, Eq. (12.3-2). For activation-limited reactions, the activation energies are roughly equal to those for gas-phase reactions. This is as expected, since the collisional activation is very similar to that of gaseous reactions. In the case of diffusion-limited reactions, the temperature dependence of the rate constant is governed by the diffusion coefficients. Diffusion coefficients in liquids commonly have a temperature dependence given by Eq. (10.4-5), which is also of the same form as the Arrhenius formula:

$$D = D_0e^{-E_{a,d}/RT} \qquad (12.3\text{-}19)$$

The activation energies are somewhat smaller than for activation-limited reactions, often near the values for the energies of activation for diffusion processes.

EXAMPLE 12.9

For the reaction

$$2\text{I} \rightarrow \text{I}_2$$

in carbon tetrachloride, the value of the rate constant at 23°C is $7.0 \times 10^6\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}$. At 30°C, the value is $7.7 \times 10^6\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}$. Find the activation energy and compare it with the activation energy for the viscosity of carbon tetrachloride in Example 10.17.

Solution

$$E_a = \frac{R\ln(k_2/k_1)}{\dfrac{1}{T_1} - \dfrac{1}{T_2}} = \frac{(8.3145\ \text{J K}^{-1}\text{mol}^{-1})\ln\left(\dfrac{7.7 \times 10^6\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}}{7.0 \times 106\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1}}\right)}{\dfrac{1}{296\ \text{K}} - \dfrac{1}{303\ \text{K}}}$$

$$= 10200\ \text{J mol}^{-1}$$

This value is nearly the same as that of Example 10.17, $10400\ \text{J mol}^{-1}$.

PROBLEMS

Section 12.3: The Temperature Dependence of Rate Constants

12.7 The first-order rate constant for the thermal decomposition of 3-methylcyclobutanone has the values[7]

T/K	$k/10^{-4}\ \text{s}^{-1}$	T/K	$k/10^{-4}\ \text{s}^{-1}$
552.24	0.4259	589.05	6.459
561.81	0.8936	596.96	11.201
570.41	1.707	606.14	20.83
579.35	3.207		

a. Find the value of the activation energy and the value of the preexponential factor.

b. Find the value of the rate constant at 600.0 K.

c. Find the time for 80.0% of the reactant to react at 600.0 K.

12.8 The rate constant for the gas-phase thermal decomposition of ethyl bromide (bromoethane) is equal to $0.1068\ \text{s}^{-1}$ at 500°C and equal to $6.4529\ \text{s}^{-1}$ at 600°C. Find the parameters A and E_a in the Arrhenius expression for this rate constant.

12.9 For the reaction

$$\text{H}_2 + \text{I}_2 \longrightarrow 2\text{HI}$$

at 373.15 K, the rate constant is equal to $8.74 \times 10^{-15}\ \text{L mol}^{-1}\ \text{s}^{-1}$. At 473.15 K, it is equal to $9.53 \times 10^{-10}\ \text{L mol}^{-1}\ \text{s}^{-1}$. Find the value of the parameters A and E_a in the Arrhenius expression for the rate constant.

12.10 The gas-phase reaction

$$2\text{N}_2\text{O}_5 \longrightarrow 4\text{NO}_2 + \text{O}_2$$

obeys first-order kinetics. The half-life of this reaction equals 89500 s at 273.15 K and equals 795 s at 323.15 K.

a. Find the values of the preexponential factor and the activation energy in the Arrhenius formula

b. Find the fraction of N_2O_5 molecules remaining after 1.00 hour in a reaction carried out at 298.15 K.

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[7] H. M. Frey, H. P. Watts, and I. D. R. Stevens, *J. Chem. Soc. Faraday Trans.*, 2, **83**, 601 (1987).

12.11 The gas-phase decomposition of acetaldehyde, CH_3CHO, obeys second-order kinetics. Some values of the rate constant are:

T/K	$k/\text{L mol}^{-1}\text{s}^{-1}$	T/K	$k/\text{L mol}^{-1}\text{s}^{-1}$
703	0.0110	811	0.79
733	0.0352	836	2.14
759	0.105	865	4.95
791	0.343		

a. Find the activation energy and the preexponential factor.

b. Find the value of the rate constant at 500°C.

c. If the initial pressure of pure acetaldehyde is equal to 0.500 atm at 500°C, find the time for 50.0% of the acetaldehyde to react.

12.12 For the reaction of I_2 and $N_2CHCO_2C_2H_5$ in CCl_4 at 298.15 K, $k = 3.28 \times 10^{-4}\ \text{L mol}^{-1}\ \text{s}^{-1}$, and at 323.15 K, $k = 4.60 \times 10^{-3}\ \text{L mol}^{-1}\ \text{s}^{-1}$. Find the activation energy and the preexponential factor in the Arrhenius expression. Do you think that the reaction is diffusion-controlled or activation-controlled? Explain your answer.

12.13 The hydrolysis of 2-chlorooctane in 80% ethanol obeys pseudo first-order kinetics. At 0°C the rate constant equals $1.06 \times 10^{-5}\ \text{s}^{-1}$ and at 25°C it equals $3.19 \times 10^{-4}\ \text{s}^{-1}$.

a. Find the values of the parameters in the Arrhenius formula for this reaction.

b. Find the value of k at 15°C.

Find the half-time of the reaction at 15°C, neglecting any back reaction.

12.14 The decomposition of benzenediazonium fluorborate in aqueous HCl solution obeys pseudo first-order kinetics. The rate constant is measured to be equal to $4.04 \times 10^{-5}\ \text{s}^{-1} \pm 0.12 \times 10^{-5}\ \text{s}^{-1}$ at 25°C and equal to $3.18 \times 10^{-4}\ \text{s}^{-1} \pm 0.09 \times 10^{-4}\ \text{s}^{-1}$ at 40°C. Calculate the activation energy and estimate the error in the activation energy, assuming that the errors in the temperature are negligible.

12.15 **a.** The rate constant for the bimolecular elementary gaseous process

$$CO + O_2 \longrightarrow CO_2 + O$$

is equal to $1.22 \times 10^{5}\ \text{L mol}^{-1}\ \text{s}^{-1}$ at 2500 K and is equal to $3.66 \times 10^{5}\ \text{L mol}^{-1}\ \text{s}^{-1}$ at 2800 K. Find the value of the activation energy and the value of the preexponential factor.

b. Assuming a hard-sphere diameter of 350 pm for O_2 and a hard-sphere diameter of 360 pm for CO, calculate the value of the steric factor in the collision theory.

12.16 Apply the collision theory to calculate the rate constant for the gas-phase reaction

$$2NO \longrightarrow N_2 + O_2$$

at 500.0 K. The effective hard-sphere diameter of NO molecules is 205 pm. Assume that E_c is equal to $293\ \text{kJ mol}^{-1}$ and that the steric factor is equal to 1.

12.4 Reaction Mechanisms and Rate Laws

There is no direct way to take an experimentally determined rate law for a chemical reaction and deduce the correct mechanism from it. For example, the reaction

$$H_2 + I_2 \longrightarrow 2HI$$

is second order overall, first order with respect to each reactant. The rate law could correspond to a bimolecular elementary reaction, and this was once thought to be the case. The reaction is now thought to proceed by several competing mechanisms, including the elementary mechanism.[8]

Although we cannot directly deduce a mechanism from a rate law, we can often deduce a rate law from an assumed mechanism and can then compare this equation with the experimental rate law. If the two do not match, the proposed mechanism must

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[8] K. J. Laidler, *op. cit.*, p. 297ff (note 3); Sullivan, *J. Chem. Phys.*, **46**, 73 (1967).

be incorrect. If they match, the mechanism might be correct, although other mechanisms might give the same rate law. There are sometimes other types of experiments that can be done, including direct detection of reactive intermediates, molecular beam experiments, and radioactive tracer experiments. However, we must regard even a well-accepted mechanism as tentative.

Since a proposed mechanism consists of elementary steps, we can write a rate law for each step from the fact that for an elementary process the order equals the molecularity. Every multistep mechanism leads to a set of simultaneous differential equations analogous to those for the simple mechanism of Eq. (11.5-1). There is one independent differential equation for each elementary step of the mechanism.

Consider the reaction of Eq. (12.1-1):

$$2NO_2 + O_3 \longrightarrow N_2O_5 + O_2$$

If the reaction were elementary, the rate law for the forward reaction would be:

$$\text{rate} = \frac{d[N_2O_5]}{dt} = -\frac{d[O_3]}{dt} = k[NO_2]^2[O_3] \quad \begin{array}{l}\text{(rate law for the}\\ \text{one-step mechanism)}\end{array} \tag{12.4-1}$$

This rate law does not agree with the experimentally determined rate law, which is second order overall and first order with respect to each reactant.

The accepted mechanism of the forward reaction is

$$\begin{aligned} &(1) \quad NO_2 + O_3 \longrightarrow NO_3 + O_2 \\ &(2) \quad NO_3 + NO_2 \longrightarrow N_2O_5 \end{aligned} \tag{12.4-2}$$

where the reverse reactions of both steps are assumed to be negligible. For this mechanism we can write two simultaneous differential equations. One possible choice is

$$\frac{d[O_3]}{dt} = -k_1[NO_2][O_3] \tag{12.4-3a}$$

$$\frac{d[NO_5]}{dt} = k_2[NO_3][NO_2] \tag{12.4-3b}$$

We have some choice as to which concentration time derivatives are used in writing the equations, but for a two-step mechanism there are only two independent differential equations.

Exercise 12.8

Write the differential equation for $d[NO_3]/dt$ (it will have two terms on the right-hand side) and show that the right-hand side of this equation is equal to a linear combination (weighted sum or difference) of the right-hand sides of Eqs. (12.4-3a) and (12.4-3b), and that this equation is therefore not independent of the other two equations.

We do not attempt an exact solution of the set of equations in Eq. (12.4-3), but introduce two approximation schemes.

The Rate-Limiting Step Approximation

Let us assume that the second step of the mechanism in Eq. (12.4-3) is much more rapid than the first step. We mean by this assumption that the NO_3 produced by the first step is immediately consumed by the second step, which has a large rate constant. The rate of the second step is controlled by the first step since the second step cannot consume the NO_3 more rapidly than it is formed by the first step. We call the slow first step the *rate-limiting step* or *rate-determining step*. The second step does not affect the rate law of the forward reaction, which is just the differential equation of the slow first step:

$$-\frac{d[O_3]}{dt} = k_1[NO_2][O_3]$$

This rate law agrees with experiment. The mechanism of Eq. (12.1-2) is possibly correct, but other mechanisms might be found that produce the same rate law.

If a step other than the first step is rate-limiting, the steps prior to the rate-determining step will play a role in determining the rate law, but any steps after the rate-limiting step will play no role in determining the forward rate. We illustrate this with the gas-phase reaction

$$2O_3 \longrightarrow 3O_2$$

This reaction is thought to proceed by the mechanism

$$\begin{array}{lll} (1) & O_3 + M \rightleftharpoons O_2 + O + M & \text{(fast)} \\ (2) & O + O_3 \longrightarrow 2\,O_2 & \text{(slow)} \end{array} \qquad (12.4\text{-}4)$$

where M stands for any molecule, such as an O_2 molecule or a molecule of another substance that is present. An inelastic collision with the molecule M is needed to provide the energy for breaking the bond in the O_3 molecule. We assume that the second step is rate-determining. We do not include the reverse reaction for the rate-determining step and will obtain only the forward rate law. The rate differential equation for the second step is

$$\left.\frac{d[O_2]}{dt}\right|_{\text{step 2}} = 2k_2[O_3][O] \qquad (12.4\text{-}5)$$

where the subscript means that only the contribution of step 2 to the production of O_2 is included. The factor 2 is included because two molecules of O_2 occur in the chemical equation for the second step.

We now replace the differential equation for the first step by an algebraic equation. Both the forward and the reverse reaction of the first step are assumed to be rapid compared with the second step. We invoke the *equilibrium approximation* or *quasi-equilibrium approximation*, which is that all steps prior to the rate-limiting step are assumed to be at equilibrium. With this approximation the forward and reverse rates of the first step are set equal to each other:

$$k_1[O_3][M] = k_1'[O_2][O][M]$$

where the rate constant for a reverse reaction is labeled with a prime ($'$). This is equivalent to

$$K_1 = \frac{k_1}{k_1'} = \frac{[O_2][O][M]}{[O_3][M]} = \frac{[O_2][O]}{[O_3]} \qquad (12.4\text{-}6)$$

where K_1 is the equilibrium constant for the step (ignoring activity coefficients). This corresponds to the assumption that the slow second step removes a product of step 1 so slowly that step 1 can nearly relax to equilibrium as each product molecule is removed.

Equation (12.4-6) is now solved for [O]:

$$[\mathrm{O}] = K_1 \frac{[\mathrm{O_3}]}{[\mathrm{O_2}]}$$

This formula is substituted into Eq. (12.4-5) to obtain

$$\left.\frac{d[\mathrm{O_2}]}{dt}\right|_{\text{step 2}} = 2k_2[\mathrm{O_3}][\mathrm{O}] = 2k_2 \frac{k_1[\mathrm{O_3}]^2}{k_1'\,[\mathrm{O_2}]} = 2k_2 K_1 \frac{[\mathrm{O_3}]^2}{[\mathrm{O_2}]}$$

We now write the rate law for the reaction by noting that step 1 produces one molecule of O_2 for every two molecules produced by step 2:

$$\text{rate} = \frac{1}{3}\frac{d[\mathrm{O_2}]}{dt} = \frac{1}{3}\left(\left.\frac{d[\mathrm{O_2}]}{dt}\right|_{\text{step 2}} + \left.\frac{d[\mathrm{O_2}]}{dt}\right|_{\text{step 1}}\right)$$

$$\left(\frac{1}{3}\right)\left(\frac{3}{2}\right)\left.\frac{d[\mathrm{O_2}]}{dt}\right|_{\text{step 2}} = \left(\frac{1}{3}\right)\left(\frac{3}{2}\right)2k_2\frac{k_1[\mathrm{O_3}]^2}{k_1'\,[\mathrm{O_2}]} = k_2 K_1 \frac{[\mathrm{O_3}]^2}{[\mathrm{O_2}]} \tag{12.4-7}$$

The forward rate of the first step exceeds the reverse rate by an amount equal to half of the rate of step 2. Since both the forward and the reverse rate of the first step must be large compared to the rate of the second step, the forward and reverse rates are still nearly equal to each other. The concentration of O_2 (a product) occurs in this forward rate law, which holds only if some O_2 is already present. In general a product will occur in a forward rate law only if it is produced in a step prior to the rate-limiting step.

Exercise 12.9

For the gas-phase reaction

$$2\mathrm{NO} + 2\mathrm{H_2} \longrightarrow \mathrm{N_2} + 2\mathrm{H_2O}$$

the mechanism has been proposed

(1) $2\mathrm{NO} + \mathrm{H_2} \rightleftharpoons \mathrm{N_2} + \mathrm{H_2O_2}$
(2) $\mathrm{H_2O_2} + \mathrm{H_2} \longrightarrow 2\mathrm{H_2O}$

a. Find the rate law if the second step is rate-limiting.
b. Find the rate law if the reverse reaction of step 1 is omitted and this step is rate-limiting.

We can summarize the rate-limiting step approximation: If the first step is rate-limiting, the rate law is the rate law of the first step. If a step after the first step is rate-limiting, the rate law of the rate-limiting step is written. The concentrations of any reactive intermediates in the rate law of the rate-limiting step are replaced by expressions obtained by assuming that the steps prior to the rate-limiting step are at equilibrium. The result is the final approximate rate law.

The Steady-State Approximation

This approximation, which is also called the *quasi-steady-state approximation*, consists of the assumption that the rates of change of the concentrations of all *reactive* *intermediates* are negligibly small. We say that the reactive intermediates are approximately in a “steady state.” This is generally a good approximation if the concentrations of the intermediates are small since small variables have small time derivatives if they do not oscillate rapidly. Numerical simulations of sets of simultaneous rate differential equations have shown that the steady-state approximation often gives quite accurate results.[9] Improvements on the simple steady-state approximation have been developed.[10]

EXAMPLE 12.10

Apply the steady-state approximation to the mechanism of Eq. (12.4-4).

Solution

There is one independent equation for each step in any mechanism. One equation must be written for the rate of change of the concentration of a reactant or product. The other equations must be for the rate of change of concentrations of reactive intermediates. We write the two equations

$$\frac{d[\mathrm{O_2}]}{dt} = k_1[\mathrm{O_3}][\mathrm{M}] - k_1'[\mathrm{O_2}][\mathrm{O}][\mathrm{M}] + 2k_2[\mathrm{O}][\mathrm{O_3}] \tag{12.4-8a}$$

$$\frac{d[\mathrm{O}]}{dt} = k_1[\mathrm{O_3}][\mathrm{M}] - k_1'[\mathrm{O_2}][\mathrm{O}][\mathrm{M}] - k_2[\mathrm{O}][\mathrm{O_3}] \tag{12.4-8b}$$

We invoke the steady-state approximation by setting $d[\mathrm{O}]/dt$ approximately equal to zero:

$$k_1[\mathrm{O_3}][\mathrm{M}] - k_1'[\mathrm{O_2}][\mathrm{O}][\mathrm{M}] - k_2[\mathrm{O}][\mathrm{O_3}] \approx 0 \tag{12.4-8c}$$

We now have one differential equation and one algebraic equation. We subtract Eq. (12.4-8c) from Eq. (12.4-8a) to obtain a simpler differential equation:

$$\frac{d[\mathrm{O_2}]}{dt} = 3k_2[\mathrm{O}][\mathrm{O_3}] \tag{12.4-8d}$$

We solve Eq. (12.4-8c) for [O]:

$$[\mathrm{O}] = \frac{k_1[\mathrm{O_3}][\mathrm{M}]}{k_1'[\mathrm{O_2}][\mathrm{M}] + k_2[\mathrm{O_3}]} \tag{12.4-9}$$

We substitute this equation into Eq. (12.4-8d) to obtain the rate law

$$\frac{1}{3}\frac{d[\mathrm{O_2}]}{dt} = k_2[\mathrm{O_3}]\frac{k_1[\mathrm{O_3}][\mathrm{M}]}{k_1'[\mathrm{O_2}][\mathrm{M}] + k_2[\mathrm{O_3}]} = \frac{k_1k_2[\mathrm{O_3}]^2[\mathrm{M}]}{k_1'[\mathrm{O_2}][\mathrm{M}] + k_2[\mathrm{O_3}]} \tag{12.4-10}$$

Comparison of Eq. (12.4-10) with Eq. (12.4-7) shows that if

$$k_1'[\mathrm{O_2}][\mathrm{M}] \gg k_2[\mathrm{O_3}]$$

then Eq. (12.4-10) becomes the same as Eq. (12.4-7). This corresponds to the assumption on which the rate-limiting step approximation was based, that the forward and reverse rates of the first step are much larger than the rate of the second step.

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[9] L. A. Farrow and D. Edelson, *Int. J. Chem. Kinet.*, **6**, 787 (1974); V. Viossat and R. I. Ben-Aim, *J. Chem. Educ.*, **70**, 732 (1993); G. I. Gellene, *J. Chem. Educ.*, **72**, 196 (1995); R. A. B. Bond, B. S. Martincigh, J. R. Mika, and R. H. Simoyi, *J. Chem. Educ.*, **75**, 1158 (1998); V. Viossat and R. I. Ben-Aim, *J. Chem. Educ.*, **75**, 1165 (1998).

[10] See for example L. O. Jay, A. Sandu, F. A. Potra, and G. R. Carmichael, *SIAM Journal of Scientific Computing*, **18**, 182 (1997).

Exercise 12.10

Apply the steady-state approximation to the reaction of Exercise 12.9.

a. Find the rate law if the steady-state approximation is used without the reverse of step 1.

b. Find the rate law if the steady-state approximation is used with inclusion of the reverse of step 1.

c. Under what circumstances would the rate laws of parts a and b of Exercise 12.9 be obtained?

The Lindemann Mechanism

There is a problem with unimolecular gas-phase reactions that was recognized in the late 1800s. It is unreasonable to assume that a single molecule could undergo any process that breaks or forms chemical bonds without transferring energy to it or from it. For a time there was a theory called the *radiation theory*, which asserted that the necessary energy to break a bond in a unimolecular process came from the absorption of radiation. However, unimolecular reactions can occur in the absence of ultraviolet radiation, and visible and infrared radiation do not have enough energy to break chemical bonds. Around 1920 Lindemann[11] proposed that unimolecular processes are neither strictly unimolecular nor strictly elementary. Consider a class of gas-phase reactions represented by

$$\mathrm{A} \longrightarrow \mathrm{B} + \mathrm{C} \tag{12.4-11}$$

An example of a reaction in this class is the thermal decomposition of cyclopentene to form cyclopentadiene and hydrogen:

$$\mathrm{C_5H_8} \longrightarrow \mathrm{C_5H_6} + \mathrm{H_2}$$

The forward reaction for this class of reactions is found experimentally to be described by the following rate law:

$$\text{rate} = \frac{d[\mathrm{B}]}{dt} = \frac{k[\mathrm{A}]^2}{k' + k''[\mathrm{A}]} \tag{12.4-12}$$

where k, k', and k'' are temperature-dependent parameters.

Lindemann proposed the following mechanism, which was also advanced by Christiansen:[12]

$$(1) \quad \mathrm{A} + \mathrm{A} \rightleftharpoons \mathrm{A}^* + \mathrm{A} \tag{12.4-13a}$$

$$(2) \quad \mathrm{A}^* \longrightarrow \mathrm{B} + \mathrm{C} \tag{12.4-13b}$$

The symbol A* stands for a molecule of A that is in an excited state due to energy gained through the inelastic collision of step 1. If another substance, M, is present, Eq. (12.4-13a) can be replaced by

$$(1) \quad \mathrm{A} + \mathrm{M} \rightleftharpoons \mathrm{A}^* + \mathrm{M} \tag{12.4-13c}$$

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[11] F. A. Lindemann, *Trans. Faraday Soc.*, **17**, 598 (1922).

[12] J. S. Christiansen, Ph.D. Dissertation, University of Copenhagen, 1921.

One possibility is that the inelastic collision in step 1 excites various vibrations in the A molecule that can eventually combine to produce a transition state (activated complex) of some kind. We write two differential equations:

$$\frac{d[\mathrm{A}^*]}{dt} = k_1[\mathrm{A}]^2 - k_1'[\mathrm{A}][\mathrm{A}^*] - k_2[\mathrm{A}^*] \tag{12.4-14}$$

$$\frac{d[\mathrm{B}]}{dt} = k_2[\mathrm{A}^*] \tag{12.4-15}$$

where we follow the practice of labeling rate constants by the number of the step, with reverse rate constants labeled with a prime symbol ($'$). Imposing the steady-state approximation by setting $d[\mathrm{A}^*]/dt$ equal to zero gives

$$k_1[\mathrm{A}]^2 - k_1'[\mathrm{A}][\mathrm{A}^*] - k_2[\mathrm{A}^*] = 0$$

We solve this equation for [A*] to obtain

$$[\mathrm{A}^*] = \frac{k_1[\mathrm{A}]^2}{k_2 + k_1'[\mathrm{A}]} \tag{12.4-16}$$

We substitute this equation into Eq. (12.4-15) to give

$$\text{rate} = \frac{d[\mathrm{B}]}{dt} = \frac{k_1 k_2[\mathrm{A}]^2}{k_2 + k_1'[\mathrm{A}]} \tag{12.4-17}$$

This equation agrees with Eq. (12.4-12), with the parameters k, k', and k'' identified in terms of the rate constants for the steps of the mechanism.

Exercise 12.11

Derive the rate law that results if Eq. (12.4-13a) is replaced by Eq. (12.4-13c).

We write Eq. (12.4-17) in the form

$$\text{rate} = \frac{d[\mathrm{B}]}{dt} = \frac{k_1 k_2[\mathrm{A}]}{k_2 + k_1'[\mathrm{A}]}[\mathrm{A}] = k_{\mathrm{uni}}[\mathrm{A}] \tag{12.4-18}$$

where k_{uni} depends on [A] as indicated. If the pressure or concentration of substance A is large enough that $k_1'[\mathrm{A}] \gg k_2$, k_{uni} approaches a constant and the rate law is first order, which corresponds to our general assumption about unimolecular elementary reactions. If the pressure or concentration of substance A is small enough that $k_2 \gg k_1'[\mathrm{A}]$, the rate law approaches second order. This region of low pressure or concentration is called the *fall-off region*.

EXAMPLE 12.11

a. Find the rate law predicted by the mechanism of Eq. (12.4-13) if the second step is rate-determining. What condition turns the expression of Eq. (12.4-14) into this result?

b. Find the rate law predicted by the mechanism of Eq. (12.4-13) if the forward reaction of the first step is rate-determining.

Solution

a. The equilibrium approximation gives

$$K_1 = \frac{k_1}{k_1'} = \frac{[A][A^*]}{[A]^2} = \frac{[A^*]}{[A]} \tag{12.4-19}$$

When Eq. (12.4-19) is substituted into Eq. (12.4-15), we obtain the first-order rate law:

$$\text{rate} = \frac{d[B]}{dt} = k_2K_1[A] = \frac{k_2k_1}{k_1'}[A] \tag{12.4-20}$$

which is the same as Eq. (12.4-14) if the k_2 term in the denominator of the expression in Eq. (12.4-14) is deleted.

b. The rate law is second order in the case that $k_2 \gg k_1'[A]$:

$$\text{rate} = -\frac{d[A]}{dt} = k_1[A]^2 \tag{12.4-21}$$

Most unimolecular processes are apparently observed in the first-order (high-pressure or high-concentration) region, and we will continue to assume first-order kinetics for unimolecular steps in multistep mechanisms. Most proposed mechanisms do not include unimolecular steps, and there are not very many reactions known to have a one-step unimolecular mechanism. The first such reaction discovered was the isomerization of cyclopropane to propene. Others are the dissociation of molecular bromine and the decomposition of sulfuryl chloride.[13]

Mechanisms with More than Two Steps

If a proposed mechanism has three steps and if the third step is rate-limiting, the first two steps are assumed to be at equilibrium. Algebraic equations are written for these equilibria. If the steady-state approximation is applied, two differential equations for the rates of change of two reactive intermediates' concentrations are replaced by algebraic equations. In either case, there are two algebraic equations and a single differential equation. Mechanisms with four or more steps are treated analogously.

EXAMPLE 12.12

Find the rate law for the liquid-phase mechanism[a]

$$\begin{aligned}
&(1) \quad H^+ + HNO_2 + NO_3^- \rightleftharpoons N_2O_4 + H_2O && \text{(fast)} \\
&(2) \quad N_2O_4 \rightleftharpoons 2NO_2 && \text{(fast)} \\
&(3) \quad NO_2 + Fe(CN)_6^{3-} \longrightarrow \text{further intermediates} && \text{(slow)}
\end{aligned} \tag{12.4-22}$$

assuming that step (3) is rate-limiting.

[a] M. V. Twigg, *Mechanisms of Inorganic and Organometallic Reactions*, Plenum Press, New York, 1983, p. 39.

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[13] K. J. Laidler, *op. cit.*, pp. 150ff (note 3).

Solution

We write equilibrium expressions for steps (1) and (2):

$$K_1 = \frac{k_1}{k_1'} = \frac{[N_2O_4][H_2O]}{[H^+][HNO_2][NO_3^-]} \tag{12.4-23}$$

$$K_2 = \frac{k_2}{k_2'} = \frac{[NO_2]^2}{[N_2O_4]} \tag{12.4-24}$$

The rate differential equation for step (3) is

$$\text{rate} = k_3[NO_2][\text{fer}] \tag{12.4-25}$$

where [fer] stands for the concentration of the hexacyano iron(III) ion, $Fe(CN)_6^{3-}$, also known as the ferricyanide ion. Equations (12.4-23) and (12.4-24) are solved simultaneously. From Eq. (12.4-24)

$$[NO_2] = (K_2[N_2O_4])^{1/2} \tag{12.4-26}$$

From Eq. (12.4-23)

$$[N_2O_4] = \frac{K_1[H^+][HNO_2][NO_3^-]}{[H_2O]} \tag{12.4-27}$$

Equation (12.4-27) is substituted into Eq. (12.4-26) and the resulting equation is substituted into Eq. (12.4-25). The result is

$$\begin{aligned}\text{rate} &= \left(\frac{k_3K_2K_1[H^+][HNO_2][NO_3^-]}{[H_2O]}\right)^{1/2}[\text{fer}] \\ &= k_{\text{app}}[H^+]^{1/2}[HNO_2]^{1/2}[NO_3^-]^{1/2}[\text{fer}] \end{aligned} \tag{12.4-28}$$

We have incorporated the concentration of H_2O into k_{app}, the apparent rate constant, since the concentration of water is nearly constant in dilute aqueous solutions. The reaction is pseudo 5/2 order overall.

Exercise 12.12

Apply the steady-state approximation to the mechanism of Example 12.12. Omit the reverse reaction in step 2.

EXAMPLE 12.13

The following is a famous gas-phase reaction, with a mechanism proposed by Ogg.[a]

$$2N_2O_5 \longrightarrow 4NO_2 + O_2 \tag{12.4-29}$$

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[a] R. A. Ogg, Jr., *J. Chem. Phys.*, **15**, 337, 613 (1947).

The proposed mechanism is

$$\begin{aligned}&(1) \quad N_2O_5 \rightleftharpoons NO_2 + NO_3\\ &(2) \quad NO_2 + NO_3 \longrightarrow NO + O_2 + NO_2\\ &(3) \quad NO + NO_3 \longrightarrow 2NO_2\end{aligned} \tag{12.4-30}$$

Find the rate law using the steady-state approximation.

Solution

We write three differential equations and impose the steady-state approximation on the reactive intermediates NO_3 and NO:

$$-\frac{d[N_2O_5]}{dt} = k_1[N_2O_5] - k_1'[NO_2][NO_3] \tag{12.4-31}$$

$$\frac{d[NO_3]}{dt} = k_1[N_2O_5] - k_1'[NO_2][NO_3] - k_2[NO_2][NO_3] - k_3[NO][NO_3] \approx 0 \tag{12.4-32a}$$

$$\frac{d[NO]}{dt} = k_2[NO_2][NO_3] - k_3[NO][NO_3] \approx 0 \tag{12.4-32b}$$

The second equalities in Eqs. (12.4-32a) and (12.4-32b) give two simultaneous algebraic equations, which can be solved for $[NO_3]$ and [NO]. The results are

$$[NO] = \frac{k_2[NO_2]}{k_3} \tag{12.4-33a}$$

and

$$[NO_3] = \frac{k_1[N_2O_5]}{(k_1' + 2k_2)[NO_2]} \tag{12.4-33b}$$

When these two equations are substituted into Eq. (12.4-31), we obtain

$$\text{rate} = \frac{2k_1k_2}{k_1' + 2k_2}[N_2O_5] = k_{\text{app}}[N_2O_5] \tag{12.4-34}$$

so that the reaction is first order. Although the steady-state approximation usually leads to a rate law with a two-term denominator, this rate law corresponds to a definite order.

Exercise 12.13

a. Verify Eq. (12.4-34).

b. Assume that the second step of the mechanism of Example 12.13 is rate-limiting. Find the rate law for the reaction.

c. What assumptions will cause the steady-state result to become the same as the result of part b?

Deducing a Mechanism from a Rate Law

It is not a routine matter to decide what mechanism to propose once a rate law has been determined. However, you can sometimes use the following procedure:[14]

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[14] J. O. Edwards, E. F. Greene, and J. Ross, *J. Chem. Educ.*, **45**, 381 (1968).

A. Construct a possible set of steps.

   1. The steps must add up to the correct stoichiometry (possibly multiplying one or more of the steps by constants before adding).
   2. If the mechanism has two steps, there must be at least one reactive intermediate. Three steps require two reactive intermediates, etc. Reactive intermediates must cancel in the addition of the steps: They must occur on the right-hand side of one step equation and on the left-hand side of a later step equation.
   3. Let your knowledge of chemistry guide the choice of a proposed mechanism.

      i. The breaking of a weak bond is more likely than the breaking of a strong bond.
      ii. Reactive intermediates should have reasonable structures. In a gas-phase reaction, reactive intermediates with nonzero charges are not very likely, but free radicals are more likely. In a reaction in an aqueous solution, intermediates with nonzero charges are more likely than are free radicals.

B. Choose the rate-limiting step approximation or the quasi-steady-state approximation.

   1. If the experimental rate law has definite orders, try the rate-limiting step approximation.

      i. If no products appear in the rate law for the forward reaction, it is possible that the first step is the rate-limiting step.
      ii. If there are some reactants that do not appear in the rate law for the forward reaction, these substances occur only in steps after the rate-limiting step.
      iii. If negative orders or fractional orders occur in the rate law, the rate-limiting step cannot be the first step.
      iv. Substances with positive orders have a larger sum of stoichiometric coefficients on the left-hand sides of step equations up to and including the rate-limiting step, and substances with negative orders have a larger sum of stoichiometric coefficients on the right-hand sides of step equations prior to the rate-limiting step.

   2. If the rate law has a denominator with two or more terms, try the steady-state approximation.

C. Deduce the rate law for your proposed mechanism and compare it with the experimental rate law. If it does not agree, try again with another proposed mechanism.

Let us examine a few hypothetical examples.

EXAMPLE 12.14

If the stoichiometry of the reaction is

$$aA + bB \longrightarrow cC + dD \qquad (12.4\text{-}35)$$

and if the rate law is

$$\text{rate} = k_i[A]^a[B]^b \qquad (12.4\text{-}36)$$

find a mechanism that conforms to this rate law.

Solution

The mechanism could be

$$(1) \quad aA + bB \longrightarrow \text{reactive intermediates (slow, rate-limiting)}$$

$$(2) \quad \text{reactive intermediates} \longrightarrow cC + dD \text{ (fast)}$$

However, if $a + b > 3$, this is not very likely, since collisions of more than three particles are unlikely. If $a = 1$ and $b = 3$, a possible mechanism is

$$(1) \quad A + B \rightleftharpoons F \quad \text{(fast)}$$

$$(2) \quad F + B \rightleftharpoons G \quad \text{(fast)}$$

$$(3) \quad G + B \longrightarrow \text{further intermediates or products} \quad \text{(slow)}$$

where F and G are reactive intermediates.

Exercise 12.14

Assuming that step 3 is rate-limiting, show that the above mechanism leads to the rate law

$$\text{rate} = k[A][B]^3$$

EXAMPLE 12.15

If the stoichiometry of a reaction is

$$B + F \longrightarrow D + \text{other products} \tag{12.4-37}$$

and if the rate law is

$$\text{rate} = k_{\text{app}}[B]^{a+b}[F]^a[D]^{-a}$$

find a mechanism that conforms to this rate law.

Solution

The first step in the mechanism cannot be rate-limiting. The following mechanism can produce this rate law:

$$\begin{aligned} &(1) \quad B + F \rightleftharpoons A + D && \text{(fast in both directions)} \\ &(2) \quad aA + bB \longrightarrow \text{products} && \text{(slow, rate-limiting)} \end{aligned} \tag{12.4-38}$$

where A is a reactive intermediate. The equilibrium approximation applied to the first step gives

$$[A] = K_1 \frac{[B][F]}{[D]}$$

so that the rate expression is

$$\text{rate} = k_2\left(K_1 \frac{[B][F]}{[D]}\right)^a [B]^b = k_{\text{app}}[B]^{a+b}[F]^a[D]^{-a} \tag{12.4-39}$$

EXAMPLE 12.16

The stoichiometry of a reaction is

$$\mathrm{B} + 2\mathrm{F} + \mathrm{H} \longrightarrow \mathrm{D} + \text{other products}$$

and its rate law is

$$\text{rate} = k_{\text{app}}\frac{[\mathrm{B}][\mathrm{F}]^2[\mathrm{H}]}{[\mathrm{D}]}$$

Propose a mechanism.

Solution

The first step cannot be rate-limiting because of the presence of [D] in the denominator of the rate law. The following three-step mechanism corresponds to this rate law if the third step is rate-limiting:

$$\begin{array}{llll} (1) & \mathrm{B} + \mathrm{F} \rightleftharpoons \mathrm{A} + \mathrm{D} & \text{(fast)} & \\ (2) & \mathrm{F} + \mathrm{H} \rightleftharpoons \mathrm{G} & \text{(fast)} & \qquad (12.4\text{-}40) \\ (3) & \mathrm{A} + \mathrm{G} \longrightarrow \text{products} & \text{(slow)} & \end{array}$$

The rate law corresponding to this mechanism is

$$\text{rate} = k_3\left(K_1[\mathrm{B}][\mathrm{F}][\mathrm{D}]^{-1}\right)(K_2[\mathrm{F}][\mathrm{H}]) = k_3K_1K_2\frac{[\mathrm{B}][\mathrm{F}]^2[\mathrm{H}]}{[\mathrm{D}]} \qquad (12.4\text{-}41)$$

in agreement with the given rate law.

Exercise 12.15

Verify Eq. (12.4-41).

EXAMPLE 12.17

For the gaseous reaction

$$4\mathrm{HNO_3} \longrightarrow 4\mathrm{NO_2} + 2\mathrm{H_2O} + \mathrm{O_2} \qquad (12.4\text{-}42)$$

the rate law is found to be

$$\text{rate} = k_{\text{app}}[\mathrm{HNO_3}]^2[\mathrm{NO_2}]^{-1} \qquad (12.4\text{-}43)$$

Propose a possible mechanism.

Solution

We must have NO_2 on the right-hand side of some step prior to a rate-limiting step. One possibility is

$$\begin{array}{llll} (1) & \mathrm{HNO_3} \rightleftharpoons \mathrm{HO} + \mathrm{NO_2} & \text{(fast)} & \\ (2) & \mathrm{HO} + \mathrm{HNO_3} \longrightarrow \text{further intermediates/products} & \text{(slow)} & \qquad (12.4\text{-}44) \\ (3) & \text{further steps} & \text{(no effect on rate law)} & \end{array}$$

with step 2 assumed to be rate-limiting. The steps following step 2 do not affect the rate law.

Exercise 12.16

a. Show that the proposed mechanism in the previous example leads to the correct rate law.

b. If H_2O and NO_3 are the products of step 2, and if no further HNO_3 enters in later steps, propose steps 3 and 4 to complete the mechanism and give the correct stoichiometry.

Fractional orders can occur if one of the substances in the rate-limiting step is produced in a previous step with a stoichiometric coefficient greater than unity, as in Eq. (12.4-28).

The Temperature Dependence of Rates of Nonelementary Reactions

The rate law of a reaction corresponding to an assumed mechanism contains the rate constants of some or all of the steps of the mechanism. If the temperature dependence of these rate constants is known, the temperature dependence of the overall rate can be deduced. The rate law for the ozone decomposition of Eq. (12.4-4) is given by Eq. (12.4-7):

$$\text{rate} = \frac{1}{3}\left(\frac{d[\mathrm{O_2}]}{dt}\right) = k_{\text{app}}\frac{[\mathrm{O_3}]^2}{[\mathrm{O_2}]} = k_2\frac{k_1[\mathrm{O_3}]^2}{k_1'[\mathrm{O_2}]} \tag{12.4-45}$$

If each of the elementary rate constants is governed by the Arrhenius formula, Eq. (12.3-2), then the temperature dependence of the overall rate constant, k_{app}, is given by

$$\begin{aligned} k_{\text{app}} &= \frac{A_2A_1}{A_{1'}}\frac{e^{-E_{\text{a}2}/RT}e^{-E_{\text{a}1}/RT}}{e^{-E_{\text{a}1'}/RT}} = A_{\text{app}}\exp\left(-\frac{E_{\text{a}2}+E_{\text{a}1}-E_{\text{a}1'}}{RT}\right) \\ &= A_{\text{app}}\exp\left(-\frac{E_{\text{a,app}}}{RT}\right) \end{aligned} \tag{12.4-46}$$

where the apparent activation energy $E_{\text{a,app}}$ is

$$E_{\text{a,app}} = E_{a2} + E_{a1} - E_{a1'}$$

Since the ratio k_1/k_1' is equal to an equilibrium constant for the first step, we can rewrite Eq. (12.4-46) as

$$k_{\text{app}} = A_2\exp\left(-\frac{E_{\text{a}2}+\Delta G_1^\circ}{RT}\right) \tag{12.4-47}$$

It is possible that the apparent activation energy of a reaction with a multistep mechanism is negative. This occurs in the recombination of iodine atoms to form I_2, as described in Problem 12.41.

Exercise 12.17

The temperature dependence of a rate law corresponding to a steady-state approximation is more complicated than that of the previous example. Write the temperature dependence of the apparent first-order rate constant for the decomposition of N_2O_5 given in Eq. (12.4-34).

PROBLEMS

Section 12.4: Reaction Mechanisms and Rate Laws

12.17 The formation of phosgene

$$CO + Cl_2 \rightleftharpoons COCl_2$$

is thought to proceed by the mechanism[15]

$$\begin{array}{ll} (1) & Cl_2 \rightleftharpoons 2\,Cl \\ (2) & Cl + CO \rightleftharpoons COCl \\ (3) & COCl + Cl\,_2 \rightleftharpoons COCl_2 + Cl \end{array}$$

a. Find the forward rate law, assuming step (3) to be rate-limiting.

b. Find the reverse rate law, assuming step (3) to be rate-limiting.

c. Show that these expressions are consistent with the equilibrium constant expression.

d. Find the forward rate law, assuming the steady-state approximation.

12.18 For the reaction

$$4HNO_3 \longrightarrow 4NO_2 + 2H_2O + O_2$$

a proposed mechanism is

$$\begin{array}{ll} (1) & HNO_3 \rightleftharpoons HO + NO_2 \\ (2) & HO + HNO_3 \longrightarrow \text{further intermediates} \end{array}$$

where the second step is assumed to be rate-limiting. Find the rate law predicted by this mechanism.

12.19 An alternative mechanism for the reaction of Problem 12.17 is

$$\begin{array}{ll} (1) & Cl_2 \rightleftharpoons 2Cl \\ (2) & Cl + Cl_2 \rightleftharpoons Cl_3 \\ (3) & Cl_3 + CO \rightleftharpoons COCl_2 + Cl \end{array}$$

a. Find the forward rate law, assuming step (3) to be rate-limiting.

b. Find the reverse rate law, assuming step (3) to be rate-limiting.

c. Show that these expressions are consistent with the equilibrium constant expression.

12.20 The gas-phase reaction

$$C_2H_6 + H_2 \rightleftharpoons 2\,CH_4$$

is thought to proceed by the mechanism

$$\begin{array}{ll} (1) & C_2H_6 \rightleftharpoons 2\,CH_3 \\ (2) & CH_3 + H_2 \longrightarrow CH_4 + H \\ (3) & H + C_2H_6 \longrightarrow CH_4 + CH_3 \end{array}$$

where the back reactions for steps 2 and 3 are negligible.

a. Find the rate law assuming the quasi-steady-state approximation.

b. Find the rate law assuming that step 2 is rate-limiting.

12.21 Consider the hypothetical reaction:

$$A + 2B \longrightarrow C + D$$

Assume that the forward rate law is

$$\text{rate} = -\frac{d[A]}{dt} = k[A][B]^2$$

Propose two different mechanisms that conform to this rate law. Which of these two mechanisms is more plausible?

12.22 A plausible mechanism for the reaction of H_2 and I_2 is[16]

$$\begin{array}{ll} (1) & I_2 \rightleftharpoons 2I \\ (2) & H_2 + I \rightleftharpoons H_2I \\ (3) & H_2I + I \rightleftharpoons 2HI \end{array}$$

a. Obtain the rate law for the forward reaction for this mechanism using the steady-state approximation (omit the reverse reaction of step 3). The experimental rate law is second order, and the reaction was thought for many decades to be elementary.

b. Obtain the rate law for the reverse reaction using the steady-state approximation.

c. Equate the forward and reverse rates to obtain an expression for the equilibrium constant.

12.23 Obtain the rate law for the forward reaction for the mechanism of the previous problem assuming that step 3 is rate-limiting.

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[15] K. J. Laidler, *op. cit.*, p. 301ff (note 3).

[16] J. H. Sullivan, *J. Chem. Phys.*, **46**, 73 (1967).

12.24 For the reaction

$$3HNO_2 \longrightarrow H_2O + 2NO + H^+ + NO_3^-$$

assume the mechanism

$$\begin{array}{ll} (1) & 2HNO_2 \rightleftharpoons NO + NO_2 + H_2O \\ (2) & 2NO_2 \rightleftharpoons N_2O_4 \\ (3) & N_2O_4 + H_2O \longrightarrow HNO_2 + H^+ + NO_3^- \end{array}$$

Find the rate law, assuming the third step to be rate-limiting.

12.25 **a.** Using the steady-state approximation, find the rate law corresponding to the mechanism

$$\begin{array}{ll} (1) & NO_2NH_2 + OH^- \rightleftharpoons H_2O + NO_2NH^- \\ (2) & NO_2NH^- \longrightarrow N_2O + OH^- \end{array}$$

b. Tell how you would determine experimentally whether one or the other of the two steps is rate-determining.

12.26 The reaction equation for the nitration of an aromatic compound in an acidic solution can be written

$$ArH + HNO_3 \longrightarrow ArNO_2 + H_2O$$

where Ar stands for an aromatic group such as the phenyl group, C_6H_5. A proposed mechanism is[17]

$$\begin{array}{ll} (1) & HNO_3 + HA \rightleftharpoons H_2NO_3^+ + A^- \\ (2) & H_2NO_3^+ \rightleftharpoons H_2O + NO_2^+ \\ (3) & NO_2^+ + ArH \longrightarrow ArNO_2H^+ \\ (4) & ArNO_2H^+ + A^- \longrightarrow ArNO_2 + HA \end{array}$$

where HA represents a weak acid such as HSO_4^-.

a. Find the rate law assuming that step (2) is rate-limiting.

b. Find the rate law assuming that step (3) is rate-limiting.

c. Find the rate law assuming the steady-state approximation.

12.27 The reaction

$$2NO + 2H_2 \longrightarrow N_2 + 2\,H_2O$$

is found to be second order in NO and first order in H_2 (third order overall). Propose a mechanism that gives this rate law.

12.28 The reaction

$$2Cl_2O + 2N_2O_5 \longrightarrow 2NO_3Cl + 2NO_2Cl + O_2$$

is found to be zero order with respect to Cl_2O and first order with respect to N_2O_5. Devise a mechanism for the reaction that corresponds to this rate law.

12.29 The reaction

$$2NO_2Cl \longrightarrow 2NO_2 + Cl_2$$

is assumed to have the mechanism

$$\begin{array}{ll} (1) & NO_2Cl \rightleftharpoons NO_2 + Cl \\ (2) & Cl + NO_2Cl \longrightarrow NO_2 + Cl_2 \end{array}$$

a. Find the rate law assuming the second step to be rate-limiting.

b. Find the rate law assuming the steady-state approximation.

12.30 **a.** Find the rate law for the reaction

$$2NO(g) + O_2(g) \longrightarrow N_2O_4(g)$$

assuming the mechanism

$$\begin{array}{ll} (1) & NO + O_2 \rightleftharpoons NO_3 \quad \text{(fast)} \\ (2) & NO_3 + NO \longrightarrow N_2O_4 \\ & \text{(slow, rate-limiting)} \end{array}$$

b. Propose a different two-step mechanism that corresponds to the same rate law.

c. Find the rate law for the same mechanism using the steady-state approximation.

12.31 For the reaction

$$2ICl + H_2 \longrightarrow I_2 + 2HCl$$

the forward rate law is found to be

$$\text{rate} = \frac{d[I_2]}{dt} = k[ICl][H_2]$$

Propose a mechanism that predicts this rate law.

12.32 For the reaction

$$2ICl + H_2 \longrightarrow I_2 + 2HCl$$

a proposed mechanism is

$$\begin{array}{lll} (1) & 2\,ICl \rightleftharpoons I_2 + Cl_2 & \text{(fast in both directions)} \\ (2) & H_2 + Cl_2 \longrightarrow 2\,HCl & \text{(slow, rate-limiting)} \end{array}$$

Find the rate law that corresponds to this mechanism.

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[17] R. J. Gillespie, E. D. Hughes, C. K. Ingold, and R. I. Reed, *Nature*, **163**, 599 (1949).

12.33 **a.** Find the rate law for the reaction

$$H^+ + I^- + H_2O_2 \rightleftharpoons H_2O + HIO$$

assuming the mechanism

$$\begin{array}{ll} (1) & H^+ + H_2O_2 \rightleftharpoons H_3O_2^+ \quad \text{(fast)} \\ (2) & H_3O_4^+ + I^- \longrightarrow H_2O + HIO \\ & \text{(slow, rate-limiting)} \end{array}$$

b. Find the rate law assuming the mechanism

$$\begin{array}{ll} (1) & H^+ + I^- \rightleftharpoons HI \\ (2) & H_2O_2 + HI \longrightarrow H_2O + HIO \\ & \text{(slow, rate-limiting)} \end{array}$$

12.34 The reaction

$$H_2O_2 + 3I^- + 2\,H^+ \longrightarrow 2H_2O + I_3^-$$

obeys the rate law[18]

$$-\frac{d[H_2O_2]}{dt} = k_1[H_2O_2][I^-] + k_2[H_2O_2][I^-][H^+]$$

The two terms presumably correspond to two competing mechanisms. Propose a reasonable mechanism for the first term, and two different reasonable mechanisms for the second term.

12.35 The hypothetical reaction

$$2A \longrightarrow 2B + C$$

obeys the rate law

$$\text{rate} = \frac{d[C]}{dt} = k\frac{[A]^2}{[B]}$$

Propose a mechanism consistent with this rate law.

12.5 Chain Reactions

Chain mechanisms involve reactive intermediates that are called *chain carriers*. A chain mechanism usually contains an *initiation step*, in which chain carriers are formed; one or more *chain propagation steps* in which products are formed and in which chain carriers are produced as well as being consumed; and a *chain termination step* in which chain carriers are consumed without being replaced. Since chain carriers are produced as well as being consumed, the reaction can continue without further initiation steps.

The following gas-phase reaction has been identified as a chain reaction:

$$H_2 + Br_2 \longrightarrow 2HBr \tag{12.5-1}$$

The empirical rate law for the forward reaction in the presence of some HBr is

$$-\frac{d[H_2]}{dt} = \frac{k_a[H_2][Br_2]^{1/2}}{1 + k_b[HBr]/[Br_2]} \tag{12.5-2}$$

where k_a and k_b are temperature-dependent parameters. The accepted mechanism for the forward reaction is[19]

$$\begin{array}{ll} (1) & Br_2 \rightleftharpoons 2\,Br \\ (2) & Br + H_2 \rightleftharpoons HBr + H \\ (3) & H + Br_2 \longrightarrow HBr + Br \end{array} \tag{12.5-3}$$

Step 1 is the initiation step. The forward reactions of steps 2 and 3 are chain propagation steps, producing the two chain carriers, Br and H. The reverse reaction of step 1 is the termination step. The reverse reactions of steps 2 and 3 regenerate chain carriers but consume the product. They are called *inhibition processes*.

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[18] D. Benson, *Mechanisms of Inorganic Reactions in Solution*, McGraw-Hill, New York, 1968, p. 6ff.

[19] K. J. Laidler, *op. cit.*, p. 291ff (note 3).

Once bromine atoms are formed in the initiation step, the reaction can proceed without further initiation. The *chain length* γ is defined as the average number of times the cycle of the two propagation steps is repeated for each initiation step. It is possible to have a chain length as large as 10^6. In this reaction, the initiation step gives two Br atoms, and each of these gives two molecules of HBr per cycle, so that the number of molecules of product for each initiation step is equal to 4 times the chain length.

To obtain the rate law we apply the steady-state approximation. For a three-step mechanism we must write three differential equations. We choose the time derivatives of $[H_2]$ and the concentrations of the two chain carriers [H] and [Br]. We choose $[H_2]$ instead of $[Br_2]$ or [HBr] because H_2 occurs in only one step of the mechanism and will give a simpler differential equation. The simultaneous differential equations are

$$-\frac{d[H_2]}{dt} = k_2[Br][H_2] - k_2'[HBr][H] \tag{12.5-4a}$$

$$\begin{aligned}\frac{d[Br]}{dt} = 2k_1[Br_2] - k_2[Br][H_2] + k_3[H][Br_2] \\ + k_2'[HBr][H] - 2k_1'[Br]^2 \approx 0\end{aligned} \tag{12.5-4b}$$

$$\frac{d[H]}{dt} = k_2[Br][H_2] - k_2'[HBr][H] - k_3[H][Br_2] \approx 0 \tag{12.5-4c}$$

We have applied the steady-state approximation and set the time derivatives of the concentration of the chain carriers H and Br equal to zero. To solve the algebraic versions of Eqs. (12.5-4b) and (12.5-4c), we add Eqs. (12.5-4b) and (12.5-4c) to give

$$k_1[Br_2] - k_1'[Br]^2 = 0 \tag{12.5-5a}$$

which is the same as

$$[Br] = \left(\frac{k_1}{k_1'}\right)^{1/2} [Br_2]^{1/2} \tag{12.5-5b}$$

Equation (12.5-5b) is the same equation that would result from assuming that step 1 is at equilibrium. The relation of Eq. (12.5-5b) is substituted into Eq. (12.5-4b) or Eq. (12.5-4c) to give (after several steps of algebra)

$$[H] = \frac{k_2\left(k_1/k_1'\right)^{1/2} [H_2][Br_2]^{1/2}}{k_3[Br_2] + k_2'[HBr]} \tag{12.5-6}$$

We now simplify Eq. (12.5-4a) by noticing that the first two terms in Eq. (12.5-4c) are the same as the two terms on the right-hand side of Eq. (12.5-4a), so that

$$-\frac{d[H_2]}{dt} = k_3[H][Br_2]$$

When Eq. (12.5-6) is substituted into this equation, we have

$$-\frac{d[H_2]}{dt} = \frac{k_2\left(k_1/k_1'\right)^{1/2} [H_2][Br_2]^{1/2}}{1 + \dfrac{k_2'[HBr]}{k_3[Br_2]}} \tag{12.5-7}$$

which reproduces the empirical rate law with the following expressions for the empirical parameters:

$$k_a = k_2\left(\frac{k_1}{k_1'}\right)^{1/2} \tag{12.5-8a}$$

$$k_b = \frac{k_2'}{k_3} \tag{12.5-8b}$$

Exercise 12.18

Verify Eqs. (12.5-6) and (12.5-7).

Photochemical Chain Reactions

The energy to break the Br–Br bond in the initiation step of a chain reaction can be supplied by ultraviolet light instead of by an inelastic molecular collision.

Exercise 12.19

The Br–Br bond energy in Table A.9 of Appendix A is 193 kJ mol^{-1}. Calculate the minimum frequency and maximum wavelength of light with sufficient energy per photon to break a Br–Br bond.

The initiation step and the termination step of the photochemically initiated reaction of H_2 and Br_2 are

$$\begin{aligned} &(1) \quad Br_2 + h\nu \longrightarrow 2\,Br \\ &(1') \quad 2Br \longrightarrow Br_2 \end{aligned} \tag{12.5-9}$$

where we use the expression for the energy of a photon, $h\nu$, as a symbol for the photon. The rest of the mechanism is just as in Eq. (12.5-3). The termination reaction is the same as before.

The Laws of Photochemistry

Photochemical reactions are described by two empirical laws. The first is the *Grotthuss–Draper law*, which states that only absorbed radiation is effective in producing a photochemical change. A large intensity of incident light will not produce a photochemical effect if none of it is absorbed. The second law is the *Stark–Einstein law of photochemical equivalence*, which states that for each photon absorbed, one molecule undergoes the initial photochemical process. With high-intensity laser light a molecule can absorb several photons in a single photochemical process, and this provides an exception to the Stark–Einstein law.[20]

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[20] See, for example, L. Li, M. Wu, and P. M. Johnson, *J. Chem. Phys.*, **86**, 1131 (1987).

The Rate Law of the Photochemical Reaction

The rate of the initiation step of Eq. (12.5-9) is proportional to the rate at which photons are absorbed. We let J be the average rate of absorption of light, measured in *einsteins* per unit volume per second (one einstein is 1 mol of photons). The rate of photochemical production of Br atoms is equal to $2J$, so that the steady-state equation for Br atoms is now

$$\frac{d[\mathrm{Br}]}{dt} = 2J - k_2[\mathrm{Br}][\mathrm{H_2}] + k_3[\mathrm{H}][\mathrm{Br_2}] + k_2'[\mathrm{HBr}][\mathrm{H}] - 2k_1'[\mathrm{Br}]^2 \approx 0 \qquad (12.5\text{-}10)$$

We neglect the collisional (thermal) production of Br atoms, which is much slower than the photochemical production. The steady-state equation for [H] is still Eq. (12.5-4c): When this equation is added to Eq. (12.5-10), we obtain

$$J - k_1'[Br]^2 = 0 \qquad (12.5\text{-}11)$$

Equation (12.5-11) is combined with Eq. (12.5-5) and substituted into Eq. (12.5-7) to obtain the rate law

$$-\frac{d[\mathrm{H_2}]}{dt} = \frac{k_2\left(1/k_1'\right)^{1/2}[\mathrm{H_2}]J^{1/2}}{1 + \dfrac{k_2'[\mathrm{HBr}]}{k_3[\mathrm{Br_2}]}} \qquad (12.5\text{-}12)$$

which agrees with experiment.

Exercise 12.20

Verify Eq. (12.5-12).

The *quantum yield* Φ of a photochemical reaction is defined as the number of molecules of product produced per photon absorbed. It is also equal to the number of moles of product per einstein of photons absorbed. The quantum yields of photochemical reactions can range from nearly zero to about 10^6. Quantum yields greater than unity ordinarily indicate a chain reaction.

Reaction of Hydrogen with the Other Halogens

Hydrogen reacts in the gas phase with chlorine or iodine as well as with bromine, but there are differences between the three reactions. The reaction of hydrogen with chlorine is inhibited by oxygen. An approximate rate expression for the thermally initiated reaction is

$$\frac{d[\mathrm{HCl}]}{dt} = \frac{k_{\mathrm{l}}J[\mathrm{H_2}][\mathrm{Cl_2}]^2}{k_{\mathrm{m}}[\mathrm{Cl_2}] + [\mathrm{O_2}]([\mathrm{H_2}] + k_{\mathrm{n}}[\mathrm{Cl_2}])} \qquad (12.5\text{-}13a)$$

where k_{l}, k_{m}, and k_{n} are temperature-dependent parameters. An approximate empirical rate law for the photochemical reaction is[21]

$$\frac{d[\mathrm{HCl}]}{dt} = \frac{k_{\mathrm{a}}J[\mathrm{H_2}][\mathrm{Cl_2}]}{k_{\mathrm{b}}[\mathrm{C1_2}] + [\mathrm{O_2}]([\mathrm{H_2}] + k_{\mathrm{c}}[\mathrm{Cl_2}])} \qquad (12.5\text{-}13b)$$

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[21] K. L. Laidler, *op. cit.*, p. 295ff (note 3).

where k_a, k_b, and k_c are temperature-dependent parameters. In the complete absence of oxygen, the photochemical reaction becomes first order in hydrogen and zero order in chlorine (except for the dependence of J on the concentration of chlorine). However, k_b is sufficiently small that partial pressures of oxygen down to a few hundredths of a torr are effective in inhibiting the reaction. Another difference between the hydrogen–chlorine reaction and the hydrogen–bromine reaction is that the recombination of chlorine atoms, analogous to process $1'$ in Eq. (12.5-9) is unimportant, whereas termination of chains by combination of chlorine atoms with the surface of the reaction vessel and with other molecules (such as oxygen) is important. In the thermally initiated reaction the dissociation of the Cl_2 molecules at the surface of the reaction vessel is apparently important.[22] A third difference is that the hydrogen–chlorine reaction gives off enough heat that the reaction mixture can heat up, speeding up the reaction and causing an explosion. The mechanisms and the derivations of the rate laws are found in reference 3.

The hydrogen–iodine reaction was mentioned in the previous chapter:

$$H_2 + I_2 \longrightarrow 2\,HI \tag{12.5-14}$$

This reaction is not primarily a chain reaction except at high temperatures. The reaction obeys second-order kinetics and was thought at one time to proceed by a bimolecular elementary mechanism. We now know that several mechanisms compete, including the elementary mechanism. The chain mechanism analogous to Eq. (12.5-3) is dominant above 750 K but is unimportant below 600 K. The following non-chain mechanism appears to be dominant below 600 K:[23]

$$\begin{array}{lll} (1) & I_2 \rightleftharpoons 2I & \text{(fast)} \\ (2) & 2I + H_2 \longrightarrow 2HI & \text{(slow)} \end{array} \tag{12.5-15}$$

Exercise 12.21

a. Find the rate law for the mechanism of Eq. (12.5-15) using the rate-limiting step approximation.
b. Find the rate law for the mechanism of Eq. (12.5-15) using the steady-state approximation.

Branching-Chain Reactions

The combustion of hydrogen with oxygen is a chain reaction that appears to proceed by a branching-chain mechanism. This means that some propagation steps produce more chain carriers than they consume, accelerating the reaction and possibly producing an explosion. A simplified version of the accepted mechanism of the hydrogen–oxygen reaction is[24]

$$\begin{array}{lll} (1) & H_2 + \text{wall} \longrightarrow H(\text{adsorbed}) + H & \text{(initiation)} \\ (2) & H + O_2 \longrightarrow OH + O & \text{(branching)} \\ (3) & O + H_2 \longrightarrow OH + H & \text{(branching)} \\ (4) & OH + H_2 \longrightarrow H_2O + H & \text{(propagation)} \end{array}$$

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[22] R. N. Pease, *J. Am. Chem. Soc.*, **56**, 2388 (1934).

[23] K. L. Laidler, *op. cit.*, p. 295ff (note 3). See also J. H. Sullivan, *J. Chem. Phys.*, **46**, 73 (1967).

[24] S. W. Benson, *The Foundations of Chemical Kinetics*, McGraw-Hill, New York, 1960, p. 454ff.

(5) $H + O_2 + M \longrightarrow HO_2 + M$ (termination)
(6) $H + \text{wall} \longrightarrow \text{stable species}$ (termination)
(7) $HO + \text{wall} \longrightarrow \text{stable species}$ (termination)
(8) $HO_2 + \text{wall} \longrightarrow \text{stable species}$ (termination)

In step 5, M represents any molecule that can collide inelastically with H and O_2. This could be an H_2 or an O_2 molecule, but could be a molecule of another substance. Steps 2 and 3 consume one chain carrier but provide two chain carriers, so that as these steps occur the number of chain carriers increases and an explosion can occur. Since several processes at the walls of the vessel are included in the mechanism the ratio of the surface area to the volume is important in determining whether an explosion will occur.

PROBLEMS

Section 12.5: Chain Reactions

12.36 The chain mechanism for the

$$H_2 + I_2 \rightleftharpoons 2HI$$

reaction is

(1) $I_2 \rightleftharpoons 2I$
(2) $I + H_2 \rightleftharpoons HI + H$
(3) $H + I_2 \longrightarrow HI + I$

Note that no reverse reaction is included in step 3, and that the initiation step (step 1) is not included in adding the steps to obtain the stoichiometric equation.

a. Find the rate law using the steady-state approximation.

b. Find the rate law using a hybrid of the rate-limiting step approximation and the steady-state approximation: Assume that step 1 is at equilibrium, and assume a steady state for the concentration of H.

c. What must be assumed to make the results of parts a and b agree with the experimental rate law, which is first order in H_2 and in I_2 and second order overall?

12.37 The thermal decomposition of acetaldehyde follows the reaction equation $CH_3CHO \longrightarrow CH_4 + CO$. The following mechanism is proposed[25]

(1) $CH_3CHO \longrightarrow CH_3 + CHO$
(2) $CH_3CHO + CH_3 \longrightarrow CH_4 + CO + CH_3$

with the following termination steps, which make only traces of C_2H_6 and H_2 and are not included in the stoichiometric equation:

(3) $2\,CH_3 \longrightarrow C_2H_6$
(4) $2\,CHO \longrightarrow 2\,CO + H_2$

a. Find the rate law assuming that the concentration of CH_3 is steady.

b. Add a reverse reaction to step 1 and find the rate law in the steady-state approximation.

c. Johnston[26] gives a mechanism in which step 2 is replaced by the steps

(2a) $CH_3 + CH_3CHO \longrightarrow CH_3CO + CH_4$
(2b) $CH_3CO \longrightarrow CH_3 + CO$

Repeat the steady-state solution using this mechanism, again ignoring the termination steps. What must be assumed to bring the two results into agreement?

Summary of the Chapter

A chemical reaction mechanism is the sequence of elementary steps that accomplishes the reaction. A gas-phase elementary process involves a single molecular collision. A liquid-phase "elementary" process is actually preceded and followed by diffusion

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[25] J. L. Latham, *Elementary Reaction Kinetics*, 2nd ed., Butterworths, London, 1969, p. 128.
[26] H. S. Johnston, *Gas Phase Reaction Rate Theory*, Ronald Press, New York, 1966, p. 36.

processes. If the diffusion of the reactant molecules is a slow process compared to the chemical part, the reaction is called a diffusion-limited or diffusion-controlled reaction. If the rate is limited by the chemical part, the reaction is called activation-limited. In either a gaseous or liquid-state elementary process, the molecularity of a substance is equal to its order.

The empirical Arrhenius formula for the temperature dependence of elementary rate constants was presented. This empirical formula was based on an idea that "activated" molecules with high energy are necessary for the reaction to occur and that the population of molecules with a characteristic activation energy is given by the Boltzmann probability distribution. We presented the collision theory of bimolecular reaction rates, using first the assumption that all collisions with a relative kinetic energy greater than a critical value would lead to reaction.

A set of rate differential equations can be constructed for a mechanism, with one equation for each elementary step. These simultaneous differential equations cannot generally be solved analytically. We introduced two approximation schemes, the rate-limiting-step approximation and the steady-state approximation. These schemes are used to deduce an approximate rate law corresponding to a given mechanism. Example mechanisms were studied, including chain reactions, in which propagation steps are included in the mechanism. Suggestions were made for proposing a mechanism to correspond to an experimental rate law.

ADDITIONAL PROBLEMS

12.38 For the reaction

$$H_2 + I_2 \longrightarrow 2HI$$

the value of ΔU is $-8.2\,\mathrm{kJ\,mol^{-1}}$.

a. Find the value of the activation energy for the reverse reaction, using information in the chapter.

b. Using thermodynamic data and the Gibbs–Helmholtz equation, find the value of the equilibrium constant for the reaction at 373.15 K. State any assumptions.

c. Find the value of the reverse rate constant at 373.15 K, using your result from part b and data in the chapter.

12.39 The thermal decomposition of ethyl bromide (bromoethane) follows first-order kinetics, and the rate constant is reported to be equal to $0.1068\,\mathrm{s^{-1}}$ at 500°C and equal to $6.4529\,\mathrm{s^{-1}}$ at 600°C.

a. Find E_a and A in the Arrhenius formula for this reaction.

b. Find the value of the rate constant at 550°C.

c. If the initial pressure of bromoethane at 550°C is 1.000 atm, find the partial pressure of bromoethane at a reaction time of 10.00 s and at a reaction time of 100.0 s.

12.40 The decomposition of ethyl bromide (bromoethane), C_2H_5Br, in the gas phase is observed to be a first-order reaction.

a. Assuming the Lindemann mechanism, write the steps of the mechanism. The products are ethene, C_2H_4, and hydrogen bromide, HBr. What must be the case for the first-order rate law to be observed?

b. The value of the rate constant at 527°C is reported to be equal to $0.0361\,\mathrm{s^{-1}}$. Find the half-life of the reaction at this temperature. Neglect any reverse reaction.

c. If the original pressure of pure ethyl bromide is equal to 1.00 atm, find the partial pressure of each substance after an elapsed time of 60 seconds. Neglect any reverse reaction.

d. The rate constant is reported to be equal to $1.410\,\mathrm{s^{-1}}$ at 627°C. Find the value of E_a and A in the Arrhenius formula for the reaction.

12.41 The gas-phase recombination of iodine atoms proceeds in the presence of a second substance, abbreviated by M:

$$I + I + M \longrightarrow I_2 + M$$

Two mechanisms are proposed.[27] The first is

$$\begin{aligned} &(1) \quad \mathrm{I} + \mathrm{I} \rightleftharpoons \mathrm{I_2}^* \\ &(2) \quad \mathrm{I_2}^* + \mathrm{M} \longrightarrow \mathrm{I_2} + \mathrm{M} \end{aligned}$$

where I_2* represents a high-energy molecule. The second mechanism is

$$\begin{aligned} &(1) \quad \mathrm{I} + \mathrm{M} + \mathrm{M} \rightleftharpoons \mathrm{IM} + \mathrm{M} \\ &(2) \quad \mathrm{IM} + \mathrm{I} \longrightarrow \mathrm{I_2} + \mathrm{M} \end{aligned}$$

where IM represents a loosely bound molecule that is not necessarily capable of permanent existence.

a. Find the rate law for each mechanism, using the rate-limiting step approximation and assuming that the second step in each mechanism is rate-limiting.

b. It is found that the activation energy for the overall reaction is negative. If M stands for an argon atom, then the rate constant $k = 8.3 \times 10^{-33}\ \mathrm{cm^6\ s^{-1}}$ at 300 K, and $k = 1.3 \times 10^{33}\ \mathrm{cm^6\ s^{-1}}$ at 1300 K. Note that the concentrations are expressed in atoms per cubic centimeter for these values of the rate constants. Find the value of the activation energy and the value of the preexponential factor.

c. Explain the fact that the activation energy is negative.

12.42 The gas-phase reaction

$$\mathrm{H_2} + \mathrm{I_2} \rightleftharpoons 2\mathrm{HI}$$

is second order in each direction (the orders are equal to the stoichiometric coefficients). At 500 K, the value of $\Delta_f G^\circ(\mathrm{HI})$ is $-10.088\ \mathrm{kJ\ mol^{-1}}$.

a. Find the value of the equilibrium constant for the reaction at 500 K.

b. The forward rate constant is represented by the Arrhenius formula with $A = 5.47 \times 10^9\ \mathrm{L\ mol^{-1}\ s^{-1}}$ and $E_a = 170\ \mathrm{kJ\ mol^{-1}}$. Find the value of the forward rate constant at 500 K.

c. Find the value of the reverse rate constant at 500 K.

d. The value of ΔU° for the reaction is -11.244 kJ $\mathrm{mol^{-1}}$ at 500 K. Find the value of the activation energy for the reverse reaction.

12.43 Label each statement as either true or false. If a statement is true only under special circumstances, label it as false.

a. A useful rule of thumb is that the rate of a chemical reaction doubles for each increase in temperature of 10°C.

b. Every chemical reaction proceeds by a multistep mechanism.

c. Every reaction mechanism is a sequence of steps that follows each other sequentially.

d. In a typical gas-phase chemical reaction, only a small fraction of molecular collisions leads to reaction.

e. Termolecular steps are relatively rare in chemical reaction mechanisms.

f. Diffusion-limited reactions are rapid because diffusion is an inherently rapid process.

g. Only mechanisms with branching chains can lead to explosions.

12.44 For the reaction of CH_3Br and I^- in water, the Arrhenius parameters are $A = 1.68 \times 10^{10}\ \mathrm{L\ mol^{-1}\ s^{-1}}$, $E_a = 76.40\ \mathrm{kJ\ mol^{-1}}$.

a. The activation energy has almost exactly the same value if methanol is the solvent. Do you think that the reaction is diffusion-controlled or activation-controlled? Explain your answer.

b. Find the value of the rate constant at 50.0°C.

c. If the initial concentrations are both equal to $0.500\ \mathrm{mol\ L^{-1}}$, find the half-life of the reaction. Neglect any reverse reaction.

d. If the initial concentration of CH_3Br is $0.500\ \mathrm{mol\ L^{-1}}$ and that of I^- is $0.350\ \mathrm{mol\ L^{-1}}$, find the time required for 50.0% of the CH_3Br to react. Neglect any reverse reaction.

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[27] H. S. Johnston, *op. cit.*, p. 253ff. (note 26).

13

Chemical Reaction Mechanisms II: Catalysis and Miscellaneous Topics

PRINCIPAL FACTS AND IDEAS

1. Catalysts provide alternate mechanisms for chemical reactions.
2. If a reaction can occur by two or more competing mechanisms, according to the law of detailed balance, each one must separately be at equilibrium if the reaction is at equilibrium.
3. Chemical reactions can produce oscillations if autocatalytic steps occur in the mechanism of the reaction.
4. Polymers are created by covalently bonding monomer molecules together in chains or networks. The reaction kinetics of polymer formation can be studied by methods already introduced.
5. Nonequilibrium electrochemical cells can be studied by methods that we have introduced in previous chapters.
6. Reaction mechanisms can sometimes be verified by direct observation of reaction intermediates.

13.1 Catalysis

Jons Jakob Berzelius, 1779–1848, was a great Swedish chemist who dominated the field of chemistry for several decades and who invented the present system of chemical symbols for the elements.

A substance that increases the rate of a chemical reaction but does not appear in its stoichiometric equation is called a *catalyst*. This term was coined in 1836 by Berzelius from the Greek words *kata* ("wholly") and *lyein* ("to loosen").[1] Catalysis can be divided into three classes: In *homogeneous catalysis* all substances involved in the reaction, including the catalyst, occur in the same phase. In *heterogeneous catalysis* the catalyzed reaction occurs at the boundary between two phases (usually on the surface of a solid catalyst). *Enzyme catalysis* is a special case of homogeneous catalysis, which we will discuss separately. A catalyst generally provides an alternative mechanism involving the catalyst that competes with the uncatalyzed mechanism. If the catalyzed mechanism is faster than the uncatalyzed mechanism, the observed rate of the reaction is primarily due to the catalyzed mechanism, although the reaction is also still proceeding by the uncatalyzed mechanism.

Exercise 13.1

Some elementary chemistry textbooks include the statement "A catalyst lowers the activation energy of a reaction." Write a critique of this misleading statement.

Heterogeneous Catalysis

This type of catalysis occurs at a surface, usually a solid surface. Recent developments in nanotechnology have produced nanometer-size solid particles that act as efficient catalysts.[2] A solid catalyst acts by adsorbing molecules from a gas or liquid phase onto its surface, where they react. Consider a unimolecular process in the gas phase,

$$\text{A(gas)} \longrightarrow \text{products} \tag{13.1-1}$$

and a catalyzed mechanism,

$$(1) \quad \text{A(gas)} + \text{surface site} \rightleftharpoons \text{A(adsorbed)} \tag{13.1-2}$$

$$(2) \quad \text{A(adsorbed)} \longrightarrow \text{products} \tag{13.1-3}$$

If the second step is rate-limiting, the first step can be assumed to be at equilibrium. We now present a simple equilibrium theory of adsorption in order to discuss the equilibrium of the first step of this mechanism.

The Langmuir Theory of Adsorption

This theory assumes the process

$$\text{A} + \text{surface site} \rightleftharpoons \text{A(adsorbed)} \tag{13.1-4}$$

We assume that only a single layer of molecules (a *monolayer*) can be adsorbed on the surface sites. These sites might include all of the atoms of the solid surface or might be surface imperfections such as a "step" between two layers of atoms, as schematically depicted in Figure 13.1.

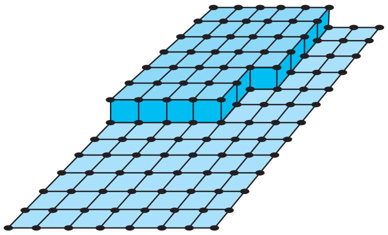

Figure 13.1 Idealized Sites on a Solid Surface.

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[1] K. J. Laidler, *Chemical Kinetics*, Harper and Row, New York, 1987, p. 229.

[2] N. Tian, Z.-Y. Zhou, S.-G. Sun, Y. Ding, and Z. L. Want, *Science*, **316**, 732 (2007).

Let θ represent the fraction of the surface sites that are occupied by adsorbed A molecules. The adsorption is assumed to be an elementary process so that the rate of adsorption is proportional to the concentration of A in the fluid phase and to $1-\theta$, the fraction of surface sites available for adsorption:

$$\text{rate of adsorption} = k_1[\text{A}](1-\theta) \tag{13.1-5}$$

where [A] is the concentration of A in the gas or liquid phase and where k_1 is a rate constant that can depend on temperature but not on [A] or θ. The desorption is also assumed to be an elementary process so that

$$\text{rate of desorption} = k_1'\theta \tag{13.1-6}$$

where k_1' is another rate constant. At equilibrium, the rate of desorption equals the rate of adsorption:

$$k_1'\theta = k_1[\text{A}](1-\theta) \tag{13.1-7}$$

This theory was devised by Irving Langmuir, 1881–1957, an American industrial chemist who won the 1932 Nobel Prize in chemistry for his work on surface chemistry.

This equation can be solved for θ to give the *Langmuir isotherm*:

$$\theta = \frac{k_1[\text{A}]}{k_1' + k_1[\text{A}]} = \frac{K[\text{A}]}{1+K[\text{A}]} \quad \text{(Langmuir isotherm)} \tag{13.1-8}$$

where K is an equilibrium constant given by

$$K = \frac{k_1}{k_1'} \tag{13.1-9}$$

The name "isotherm" is used because the formula corresponds to a fixed temperature. The value of K can be determined from a graph of the Langmuir isotherm since $1/K$ is equal to the value of [A] that corresponds to $\theta = 1/2$. Figure 13.2 schematically depicts the Langmuir isotherm for a hypothetical system.

Exercise 13.2

Show that $1/K$ equals the value of [A] that corresponds to $\theta = 1/2$.

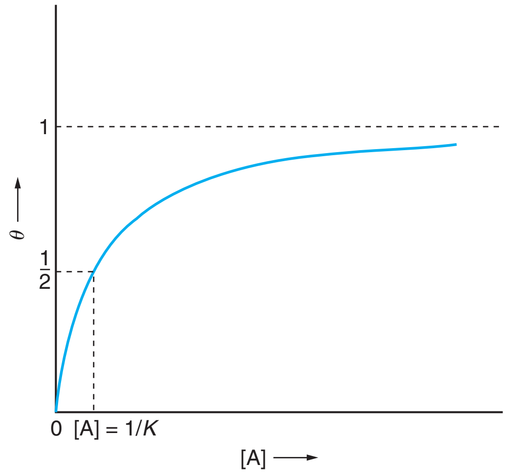

Figure 13.2 The Langmuir Isotherm.

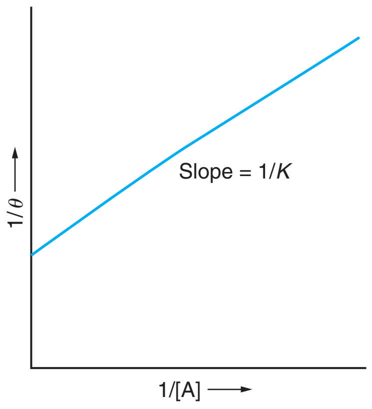

Figure 13.3 Linear Plot of the Langmuir Isotherm.

Since the total area of an adsorbing surface and the area occupied by one adsorbed molecule are probably not known, the value of θ might not be known. However, the mass adsorbed is proportional to θ, and a graph of the mass adsorbed will have the same shape as the graph of Figure 13.2. The asymptote corresponds to $\theta = 1$, allowing one to determine where $\theta = 1/2$ is located on the graph if the asymptote can be accurately located. If the data suffer from experimental errors, locating the asymptote might be difficult, so it is desirable to make a plot of a different type, as shown in Figure 13.3. In this figure, $1/\theta$ is plotted as a function of $1/[\mathrm{A}]$, corresponding to the reciprocal of Eq. (13.1-8):

$$\frac{1}{\theta} = \frac{1 + k[\mathrm{A}]}{k[\mathrm{A}]} = \frac{1}{k[\mathrm{A}]} + 1 \qquad (13.1\text{-}10)$$

If the Langmuir isotherm is obeyed, this should give a linear plot.

A plot of the reciprocal of the mass adsorbed is usually made, since this quantity is proportional to $1/\theta$. Since a plot of $1/\theta$ as a function of $1/[\mathrm{A}]$ has an intercept equal to unity, it is possible to determine the relationship between θ and the mass absorbed and then to determine the value of K from the slope of the line in the plot.

Exercise 13.3

Show that Eq. (13.1-10) is correct.

EXAMPLE 13.1

Chloroethane from the gas phase is adsorbed on a sample of charcoal at 273.15 K. The mass adsorbed for each concentration in the gas phase is

$[\mathrm{C_2H_5Cl}]/\mathrm{mol\,L^{-1}}$	0.00117	0.00294	0.00587	0.0117	0.0176
mass adsorbed/g	3.0	3.8	4.3	4.7	4.8

a. Find the value of θ for each concentration and the value of K.

b. If each chloroethane molecule occupies an area of $2.60 \times 10^{-19}\ \mathrm{m^2}$, find the effective area of the sample of charcoal.

Solution

a. Since m, the mass absorbed, is proportional to θ,

$$\frac{1}{m} = \frac{B}{\theta} = \frac{B}{K[\mathrm{C}]} + B \qquad (13.1\text{-}11)$$

where B is a proportionality constant and where we abbreviate chloromethane by C. For each data point, we calculate $1/m$ and $1/[\mathrm{C}]$.

$\frac{1}{m/\mathrm{g}}$	0.333	0.263	0.233	0.213	0.208
$\frac{1}{[\mathrm{C}]/\mathrm{mol\,L^{-1}}}$	855	340	170	85.5	56.8

Figure 13.4 shows a graph of $1/m$ as a function of $1/[\mathrm{C}]$ with the linear least-squares line. The slope of this line is equal to $1.55 \times 10^{-4}\ \mathrm{mol\,L^{-1}\,g^{-1}}$ and its intercept is equal to $0.203\ \mathrm{g^{-1}}$.

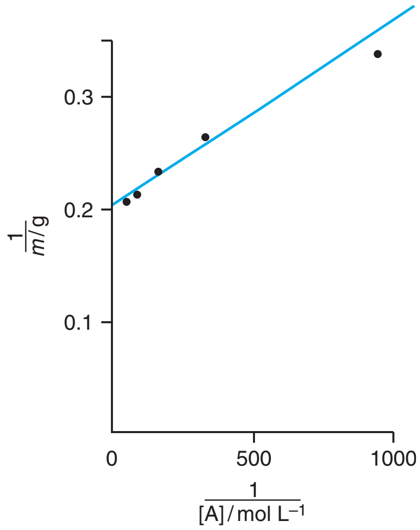

Figure 13.4 Plot of $1/m$ as a Function of $1/[\mathrm{A}]$.

$$B = 0.203\,\mathrm{g}^{-1}$$

$$K = \frac{0.203\,\mathrm{g}^{-1}}{1.55 \times 10^{-4}\,\mathrm{mol\,L^{-1}\,g^{-1}}} = 1310\,\mathrm{L\,mol}^{-1}$$

The asymptotic value of m is equal to $1/B$, or 4.93 g.

b. The effective area of the sample is obtained from the assumption that the asymptotic amount adsorbed corresponds to a full monolayer. Since the molar mass of chloroethane is equal to $64.515\,\mathrm{g\,mol}^{-1}$, the asymptotic amount adsorbed is equal to 0.0764 mol. The effective area $\mathscr{A}$ is

$$\begin{aligned}\mathscr{A} &= \left(0.260\,\mathrm{nm}^2\ \mathrm{molecule}^{-1}\right)\left(6.022 \times 10^{23}\ \mathrm{molecule\ mol}^{-1}\right)(0.0764\ \mathrm{mol})\\ &= 1.20 \times 10^{22}\ \mathrm{nm}^2 = 1.20 \times 10^{4}\ \mathrm{m}^2\end{aligned}$$

Although this area corresponds to the area of a macroscopic square 110 m on a side, charcoal can be so finely divided that this sample of charcoal might have a mass of only a few grams.

There are two classes of adsorption processes: *physical adsorption* and *chemical adsorption (chemisorption)*. In physical adsorption, the binding forces are London dispersion forces, dipole–dipole attractions, and so on. In chemical adsorption covalent chemical bonds are formed between the atoms or molecules of the surface and the atoms or molecules of the adsorbed substance. The Langmuir isotherm applies to both classes if only a monolayer of atoms or molecules can be adsorbed on the surface and if the adsorbed molecules do not dissociate. There are other isotherms that apply to the case of multiple layers.[3]

When hydrogen molecules are adsorbed on platinum they dissociate into hydrogen atoms that are covalently bonded (chemically adsorbed) to platinum atoms on the surface. In this case a different isotherm from that of Eq. (13.1-8) applies. Assume that a substance A_2 dissociates to form two adsorbed A atoms that occupy two sites on the surface:

$$\mathrm{A_2(g)} + 2\ \text{surface sites} \rightleftharpoons 2\mathrm{A(adsorbed)} \qquad (13.1\text{-}12)$$

If the adsorption is an elementary process,

$$\text{rate of adsorption} = k_1[\mathrm{A_2}](1-\theta)^2 \qquad (13.1\text{-}13)$$

If desorption is an elementary process,

$$\text{rate of desorption} = k_1'\theta^2 \qquad (13.1\text{-}14)$$

The rates of adsorption and desorption are equated and the resulting equation is solved for θ to obtain the equilibrium isotherm:

$$\theta = \frac{K^{1/2}[\mathrm{A_2}]^{1/2}}{1 + K^{1/2}[\mathrm{A_2}]^{1/2}} \quad \text{(adsorption with dissociation)} \qquad (13.1\text{-}15)$$

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[3] K. J. Laidler, *op. cit.*, p. 234 (note 1).

Exercise 13.4

Verify Eq. (13.1-15).

The Rate of a Heterogeneously Catalyzed Reaction

Consider the mechanism of Eqs. (13.1-2) and (13.1-3):

$$(1) \quad \mathrm{A} + \text{surface site} \rightleftharpoons \mathrm{A(adsorbed)} \quad \text{(fast)} \tag{13.1-16a}$$

$$(2) \quad \mathrm{A(adsorbed)} \longrightarrow \text{products} \quad \text{(slow)} \tag{13.1-16b}$$

We assume that the second step is rate-limiting. Using Eq. (13.1-8) for the assumed equilibrium of the first step, the rate is given by

$$\text{rate} = k_2\theta = \frac{k_2K[\mathrm{A}]}{1 + K[\mathrm{A}]} \tag{13.1-17}$$

For sufficiently small values of [A] the rate becomes first order in A, but for large enough values of [A] it is zero order in A. This limit corresponds to the fully covered catalytic surface so that the rate is determined by the number of surface sites and not by the concentration of A.

EXAMPLE 13.2

Derive an expression for the rate of the reaction of Eq. (13.1-16) assuming the steady-state approximation instead of the rate-limiting step approximation.

Solution

Assume that θ is approximately in a steady state:

$$\frac{d\theta}{dt} = k_1[\mathrm{A}](1-\theta) - k_1'\theta - k_2\theta \approx 0$$

$$\theta \approx \frac{k_1[\mathrm{A}]}{k_1[\mathrm{A}] + k_1' + k_2}$$

$$\text{rate} = k_2\theta = \frac{k_2k_1[\mathrm{A}]}{k_1[\mathrm{A}] + k_1' + k_2} = \frac{k_2[\mathrm{A}]}{[\mathrm{A}] + k_1'/k_1 + k_2/k_1}$$

Exercise 13.5

Tell what condition would make the result of the previous example become the same as that of Eq. (13.1-17).

EXAMPLE 13.3

Assume that a reactant $\mathrm{A_2}$ dissociates on adsorption. Find the rate law for the forward rate of the catalyzed reaction

$$\mathrm{A_2} \longrightarrow \text{products}$$

with the mechanism

(1) $A_2 + 2$ surface sites $\rightleftharpoons$ 2 A(adsorbed) (fast)
(2) A(adsorbed) $\longrightarrow$ further intermediates or products (slow)

Assume that the second step is rate-limiting.

Solution

From Eq. (13.1-15),

$$\theta = \frac{K^{1/2}[A_2]^{1/2}}{1 + K^{1/2}[A_2]^{1/2}}$$

$$\text{rate} = k_2\theta = \frac{k_2 K^{1/2}[A_2]^{1/2}}{1 + K^{1/2}[A_2]^{1/2}}$$

For the case of two substances that react with each other at a solid surface we consider two possible mechanisms. If only one of the reactants is adsorbed the mechanism is called the *Langmuir–Rideal mechanism*:

(1) A + surface site $\rightleftharpoons$ A(adsorbed) (13.1-18a)

(2) A(adsorbed) + B $\longrightarrow$ further intermediates or products (13.1-18b)

Since molecules must collide to react, this mechanism means that the B molecules from the fluid phase must collide with the adsorbed A molecules without first being adsorbed. If the second step is rate-limiting, the rate law is

$$\text{rate} = \frac{k_2 K[A][B]}{1 + K[A]} \quad \text{(Langmuir–Rideal mechanism)} \tag{13.1-19}$$

This mechanism is thought to be quite unlikely.

Exercise 13.6

Derive Eq. (13.1-19).

If both of the reacting molecules are adsorbed and if at least one of them can move around on the surface, a reaction between two adsorbed molecules can occur. This mechanism is called the *Langmuir–Hinshelwood mechanism*. It is said to occur more commonly than the Langmuir–Rideal mechanism. It can be represented by the mechanism

(1) A + surface site $\rightleftharpoons$ A(adsorbed) (13.1-20a)

(2) B + surface site $\rightleftharpoons$ B(adsorbed) (13.1-20b)

(3) A(adsorbed) + B(adsorbed) $\longrightarrow$ further intermediates or products (13.1-20c)

We assume that step 3 is rate-limiting. If both substances adsorb on the same set of sites the fraction of free sites is equal to $1 - \theta_A - \theta_B$, where θ_A is the fraction of sites with adsorbed A molecules and θ_B is the fraction of sites with adsorbed B molecules:

$$\text{rate of adsorption of A} = k_1[\text{A}](1 - \theta_A - \theta_B) \qquad (13.1\text{-}21)$$

$$\text{rate of adsorption of B} = k_2[\text{B}](1 - \theta_A - \theta_B) \qquad (13.1\text{-}22)$$

The rates of desorption are

$$\text{rate of desorption of A} = k_1'\theta_A \qquad (13.1\text{-}23)$$

$$\text{rate of desorption of B} = k_2'\theta_B \qquad (13.1\text{-}24)$$

When the rate of adsorption is equated to the rate of desorption for each substance and the resulting equations are solved simultaneously for θ_A and θ_B, we obtain the equilibrium relations:

$$\theta_A = \frac{K_1[\text{A}]}{1 + K_1[\text{A}] + K_2[\text{B}]} \qquad (13.1\text{-}25)$$

$$\theta_B = \frac{K_2[\text{B}]}{1 + K_1[\text{A}] + K_2[\text{B}]} \qquad (13.1\text{-}26)$$

where $K_1 = k_1/k_1'$ and $K_2 = k_2/k_2'$.

Exercise 13.7

Verify Eqs. (13.1-25) and (13.1-26).

If step 3 in the Langmuir–Hinshelwood mechanism is rate-limiting both absorption processes will be assumed to be at equilibrium. The rate law is

$$\text{rate} = k_3\theta_A\theta_B = \frac{k_3K_1K_2[\text{A}][\text{B}]}{(1 + K_1[\text{A}] + K_2[\text{B}])^2} \quad \text{(Langmuir–Hinshelwood mechanism)} \qquad (13.1\text{-}27)$$

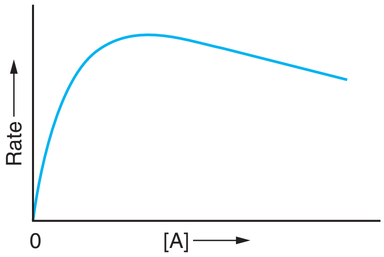

Figure 13.5 Schematic Plot of the Rate of a Catalyzed Reaction A + B → Products as a Function of [A] with Fixed [B].

Figure 13.5 shows a schematic plot of the rate as a function of [A] for a fixed value of [B]. For small values of [A] the rate is roughly proportional to [A], but as [A] is increased the rate passes through a maximum and then drops, becoming proportional to 1/[A] for large values of [A]. This decline in the rate corresponds to a value of K_1[A] that is larger than the other two terms in the denominator, so that the denominator becomes proportional to $[\text{A}]^2$. The physical reason for the decline is that as the A molecules compete more and more successfully for the surface sites, there are fewer B molecules adsorbed on the surface. The reaction then slows down because of the scarcity of adsorbed B molecules. In the reaction of CO with O_2 on platinum (one of the reactions carried out in an automobile's catalytic converter), the rate is inversely proportional to [CO].[4] This indicates that CO is bonded much more strongly on the catalyst surface than is O_2, so that K_1[CO] is much larger than the other terms in the denominator of the rate expression.

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[4] K. J. Laidler, *op. cit.*, p. 249 (note 1).

Homogeneous Catalysis

Catalytic reactions in this class occur in a single gas or liquid phase.

Gas-Phase Catalysis

An example of a gas-phase homogeneously catalyzed reaction is the decomposition of ozone

$$2O_3 \longrightarrow 3O_2 \tag{13.1-28}$$

This reaction is catalyzed by N_2O_5. The proposed catalyzed mechanism is[5]

$$\begin{aligned}
&(1) \quad N_2O_5 \longrightarrow NO_3 + NO_2 && (13.1\text{-}29a)\\
&(2) \quad NO_2 + O_3 \longrightarrow NO_3 + O_2 && (13.1\text{-}29b)\\
&(3) \quad 2NO_3 \longrightarrow 2NO_2 + O_2 && (13.1\text{-}29c)\\
&(1') \quad NO_3 + NO_2 \longrightarrow N_2O_5 && (13.1\text{-}29d)
\end{aligned}$$

The fourth step is the reverse of step 1, so we label it as $1'$. We have written it separately to emphasize that the catalyst N_2O_5 is regenerated. Step 2 must be doubled for the equations of the mechanism to add up to the stoichiometric equation.

EXAMPLE 13.4

Find the rate law for the forward reaction of the O_3 decomposition according to the above mechanism, using the steady-state approximation.

Solution

Since there are three independent steps in the mechanism, we write three differential equations: one for the rate of change of $[O_3]$, which gives the rate of the reaction, and two for the rates of change of $[NO_3]$ and $[NO_2]$. The rates of change of the reactive intermediates $[NO_3]$ and $[NO_2]$ are set equal to zero in the steady-state approximation:

$$\text{rate} = -\frac{1}{2}\frac{d[O_3]}{dt} = \frac{k_2}{2}[NO_2][O_3] \tag{13.1-30a}$$

$$\frac{d[NO_2]}{dt} = k_1[N_2O_5] - k_1'[NO_3][NO_2] + 2k_3[NO_3]^2 - k_2[NO_2][O_3] \approx 0 \tag{13.1-30b}$$

$$\frac{d[NO_3]}{dt} = k_1[N_2O_5] - k_1'[NO_3][NO_2] - 2k_3[NO_3]^2 + k_2[NO_2][O_3] \approx 0 \tag{13.1-30c}$$

Subtraction of Eq. (13.1-30c) from Eq. (13.1-30b) gives an equation that is solved to obtain

$$[NO_2] = \frac{2k_3[NO_3]^2}{k_2[O_3]} \tag{13.1-31}$$

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[5] H. S. Johnston, *Gas Phase Reaction Rate Theory*, Ronald Press, New York, 1966.

Adding Eqs. (13.1-30b) and (13.1-30c) gives an equation that is combined with Eq. (13.1-31) and solved to give

$$[\mathrm{NO}_3] = \left(\frac{k_1 k_2}{2k_1' k_3}[\mathrm{N}_2\mathrm{O}_5][\mathrm{O}_3]\right)^{1/3} \tag{13.1-32}$$

Equation (13.1-32) is substituted into Eq. (13.1-31), which is substituted into Eq. (13.1-30a) to give our solution:

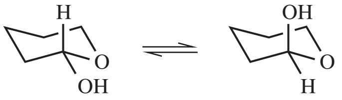
$$\begin{aligned}\text{rate} &= -\frac{1}{2}\frac{d[\mathrm{O}_3]}{dt} = k_3\left(\frac{k_1 k_2}{2k_1' k_3}[\mathrm{N}_2\mathrm{O}_5][\mathrm{O}_3]\right)^{2/3} \\ &= k_{\mathrm{app}}[\mathrm{N}_2\mathrm{O}_5]^{2/3}[\mathrm{O}_3]^{2/3}\end{aligned} \tag{13.1-33}$$

Exercise 13.8

Carry out the steps to obtain Eq. (13.1-33).

Catalysis in Solution

Various reactions are catalyzed by substances in the same phase as the reactants. A number of reactions in aqueous solutions are catalyzed by acids or bases. In *general acid catalysis* the rate depends on the concentration of unionized weak acid. In *specific hydrogen-ion catalysis* the rate depends on the concentration of hydrogen ions. Acid and base catalysis are illustrated by[6] the isomerization of α-D-glucose to β-D-glucose (or vice versa). The reaction is



(13.1-34)

where the structure on the left represents α-D-glucose. The structural formulas are abbreviated by omission of some H's and OH's.

When the reaction is carried out in pure water both the forward and reverse reactions are found to be first order. The rate law for the uncatalyzed forward reaction of the alpha isomer is

$$\text{forward rate} = k_0[\alpha] \tag{13.1-35}$$

where $[\alpha]$ stands for the concentration of the alpha isomer. The rate constant $k_0 = 0.0054\,\mathrm{min}^{-1}$ at 18°C. In the presence of a strong acid, the rate law is

$$\text{forward rate} = k_0[\alpha] + k_{\mathrm{H}^+}[\mathrm{H}^+][\alpha] \tag{13.1-36}$$

where k_0 has the same value as before and where $k_{\mathrm{H}^+} = 0.0040\,\mathrm{L\,mol^{-1}\,min^{-1}}$ at 18°C. The second term corresponds to specific hydrogen-ion catalysis, since hydrogen ions from any strong acid give the same contribution to the rate.

---

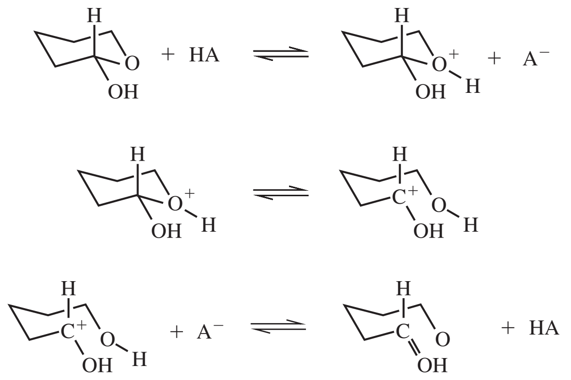
[6] S. W. Benson, *The Foundations of Chemical Kinetics*, McGraw-Hill, New York, 1990, p. 558ff.

The reaction also exhibits *specific base catalysis* so that the rate law with both catalyzed mechanisms included is

$$\text{forward rate} = k_0[\alpha] + k_{\mathrm{H}^+}[\mathrm{H}^+][\alpha] + k_{\mathrm{OH}^-}[\mathrm{OH}^-][\alpha] \qquad (13.1\text{-}37)$$

where $k_{\mathrm{OH}^-} = 3800\,\mathrm{L\,mol^{-1}\,min^{-1}}$ at 18°C. In basic solution the concentration of hydrogen ions is small and in acidic solution the concentration of hydroxide ions is small, so that only one of the last two terms will make a significant contribution in a given case. However, both terms are still present because introducing another mechanism does not shut down an existing mechanism.

The reaction also exhibits general acid catalysis. The proposed mechanism is that either the alpha or beta pyranose ring isomer of glucose is converted to the open-chain form, which can then close the ring to form either ring isomer:[7]



(13.1-38)

where HA stands for a weak acid. The alpha isomer is shown, but the mechanism for forming the open-chain structure from the beta isomer is analogous, and the mechanism for formation of either pyranose ring isomer from the open-chain structure is the reverse of this mechanism. Step 1 is thought to be rate-limiting, so that the forward reaction is predicted to be first order in α-glucose and first order in the weak acid HA:

$$\text{rate} = k_1[\alpha][\mathrm{HA}] \qquad (13.1\text{-}39)$$

Enzyme Catalysis

In cellular biological organisms nearly all chemical reactions are catalyzed by enzymes. For example, the enzyme urease catalyzes the hydrolysis of urea and the enzyme protease catalyzes the hydrolysis of proteins. Most enzymes are proteins, although some ribonucleic acids have been found to exhibit catalytic activity and have been called *ribozymes*.[8] Ribozymes usually catalyze the combination of other RNA fragments, and require the presence of divalent metal ions such as Mg^{2+}[9]. It has been thought that divalent metal ions were necessary to the function of ribozymes, but

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[7] S. W. Benson, *op. cit.*, p. 558ff (note 6).

[8] T. R. Cech, *Science*, **236**, 1532 (1987).

[9] P. Robertson and W. G. Scott, *Science*, **315**, 1549 (2007).

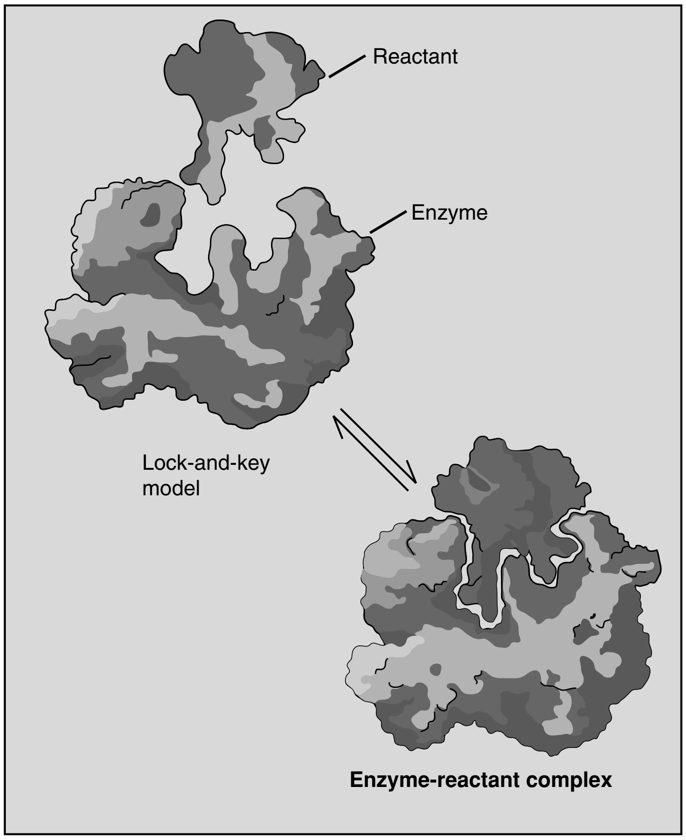

Figure 13.6 The Active Site of a Hypothetical Enzyme.

a ribozyme apparently has been found that cleaves an RNA molecule without such ions.[10]

Enzymes generally exhibit *specificity*, which means that they catalyze only specific reactions. Three kinds of specificity are recognized. The first is *absolute specificity*, which means that the enzyme catalyzes the reaction of only one substance. Urease exhibits this kind of specificity, since it will not catalyze the reaction of anything other than urea. The second kind of specificity is *group specificity*, which means that the enzyme catalyzes any of a group of reactions. Protease catalyzes the hydrolysis of various kinds of proteins, but will not catalyze the hydrolysis of fats or carbohydrates. The third kind of specificity is called *stereochemical specificity*, which means that an enzyme will catalyze the reaction of one optical isomer but not its enantiomorph. Protease catalyzes the hydrolysis of polypeptides made of L-amino acids, but not polypeptides made of D-amino acids.

A typical enzyme molecule has an *active site* at which a reactant molecule can attach itself. The active site is often like a socket into which the reactant molecule fits, like a key in a lock, as shown schematically in Figure 13.6. Once in the active site, the reactant molecule is rendered more reactive through conformational changes or polarizations produced by interaction with the enzyme. The reactant is often put into a conformation similar to a transition state.

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[10] S. R. Das and J. A. Piccirilli, *Nat. Chem. Biol.*, **1**, 45 (2005).

The Michaelis–Menten Mechanism

Michaelis and Menten proposed a mechanism for enzyme catalysis.[11] For the case of a single reactant R and a single product P,[12] this mechanism is

$$(1) \quad \mathrm{E} + \mathrm{R} \rightleftharpoons \mathrm{ER} \tag{13.1-40a}$$

$$(2) \quad \mathrm{ER} \longrightarrow \mathrm{E} + \mathrm{P} \tag{13.1-40b}$$

where E stands for the enzyme and ER stands for the enzyme-reactant complex. Many biochemistry textbooks refer to the reactant as the *substrate*, but we will continue to call it the "reactant." Since we have not included a reverse reaction for the second step, this mechanism will give a rate law for the forward reaction.

The application of the steady-state approximation to obtain the rate law for the Michaelis–Menten mechanism was first carried out by Briggs and Haldane.[13] The two differential rate equations are

$$\frac{d[\mathrm{ER}]}{dt} = k_1[\mathrm{E}][\mathrm{R}] - k_1'[\mathrm{ER}] - k_2[\mathrm{ER}] \tag{13.1-41a}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{ER}] \tag{13.1-41b}$$

The steady-state approximation is invoked by setting the right-hand side of Eq. (13.1-41a) equal to zero. An unknown but significant fraction of the enzyme is in the combined form ER, so that [E] will differ significantly from the total concentration of the enzyme, given by

$$[\mathrm{E}]_{\mathrm{total}} = [\mathrm{E}] + [\mathrm{ER}] \tag{13.1-42}$$

The total concentration of reactant is generally much larger than the enzyme concentration and is thus much larger than [ER], so that to a good approximation we can write

$$[\mathrm{R}] = [\mathrm{R}]_{\mathrm{total}} - [\mathrm{ER}] \approx [\mathrm{R}]_{\mathrm{total}} \tag{13.1-43}$$

When we substitute $[\mathrm{E}]_{\mathrm{total}} - [\mathrm{ER}]$ into the right-hand side of Eq. (13.1-41a) in place of [E], set the result equal to zero, and solve for [ER], we obtain

$$[\mathrm{ER}] = \frac{k_1[\mathrm{E}]_{\mathrm{total}}[\mathrm{R}]}{k_1' + k_2 + k_1[\mathrm{R}]} \tag{13.1-44}$$

Exercise 13.9

Verify Eq. (13.1-44).

The rate law for the forward reaction is obtained by substituting Eq. (13.1-44) into Eq. (13.1-41b). This rate law is called the *Michaelis–Menten equation*:

$$\text{forward rate} = \frac{d[\mathrm{P}]}{dt} = \frac{k_2[\mathrm{E}]_{\mathrm{total}}[\mathrm{R}]}{K_{\mathrm{m}} + [\mathrm{R}]} \quad \text{(Michaelis−Menten equation)} \tag{13.1-45}$$

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[11] L. Michaelis and M. L. Menten, *Biochem. J.*, **49**, 333 (1913).

[12] Many biochemistry textbooks denote the reactant by S (for "substrate") and its concentration by [S] instead of [R]. No good reason is given for calling a reactant a "substrate."

[13] G. E. Briggs and J. B. S. Haldane, *Biochem. J.*, **19**, 338 (1925).

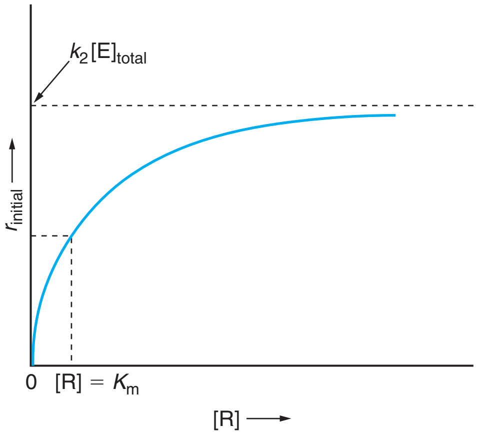

Figure 13.7 The Initial Rate as a Function of Reactant Concentration for the Michaelis–Menten Mechanism.

where

$$K_m = \frac{k' + k_2}{k_1} \tag{13.1-46}$$

The parameter K_m is called the *Michaelis–Menten constant* or the *Michaelis constant*. It is equal to a constant only if the temperature is constant. A version of the Michaelis–Menten equation can be derived with inclusion of a reverse reaction for step 2. (See Problem 13.11.) The Michaelis–Menten mechanism has also been studied without use of the steady-state approximation.[14]

Since Eq. (13.1-45) is not easily integrated, the method of initial rates is used to apply it. A number of experiments are carried out with the same concentration of enzyme but with different concentrations of reactant, and the initial rate is determined for each experiment. Figure 13.7 shows the initial rate given by Eq. (13.1-45) as a function of reactant concentration. Note the resemblance of Eq. (13.1-45) to Eq. (13.1-17), and the resemblance of Figure 13.7 to Figure 13.2. For small values of [R] the initial rate is proportional to [R] and for large values of [R] it levels off and approaches the value $k_2[E]_{total}$ asymptotically. The value of K_m can be determined by locating the asymptote and equating K_m to the value of [R] at which the initial rate is equal to one-half of the asymptotic value, as indicated in the figure. The number of reactant molecules that react per enzyme molecule per second is called the *turnover number*. Its maximum value is equal to k_2 and can range up to $10^6\ s^{-1}$.

Exercise 13.10

a. Show that the initial rate approaches the value $k_2[E]_{total}$ for large values of [R].

b. Show that K_m is equal to the value of [R] at which the initial rate is equal to half of its asymptotic value.

c. Show that the maximum value of the turnover number is equal to k_2.

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[14] N. Sundaram and P. C. Wankat, *J. Phys. Chem.*, **102**, 717 (1988).

If there is considerable experimental error in the data, it might be difficult to locate the asymptote in Figure 13.7 accurately. To avoid this problem, Eq. (13.1-46) is solved for the reciprocal of the initial rate. The result is called the *Lineweaver–Burk equation*:[15]

$$\frac{1}{r_i} = \frac{K_m}{k_2[\mathrm{E}]_{\mathrm{total}}[\mathrm{R}]} + \frac{1}{k_2[\mathrm{E}]_{\mathrm{total}}} \tag{13.1-47}$$

where the initial rate is denoted by r_i. Data on initial rates should give a straight line when $1/r_i$ is plotted as a function of $1/[\mathrm{R}]$. The slope of the line is equal to $K_m/k_2[\mathrm{E}]_{\mathrm{total}}$, the intercept on the vertical axis is equal to $1/k_2[\mathrm{E}]_{\mathrm{total}}$, and the intercept on the horizontal axis is equal to $-1/K_m$. Note the resemblance of this plot to the linear plot of the Langmuir isotherm in Figure 13.3.

Exercise 13.11

Show that the intercept of the Lineweaver–Burk plot on the horizontal axis is equal to $-1/K_m$.

EXAMPLE 13.5

The following data were gathered for the myosin-catalyzed hydrolysis of ATP at 25°C and pH 7.0:

$[\mathrm{ATP}]/\mu\mathrm{mol\ L^{-1}}$	initial rate/$\mu\mathrm{mol\ L^{-1}\ s^{-1}}$
7.5	0.067
12.5	0.095
20.0	0.119
43.5	0.149
62.5	0.185
155.0	0.191
320.0	0.195

Determine the value of the Michaelis–Menten constant.

Solution

The Lineweaver–Burk plot of the data is shown in Figure 13.8. The line drawn in the figure is the line determined by an unweighted linear least-squares procedure. The correlation coefficient for the least-squares fit is equal to 0.9975. The slope is equal to 76.58 s, and the intercept on the vertical axis is equal to $4.547\ \mathrm{L}\ \mu\mathrm{mol}^{-1}\ \mathrm{s}$. The intercept on the horizontal axis is equal to $-0.0595\ \mathrm{L}\ \mu\mathrm{mol}^{-1}$, so that the Michaelis–Menten constant is equal to $16.8\ \mu\mathrm{mol\ L^{-1}}$.

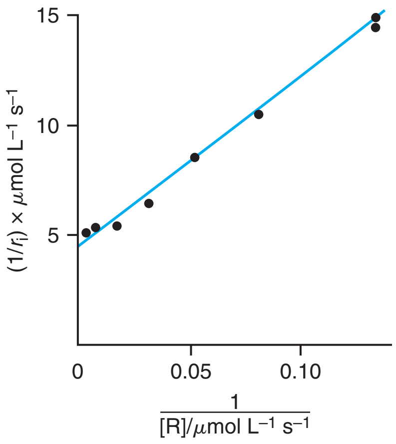

Figure 13.8 The Lineweaver–Burk Plot.

Exercise 13.12

An alternative linear plot is the Eadie plot,[a] for which Eq. (13.1-45) is put into the form

$$\frac{r_i}{[\mathrm{R}]} = \frac{r_i}{K_m} + \frac{k_2[\mathrm{E}]_{\mathrm{total}}}{K_m} \tag{13.1-48}$$

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[15] H. Lineweaver and D. Burk, *J. Am. Chem. Soc.*, **56**, 658 (1934).

Use the data of Example 13.5 to make a linear least-squares fit of $r_i/[\mathrm{R}]$ as a function of r_i. Find the value of the Michaelis–Menten constant for the reaction of Example 13.5 and compare it with the value from the Lineweaver–Burk plot of Example 13.5.

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[a] G. S. Eadie, *J. Biol. Chem.*, **146**, 85 (1942).

Enzyme Inhibition

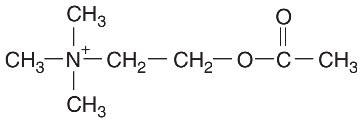
Many enzyme-catalyzed reactions are subject to *inhibition*. That is, the rate of the process is decreased by the presence of some substance, which is called an *inhibitor*. The *degree of inhibition* is defined as

$$i = 1 - \frac{r}{r_0} \tag{13.1-49}$$

where r is the rate of the catalyzed reaction in the presence of the inhibitor and r_0 is the rate in the absence of the inhibitor. A *competitive inhibitor* is one for which the degree of inhibition decreases if the reactant concentration is increased with constant concentration of the inhibitor. A *noncompetitive inhibitor* is one for which the degree of inhibition is independent of the reactant concentration, and an *anticompetitive inhibitor* is one for which the degree of inhibition increases if the concentration of the reactant is increased.

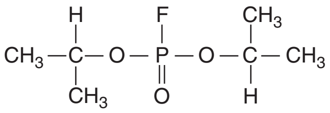
The accepted mechanism for competitive inhibition is that the inhibitor can occupy the same active site as the reactant. *Acetylcholine* is a *neurotransmitter* (a substance that diffuses across the synapse between two nerve cells and triggers a signal in the second nerve cell). This substance is hydrolyzed by the enzyme *cholinesterase*, which causes the signal to be ended by lowering the concentration of acetylcholine. Figure 13.9 shows the structural formulas of acetylcholine and of diisopropyl fluorophosphate, which is a competitive inhibitor for this hydrolysis. The diisopropyl fluorophosphate molecules compete with the acetylcholine molecules for the active sites, which inhibits the catalyzed reaction since those enzyme molecules with diisopropyl fluorophosphate molecules in their active sites are not available for acetylcholine hydrolysis. With sufficient inhibition the neurotransmitter remains in the synapse and the nerve cell transmits a signal repeatedly. If the nerve cell repeatedly stimulates a muscle to contract the muscle soon succumbs to fatigue and the organism could die. Various substances similar to diisopropyl fluorophosphate have been prepared as insecticides and as chemical warfare agents (“nerve gases”).

A proposed mechanism for a noncompetitive inhibitor is that an enzyme has a second site, other than the catalytic active site, to which the inhibitor can bind. The inhibited enzyme molecule is assumed unable to catalyze the reaction, although the active site is not occupied.



$$\mathrm{CH_3{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N^+}}{-}CH_2{-}CH_2{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}CH_3}$$

Acetylcholine



$$\mathrm{CH_3{-}\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{C}}{-}O{-}\overset{\overset{\displaystyle F}{|}}{\underset{\underset{\displaystyle O}{\|}}{P}}{-}O{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle H}{|}}{C}}{-}CH_3}$$

Diisopropyl fluorophosphate

Figure 13.9 The Structural Formulas of Acetylcholine and Diisopropyl Fluorophosphate.

PROBLEMS

Section 13.1: Catalysis

13.1 **a.** The hydrogenation of ethylene on a copper surface appears to follow the Langmuir–Hinshelwood mechanism, with the rate law

$$\text{rate} = \frac{k_a[\mathrm{H_2}][\mathrm{C_2H_4}]}{(1 + k_b[\mathrm{C_2H_4}])^2}$$

What conclusion can you draw from this rate law?

b. The same reaction on nickel appears to follow the Langmuir–Rideal mechanism. Write the rate law that you would expect to find for this case.

13.2 Apply the steady-state approximation to obtain a rate law for the reaction $A_2 \longrightarrow$ products with the assumed mechanism

(1) $A_2 + 2$ surface sites $\rightleftharpoons$ 2 A(adsorbed)

(2) A(adsorbed) $\longrightarrow$ further intermediates or products

What condition would make this rate law coincide with that obtained with the quasi-equilibrium approximation?

13.3 **a.** Derive the rate law for the reaction of a substance A that undergoes a unimolecular reaction on a catalytic surface in the case that a nonreacting substance C also adsorbs on the surface. Assume that each substance obeys the Langmuir isotherm.

b. In the case that C adsorbs more strongly than A, the catalyst can be *poisoned* by C. Poisoning can occur if lead is adsorbed on the surface of the catalyst in an automobile's catalytic converter. Find the rate law if C is much more strongly adsorbed than A.

13.4 Assume that a diatomic reactant dissociates when it is absorbed on a solid catalyst from the gas phase:

$$A_2(g) + 2 \text{ surface sites} \rightleftharpoons 2\,A(ads)$$

a. Find an expression for θ, the equilibrium fraction of surface sites occupied as a function of $[A_2]$, the concentration of A_2 in the gas phase.

b. For the reaction $A_2 + 2B \longrightarrow$ products assume the Langmuir–Rideal mechanism, which means that a B molecule in the gas phase collides with an adsorbed A atom and reacts without being adsorbed itself:

(1) $A_2(g) + 2$ surface sites $\rightleftharpoons$ 2 A(ads)

(2) A(ads) + B(g) $\longrightarrow$ products

Write the rate law, assuming the second step to be the rate-limiting step.

13.5 The following reaction is catalyzed by the bromide ion:

$$H^+ + HNO_2 + \phi NH_2 \xrightarrow{Br^-} \phi N_2^+ + 2H_2O$$

where ϕ represents the phenyl group. A proposed mechanism is

(1) $H^+ + HNO_2 \rightleftharpoons HNO_2^+$

(2) $H_2NO_2^+ + Br^- \longrightarrow ONBr + H_2O$

(3) $ONBr + \phi NH_2 \longrightarrow \phi N_2^+ + H_2O + Br^-$

a. Find the rate law, assuming the second step to be rate-limiting.

b. Find the rate law, assuming the quasi-steady-state approximation. What is the effect of assuming that the third step is much faster than the second step?

13.6 The decomposition of nitrous oxide, N_2O, on a platinum surface is apparently inhibited by the adsorption of the O_2 produced. For the case of zero initial partial pressure of O_2, the observed rate law is

$$-\frac{dP(N_2O)}{dt} = \frac{aP(N_2O)}{1 + (b/2)[P_0(N_2O) - P(N_2O)]} = \frac{aP(N_2O)}{1 + bP(O_2)}$$

where a and b are temperature-dependent parameters and where $P_0(N_2O)$ is the initial pressure of N_2O.

a. Assuming that both substances obey the Langmuir isotherm, derive this rate law, stating any necessary assumptions. Identify the parameters a and b.

b. Integrate the rate law to obtain

$$\frac{1 + bP_0}{t}\ln\left(\frac{P_0}{P_0 - x}\right) = a + b\left(\frac{x}{t}\right)$$

where $P_0 = P_0(N_2O)/2$ and where $x = P(O_2)$.

c. Following are data of Hinshelwood and Pritchard for this reaction at 741°C and for $P_0 = 190$ torr:

t/s	315	750	1400	2250	3450	5150
x/torr	10	20	30	40	50	60

Using a least-squares method, fit these data to the integrated rate law and determine the values of a and b.

13.7 The platinum-catalyzed oxidation of methanol apparently proceeds through formation of formaldehyde and then carbon monoxide.[16] The following mechanism is proposed for the oxidation of the carbon monoxide:

(1) CO(g) + surface site $\rightleftharpoons$ CO(adsorbed)

(2) O_2 + surface site $\rightleftharpoons$ O_2(adsorbed)

(3) O_2(adsorbed) + surface site $\longrightarrow$ 2O(adsorbed)

(4) CO(adsorbed) + O(adsorbed) $\longrightarrow$ CO_2(g)

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[16] R. W. McCabe and D. F. McCready, *J. Phys. Chem.*, **90**, 1428 (1986).

Find the rate law for the oxidation of CO. Use the steady-state approximation, assuming that the rates of change of θ_{CO}, θ_{O_2}, and θ_{O} are negligible. Assume that

$$1 - \theta_{\mathrm{CO}} - \theta_{\mathrm{O}_2} - \theta_{\mathrm{O}} \approx 1 - \theta_{\mathrm{CO}}$$

and neglect k_2' compared with $k_3(1 - \theta_{\mathrm{CO}})\theta_{\mathrm{O}_2}$.

13.8 The gas-phase thermal decomposition of acetaldehyde is catalyzed by I_2. The proposed mechanism is[17]

$$\begin{aligned} &(1) \quad \mathrm{CH_3CHO} + \mathrm{I_2} \rightleftharpoons \mathrm{CH_3I} + \mathrm{HI} + \mathrm{CO} \\ &(2) \quad \mathrm{CH_3I} + \mathrm{HI} \longrightarrow \mathrm{CH_4} + \mathrm{I_2} \end{aligned}$$

a. Find the rate law, using the steady-state approximation.

b. Find the rate law, assuming that the back reaction in step 1 is negligible.

c. Find the rate law, assuming that the second step is rate-limiting.

d. How would you decide which assumption is preferable?

13.9 For a homogeneously catalyzed reaction

$$\mathrm{A} + \mathrm{B} + \mathrm{C} \rightarrow \mathrm{F} + \mathrm{C}$$

where C is the catalyst, assume that the forward rate law is

$$\frac{d[\mathrm{F}]}{dt} = k[\mathrm{A}][\mathrm{B}][\mathrm{C}]$$

Integrate this rate law, assuming that [C] remains constant.

13.10 Obtain the rate law for the Michaelis–Menten mechanism of Eq. (13.1-40), assuming the second step to be rate-limiting instead of assuming the steady-state approximation.

13.11 **a.** Add the reverse reaction to the second step of the Michaelis–Menten mechanism of Eq. (13.1-40) and obtain the rate law.

b. Take the limit of the rate expression as the concentration of product approaches zero.

c. Take the limit of the rate expression as the concentration of reactant approaches zero.

d. Write an expression for the equilibrium constant of the reaction.

13.12 For the enzymatically catalyzed hydrolysis of ATP at 25°C and pH 7.0, the Michaelis–Menten constant, K_{m}, was found to equal 16.8 μmol L^{-1}, and the value of $k_2[\mathrm{E}]_{\mathrm{total}}$ was found to be 0.220 μmol $\mathrm{L}^{-1}\ \mathrm{s}^{-1}$.

a. Sketch a graph of the initial rate as a function of the initial concentration of ATP for the given data, including scales on the axes.

b. Find the initial rate at an initial ATP concentration of 30.0 μmol L^{-1}.

13.13 A certain enzymatically catalyzed reaction with negligible back reaction and a single reactant has a maximum rate of 2.34 mmol $\mathrm{L}^{-1}\ \mathrm{s}^{-1}$ at a temperature of 37°C.

a. If the rate is 1.58 mmol $\mathrm{L}^{-1}\ \mathrm{s}^{-1}$ at a reactant concentration of 12.3 mmol L^{-1} and at the same temperature and the same total enzyme concentration, find the value of K_{m} at this temperature.

b. What is the rate at a reactant concentration of 0.400 mmol L^{-1} and at the same temperature and the same total enzyme concentration?

13.14 Derive the rate law for the forward rate of the enzyme-catalyzed reaction with the mechanism

$$\begin{aligned} &(1) \quad \mathrm{E} + \mathrm{R} \rightleftharpoons \mathrm{ER} \\ &(2) \quad \mathrm{ER} \longrightarrow \mathrm{ER}' + \mathrm{P_1} \\ &(3) \quad \mathrm{ER}' \longrightarrow \mathrm{E} + \mathrm{P_2} \end{aligned}$$

where P_1 and P_2 are two different products. Comment on the relationship of your answer to the Michaelis–Menten formula.

13.15 For a fixed concentration of the enzyme succinoxidase, the following initial rates were observed. The rates are expressed as the rate of change of the absorbance at a wavelength of 250 nm.

[succinate]/mol L^{-1}	0.0100	0.00100
initial rate/s^{-1}	1.67×10^{-4}	1.13×10^{-4}

Find the value of the Michaelis–Menten constant K_{m}.

13.16 For the fumarase-catalyzed reaction

$$\text{fumarate} + \mathrm{H_2O} \longrightarrow \text{L-malate}$$

the forward-rate Michaelis–Menten equation for a single reactant is found to apply. Assume that

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[17] J. L. Latham, *Elementary Reaction Kinetics*, 2nd ed., Butterworths, London, 1969, p. 108.

$[E]_{tot} = 1.67 \times 10^{-5}$ mol L^{-1}, $K_m = 4.0 \times 10^{-6}$ mol L^{-1} and $k_2 = 4.36 \times 10^{-4}$ s^{-1}.

a. Find the initial rate for a fumarate concentration of 0.0000250 mol L^{-1}.

b. Find the initial rate for a fumarate concentration of 0.00500 mol L^{-1}.

c. Construct a graph of the initial rate as a function of fumarate concentration.

13.17 The reaction

$$CO_2 + H_2O \longrightarrow H^+ + HCO_3^-$$

is catalyzed by bovine carbonic anhydrase. At pH 7.1 and 0.5°C, $K_m = 8.23 \times 10^{-3}$ mol L^{-1} and $k_2 = 7.54 \times 10^4$ s^{-1}.

a. Find the initial rate for an initial concentration of CO_2 equal to 5.00×10^{-3} mol L^{-1} and an enzyme concentration equal to 2.8×10^{-9} mol L^{-1}.

b. Find the maximum rate for the same enzyme concentration.

13.18 For a fixed total enzyme concentration, a certain enzymatically catalyzed reaction has an initial rate of 0.0015 mol L^{-1} min^{-1} for an initial reactant concentration of 0.100 mol L^{-1} and an initial rate of 0.0020 mol L^{-1} min^{-1} with a reactant concentration of 0.200 mol L^{-1}.

a. Find the value of the Michaelis–Menten constant K_m and the maximum rate.

b. Construct a graph of the rate as a function of the reactant concentration.

c. Construct an Eadie plot for this reaction.

13.19 For the enzymatically catalyzed hydrolysis of ATP at 25°C and pH 7.0, the Michaelis–Menten constant, K_m, was found to equal 16.8 μmol L^{-1}, and the value of $k_2[E]_{total}$ was found to be 0.220 μmol L^{-1} s^{-1}.

a. Write the formula for the initial rate as a function of [ATP] with values specified for the constants.

b. Construct a graph of the initial rate as a function [ATP] for the given data, including scales on the axes.

c. Find the initial rate at an initial ATP concentration of 30.0 μmol L^{-1}.

d. Write a formula for the reciprocal of the initial rate with values for the constants.

e. Construct a Lineweaver–Burk plot for the given data. Give values for the slope and the intercept.

13.2 Competing Mechanisms and the Principle of Detailed Balance

For any reaction that proceeds by two competing mechanisms, the *principle of detailed balance* governs the rate constants for the two mechanisms: *Different mechanisms for the same reaction must give the same value of the equilibrium constant at the same temperature*. Another statement is: *At equilibrium, each mechanism must separately be at equilibrium, with canceling forward and reverse rates.* Because of this principle, *a catalyst cannot change the equilibrium constant for a reaction, and a catalyst must catalyze the reverse reaction if it catalyzes the forward reaction*.

Assume that a gaseous system containing H_2, I_2, and HI has come to equilibrium. Consider two mechanisms for the reaction of H_2 and I_2: (1) the mechanism of Eq. (12.5-15) with inclusion of a reverse reaction in step 2, and (2) the elementary mechanism:

$$(1a) \quad H_2 + I_2 \rightleftharpoons 2\,HI \qquad (13.2\text{-}1)$$

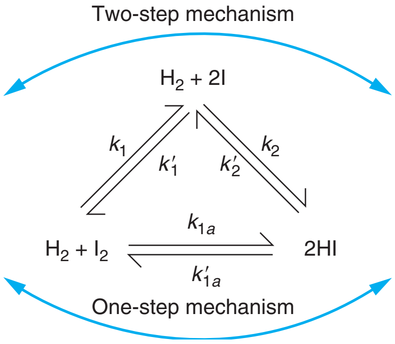

Figure 13.10 Two Mechanisms for the $H_2 + I_2$ Reaction.

Figure 13.10 shows the two pathways. Since the principle of detailed balance requires both mechanisms separately to be at equilibrium, it is not possible at equilibrium for the forward reaction of one mechanism to be canceled by the reverse reaction of the other mechanism.

Let us see what would be the consequence of assuming that equilibrium corresponds to a large forward rate of the two-step mechanism and a large reverse rate of the one-step mechanism with smaller rates for the reverse rate of the two-step mechanism and the forward rate of the one-step mechanism. If a solid substance can be found that removes iodine atoms, insertion of this substance into the reaction vessel would slow down the forward rate of the two-step reaction but would do nothing to the rate of the one-step mechanism. The system would no longer be at equilibrium and would have to change its composition to restore equilibrium. Removal of the solid substance would cause the system to return to its original equilibrium state, so that one could at will change the equilibrium composition back and forth. It would be possible to harness some of the Gibbs energy change of the forward reaction or the reverse reaction, and one would have a perpetual motion machine of the second kind, which violates the laws of thermodynamics. These two mechanisms must therefore conform to the principle of detailed balance.

By analogy with Eq. (11.4-7), the equilibrium constant for the mechanism of Eq. (13.2-1) is given by

$$K_{1a} = \frac{k_{1a}}{k'_{1a}} \tag{13.2-2}$$

By analogy with Eq. (11.5-12), the equilibrium constant for the mechanism of Eq. (12.5-15) is

$$K = \frac{k_1 k_2}{k'_1 k'_2} \tag{13.2-3}$$

Since both equilibrium constants refer to the same reaction, they must be equal:

$$\frac{k_1 k_2}{k'_1 k'_2} = \frac{k_{1a}}{k'_{1a}} \tag{13.2-4}$$

This relation provides a condition that the rate constants for the two mechanisms must obey. Of the six rate constants, only five are independent of each other. If we apply the principle of detailed balance to a catalyzed and an uncatalyzed mechanism for a given reaction, we can see that *a catalyst must catalyze the reverse reaction if it catalyzes the forward reaction*, since it cannot change the equilibrium constant of the reaction.

The principle of detailed balance is related to the *principle of microscopic reversibility*, which states that mechanical processes are time-reversible. That is, the equations governing these processes must be unchanged if the value of the time is replaced by its negative so that time appears to run backward. If it were possible to take a moving picture of the motions of molecules, the mechanical laws of motion would still apply if the movie were run backward. If equilibrium corresponded to the forward reaction of one mechanism being balanced by the reverse reaction of the other mechanism, a moving picture run backwards would be different from the same moving picture run in the forward direction.

Irreversible macroscopic processes do not obey time reversibility. A moving picture of a macroscopic diffusion process or a chemical reaction would appear to violate the second law of thermodynamics if the movie were run backwards. The entropy of the universe would seem to decrease. However, a microscopic movie of the molecular motions during the irreversible process must appear normal if run backwards. One of the most interesting questions of science: *How can irreversible macroscopic processes result from time-reversible molecular processes?* We believe that macroscopic properties are determined by microscopic properties and that macroscopic states are equivalent to averages over microstates. From our discussion of statistical entropy in Chapter 4, it is obvious that information is being lost in an irreversible process. Although much progress has been made in understanding how to average over microstates to represent a nonequilibrium macrostate, the question of how this information is lost has not yet been answered.[18]

PROBLEMS

Section 13.2: Competing Mechanisms and the Principle of Detailed Balance

13.20 A hypothetical reaction

$$\mathrm{AX} + \mathrm{B}^+ \rightleftharpoons \mathrm{A}^+ + \mathrm{BX}$$

can proceed through either of two independent mechanisms:
Elementary mechanism:

$$(1) \quad \mathrm{AX} + \mathrm{B}^+ \rightleftharpoons \mathrm{A}^+ + \mathrm{BX}$$

Two-step mechanism:

$$(2) \quad \mathrm{AX} \rightleftharpoons \mathrm{A}^+ + \mathrm{X}^-$$

$$(3) \quad \mathrm{B}^+ + \mathrm{X}^- \rightleftharpoons \mathrm{BX}$$

Given the values at some fixed temperature,

$$k_2 = 1.0 \times 10^6\ \mathrm{s}^{-1}$$

$$k_2' = 2.4 \times 10^8\ \mathrm{L\ mol^{-1}\ s^{-1}}$$

$$k_3 = 3.8 \times 10^4\ \mathrm{L\ mol^{-1}\ s^{-1}}$$

$$k_3' = 1.4 \times 10^1\ \mathrm{s}^{-1}$$

$$k_1' = 6.7 \times 10^2\ \mathrm{s}^{-1}$$

find the value of the equilibrium constant and the value of k_1 at this temperature.

13.21 Insert a reverse reaction in step 3 of Problem 12.36. Write the expression for the equilibrium constant in terms of the rate constants. Write the relation between the rate constants for the chain mechanism and the other mechanisms, using the principle of detailed balance.

13.22 Insert a reverse reaction in the second step of the mechanism of Eq. (13.1-16), assuming a single product, P, and assuming that the reverse reaction in step 2 is elementary.

a. Write an expression for the equilibrium constant of the reaction in the absence of the catalyst.

b. Write an expression for the equilibrium constant in terms of the rate constants in the assumed mechanism. Express the rate constant for the reverse reaction of step 2 in terms of the other rate constants and the equilibrium constant, using the principle of detailed balance.

13.23 Insert reverse reactions into steps 2 and 3 in the mechanism of Problem 13.14. Write an expression for the equilibrium constant for the reaction in terms of the rate constants of the three steps. Express k_3' in terms of the equilibrium constant for the uncatalyzed reaction and the other rate constants.

13.3 Autocatalysis and Oscillatory Chemical Reactions

Autocatalysis

If a product of a reaction catalyzes that reaction, the reaction is said to exhibit *autocatalysis*. The simplest hypothetical autocatalytic reaction

$$\mathrm{A} \rightarrow \mathrm{F} \qquad (13.3\text{-}1)$$

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[18] Many years ago while at a meeting, the author approached George Uhlenbeck, a prominent theoretical physicist, and asked him to comment on this question. He simply stated "Irreversibility is just a human illusion." Who knows if his opinion is correct?

corresponds to the mechanism

$$\begin{aligned} &(1) \quad \mathrm{A} + \mathrm{F} \rightleftharpoons \mathrm{C} \\ &(2) \quad \mathrm{C} \rightarrow 2\mathrm{F} \end{aligned} \tag{13.3-2}$$

where C is a reactive intermediate. Assuming that the second step is rate-limiting, the rate law is

$$\frac{d[\mathrm{F}]}{dt} = 2k_2[\mathrm{C}] = 2k_2K_1[\mathrm{A}][\mathrm{F}] = k_{\mathrm{app}}[\mathrm{A}][\mathrm{F}] \tag{13.3-3}$$

where the initial concentration of F must be nonzero for the reaction to proceed. This differential equation can be integrated. We let

$$[\mathrm{A}] = [\mathrm{A}]_0 - x$$

and

$$[\mathrm{F}] = [\mathrm{F}]_0 + x$$

where the initial concentrations are labeled with a subscript 0. The rate law now becomes

$$\frac{dx}{dt} = k_{\mathrm{app}}([\mathrm{A}]_0 - x)([\mathrm{F}]_0 + x) \tag{13.3-4}$$

or

$$\frac{dx}{([\mathrm{A}]_0 - x)([\mathrm{F}]_0 + x)} = k_{\mathrm{app}}dt \tag{13.3-5}$$

We apply the method of *partial fractions*, setting

$$\frac{1}{([\mathrm{A}]_0 - x)([\mathrm{F}]_0 + x)} = \frac{G}{[\mathrm{A}]_0 - x} + \frac{H}{[\mathrm{F}]_0 + x}$$

where a theorem of algebra guarantees that G and H are constants. We obtain two simultaneous equations for G and H by setting $x = 0$ to obtain one equation,

$$\frac{1}{[\mathrm{A}]_0[\mathrm{F}]_0} = \frac{G}{[\mathrm{A}]_0} + \frac{H}{[\mathrm{F}]_0} \tag{13.3-6a}$$

and by setting $x = [\mathrm{F}]_0$ to obtain the other equation,

$$\frac{1}{([\mathrm{A}]_0 - [\mathrm{F}]_0)2[\mathrm{F}]_0} = \frac{G}{[\mathrm{A}]_0 - [\mathrm{F}]_0} + \frac{H}{2[\mathrm{F}]_0} \tag{13.3-6b}$$

The solution to these simultaneous equations is

$$G = H = \frac{1}{[\mathrm{A}]_0 + [\mathrm{F}]_0} \tag{13.3-7}$$

so that

$$\frac{dx}{([\mathrm{A}]_0 + [\mathrm{F}]_0)([\mathrm{A}]_0 - x)} + \frac{dx}{([\mathrm{A}]_0 + [\mathrm{F}]_0)([\mathrm{F}]_0 + x)} = k_{\mathrm{app}}dt \tag{13.3-8}$$

Exercise 13.13

Solve the simultaneous equations in Eq. (13.3-6) to obtain Eq. (13.3-7).

Integration of Eq. (13.3-8) from $x = 0$ to $x = x(t') = x'$ gives

$$\frac{1}{[\mathrm{A}]_0 + [\mathrm{F}]_0} \ln\left(\frac{[\mathrm{A}]_0\big([\mathrm{F}]_0 + x'\big)}{[\mathrm{F}]_0([\mathrm{A}]_0 - x')}\right) = k_{\mathrm{app}}t' \tag{13.3-9}$$

where $x\prime = x(t')$. This expression can be solved for x':

$$x = [\mathrm{F}]_0 \frac{e^{\beta t} - 1}{1 + \frac{[\mathrm{F}]_0}{[\mathrm{A}]_0} e^{\beta t}} \tag{13.3-10}$$

where $\beta = ([\mathrm{A}]_0 + [\mathrm{F}]_0)k_{\mathrm{app}}$ and where we drop the prime symbol ($'$). The rate of the reaction begins at a small value and increases as the concentration of the product becomes larger. It then declines as the concentration of the reactant decreases. Since the mechanism does not include reverse reactions, all of the reactant will eventually be consumed and the rate will vanish.

Oscillatory Chemical Reactions

It was once thought that in any chemical reaction the concentrations of reactants would decay smoothly, that concentrations of products would rise smoothly, and that concentrations of reactive intermediates would rise and fall only once, as in the two-step mechanism of Chapter 11. The first known oscillatory chemical reaction was the iodate-catalyzed decomposition of hydrogen peroxide, discovered in 1920. In this reaction, the color of the solution (due to iodine) and the evolution of oxygen can vary in an oscillatory and nearly periodic way. The most famous oscillatory reaction is the *Belousov–Zhabotinskii reaction* (abbreviated BZ), which is the reaction of citric acid, bromate ion, and ceric ion in acidic solution. This reaction not only produces oscillations in time, but can also produce chemical waves, consisting of roughly concentric or spiral rings of different colors that move outward from various centers. The first article describing this reaction was rejected for publication, because of the common belief that chemical oscillations could not occur. However, since the 1960s chemical oscillations have been widely studied and have even become common lecture demonstrations.

We can illustrate oscillatory behavior with the *Lotka–Volterra mechanism*:

$$\begin{array}{ll} (1) & \mathrm{A} + \mathrm{X} \rightarrow 2\mathrm{X} \\ (2) & \mathrm{X} + \mathrm{Y} \rightarrow 2\mathrm{Y} \\ (3) & \mathrm{Y} \rightarrow \mathrm{P} \end{array} \tag{13.3-11}$$

This mechanism can show oscillatory behavior if A is continually replenished so that [A] remains constant: This mechanism has been used in ecology as a simple *predator–prey model*, in which A represents the food supply (grass) for prey animals (hares), represented by X. Predators (wolves) are represented by Y, and dead wolves are represented by P. The consumption of grass (A) by the hares (X) allows them to reproduce as in step 1, and the consumption of hares by wolves (Y) allows the wolves to reproduce as in step 2. Step 3 corresponds to the death of wolves by natural causes. Since no reverse steps are included, the overall reaction corresponds to the conversion of grass into dead wolves:

$$A \rightarrow P \tag{13.3-12}$$

The differential equations for this mechanism are

$$\frac{d[A]}{dt} = k_1[A][X] \tag{13.3-13a}$$

$$\frac{d[X]}{dt} = 2k_1[A][X] - k_2[X][Y] \tag{13.3-13b}$$

$$\frac{d[Y]}{dt} = k_2[X][Y] - k_3[Y] \tag{13.3-13c}$$

For the case in which [A] is held fixed, we have only Eq. (13.3-13b) and Eq. (13.3-13c) to solve simultaneously. Since we expect an oscillatory solution, we cannot apply the quasi-equilibrium approximation or the quasi-steady-state approximation. The equations must be solved numerically, using standard methods of numerical analysis to obtain the time dependence of [X] and [Y].[19] The concentrations of X and Y must satisfy the expression

$$k_2([X] + [Y]) - k_3\ln([X]) - k_1[A]\ln([Y]) = C \tag{13.3-14}$$

where C is a constant.

Exercise 13.14

Show that the foregoing expression satisfies the differential equations in Eq. (13.3-13). *Hint:* Differentiate this expression with respect to time and substitute the differential equations for [X] and [Y] into this equation.

The results can be displayed by a plot of [Y] as a function of [X]. A mathematical space with time-dependent variables plotted on the axis is called a *phase space*. If [Y] is plotted as a function of [X] for a constant value of [A], there a closed curve that is retraced over and over again as time passes, exhibiting periodic behavior. However, there are different curves for different initial states, but the oscillations predicted by the mechanism resemble the actual fluctuations in predator and prey populations in actual ecosystems.

The known mechanisms that produce oscillatory behavior have two characteristics in common. The first is autocatalysis. The product of a step must catalyze that step, as in steps 1 and 2 of the Lotka–Volterra mechanism. The second is that nonlinear differential equations occur. That is, the variables must occur with powers greater than unity or as products. A mechanism has been proposed for the BZ reaction that has 18 steps and involves 21 different chemical species.[20] A computer simulation of the 18 simultaneous rate differential equations for the mechanism has been carried out and does produce oscillatory behavior. It also exhibits the interesting behavior that all curves in phase space corresponding to different initial states eventually approach

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[19] As of 2006, the website http://tu-dresden.de/Members/thomas.petzoldt provides a program that you can run to carry out the solution to the Lotka–Volterra mechanism.

[20] R. J. Field, E. Körös, and R. M. Noyes, *J. Am. Chem. Soc.*, **94**, 8649 (1972).

a single curve, called a *limit cycle*. There is also a simplified mechanism with five steps called the *oregonator*, developed by Noyes' group at the University of Oregon.[21] This mechanism also leads to oscillatory behavior that simulates the BZ reaction fairly accurately.

PROBLEMS

Section 13.3: Autocatalysis and Oscillatory Chemical Reactions

13.24 **a.** By differentiation of Eq. (13.3-10), find an expression for the rate of the autocatalyzed reaction of Eq. (13.3-1).

b. Find an expression for the time at which the rate has its maximum value.

13.25 **a.** Construct an accurate graph of x as a function of t for the function of Eq. (13.3-10). Take the case that $[\mathrm{A}]_0 = 1.000\,\mathrm{mol\,L^{-1}}$, $[\mathrm{F}]_0 = 0.100\,\mathrm{mol\,L^{-1}}$, and $k_{\mathrm{app}} = 1.00\,\mathrm{L\,mol^{-1}\,s^{-1}}$.

b. Construct an accurate graph of the rate of the reaction for the case of part a.

13.26 **a.** Plot the curve in phase space representing the solution of Eq. (13.3-14) for $C = 1.00\,\mathrm{mol\,L^{-1}}$, $[\mathrm{A}] = 1.00\,\mathrm{mol\,L^{-1}}$, $k_1 = 1.00\,\mathrm{L\,mol^{-1}\,s^{-1}}$, $k_2 = 0.5\,\mathrm{L\,mol^{-1}\,s^{-1}}$, and $k_3 = 0.1.00\,\mathrm{s^{-1}}$. One way to proceed is to solve Eqs. (13.3-13a) and (13.3-13c) numerically by writing a computer program using either Euler's method or the Runge–Kutta method.[22]

b. Construct plots of [X] and [Y] as a function of time, using the program of part a.

13.4 The Reaction Kinetics of Polymer Formation

The word *polymer* comes from *poly*, meaning "many," and *meros*, meaning "parts." Polymer molecules are formed from small molecules (monomers) that react to form covalently bonded chains or networks. Synthetic polymers such as polyethylene, nylon, and polyesters are found in many manufactured products. There are also many naturally occurring polymers, including natural rubber, proteins, starches, celluloses, and nucleic acids. The properties of polymers are determined by their molecular structures, and the properties of synthetic polymers can be tailored to specific applications. The "Macrogalleria" website http://www.psrc.usm.edu/macrog maintained by the Polymer Science Department of the University of Southern Mississippi provides a great deal of information about polymers, including a video of the action of the Zeigler–Natta catalyst that is used to form synthetic rubber that is identical to natural rubber.

Some polymers, such as polyethylene, polystyrene, and polypropylene, have chainlike molecules. These polymers usually soften when heated and are sometimes called *thermoplastic polymers*. Other polymers are made up of networks instead of chains. Some of the network polymers have long chains with short chains (cross links) fastening two or more chains together, and others, such as Bakelite, have networks that are bonded in two or three dimensions. These polymers are sometimes called thermosetting because they are usually formed at high temperatures.

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[21] R. J. Field and R. M. Noyes, *J. Chem. Phys.*, **60**, 1877 (1974). If you search for "oregonator" in Google or any other search engine, you will find links to programs that will solve the kinetic equations for you.

[22] See R. G. Mortimer, *Mathematics for Physical Chemistry*, Elsevier/Academic Press, San Diego, 2005, p. 260ff, or any numerical analysis textbook.

Synthetic polymers are also classified by the type of reaction that forms them. Two major classes are *condensation polymers* and *addition polymers*. When a monomer unit is added to a condensation polymer chain there is a small molecule (often water) produced in addition to the lengthened chain. In an addition polymer there is no other product besides the chain. The monomer of an addition polymer generally has a carbon–carbon double bond that opens up to bond with other monomers and form a chain of covalently bonded carbon atoms. Two common examples of condensation polymers are nylon and polyester and two common examples of addition polymers are polyethylene and polystyrene.

Polymerization Kinetics

We discuss the reaction kinetics of condensation polymerization, but addition polymerization can be discussed in much the same way.[23] Consider the formation of a *polyester* from a monomer diacid, HOOC–X–COOH, and a monomer dialcohol, HO–Y–OH, where X and Y represent two hydrocarbon chains. The first step in the polymerization is

$$\mathrm{HOOC{-}X{-}COOH{+}HO{-}Y{-}OH \longrightarrow HOOC{-}X{-}COO{-}Y{-}OH{+}H_2O} \tag{13.4-1}$$

The principal product is an ester, but it also has one carboxyl group and one hydroxyl group, so it can react with a second diacid at one end and with a second dialcohol at the other end, and so on to form a chain. Two chains of any length can also bond together to form a longer chain. A long chain with the repeating unit –OOC–X–COO–Y– is eventually formed. This chain is terminated by adding a hydroxyl group at the Y– end and a hydrogen atom at the –OOC end so that it has a hydroxyl group at one end and a carboxyl group at the other.

To proceed with the solution of the rate differential equations for the polymerization reactions, we make some simplifying assumptions. We first assume that the rate coefficients for all condensation reactions have the same value, irrespective of the length of the chain involved. This approximation is commonly justified by the assertion that the behavior of a functional group in a “cage” of neighboring molecules or groups is nearly independent of the length of the chain to which the functional group is attached since the functional group is nearly immobilized in any event. We begin with a stoichiometric mixture that has equal concentrations of diacid and dialcohol and a small concentration of a catalyst. We let c represent the sum of the concentrations of all types of molecules other than catalyst or solvent molecules. At $t = 0$, when the polymerization reaction begins, $c = c_0$ and the diacid concentration and dialcohol concentration are both equal to $c_0/2$. There are two carboxyl groups on each diacid molecule, so that the initial concentration of carboxyl groups is equal to c_0 and the initial concentration of hydroxyl groups is also equal to c_0. We assume that the reaction occurs in a nonpolar solvent so that the water that is formed is insoluble in the reaction solution and is removed as it is formed. Each time a condensation reaction occurs, one free carboxyl group disappears and one free hydroxyl group disappears, and the number of molecules decreases by unity. As c changes it remains equal to the concentration of free (unesterified) carboxyl groups, and also to the concentration of free hydroxyl groups.

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[23] See H. R. Allcock and F. W. Lampe, *Contemporary Polymer Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1981, p. 245ff, or C. Tanford, *Physical Chemistry of Macromolecules*, Wiley, New York, 1961, p. 588ff for the standard treatments of both types of polymerization.

We assume that the reaction is first order in the diacid, first order in the dialcohol, and first order in the catalyst. We also assume that the reverse reaction and the uncatalyzed reaction can be neglected. The forward rate differential equation is

$$\frac{dc}{dt} = -k_{\mathrm{f}}[\mathrm{cat}]c^2 = -k'c^2 \tag{13.4-2}$$

where [cat] is the concentration of the catalyst. We let

$$k' = k_{\mathrm{f}}[\mathrm{cat}] \tag{13.4-3}$$

We assume that the volume of the system does not change significantly, and since the catalyst is not consumed, k' is a constant at constant temperature. Equation (13.4-2) is the same as Eq. (11.2-8) except for the symbols used. Transcription of Eq. (11.2-11) with the proper replacement of symbols gives the solution:

$$\frac{1}{c} = \frac{1}{c_0} + k't \tag{13.4-4}$$

We define the variable p, the fraction of carboxyl groups that have reacted:

$$p = \frac{c_0 - c}{c_0} = 1 - \frac{c}{c_0} \tag{13.4-5}$$

Equation (13.4-4) can be written in the form

$$p = \frac{k'c_0t}{1 + k'c_0t} \tag{13.4-6}$$

which is equivalent to

$$\frac{1}{1-p} = 1 + k'c_0t \tag{13.4-7}$$

Exercise 13.15

Verify Eqs. (13.4-6) and (13.4-7).

Exercise 13.16

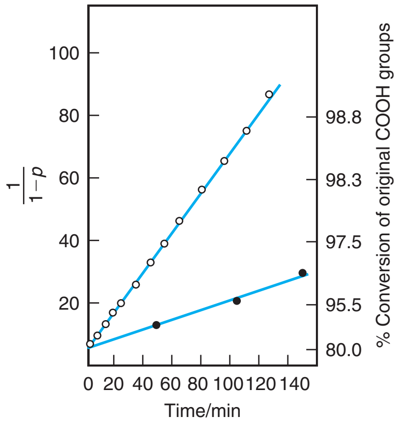
Construct an accurate graph of p as a function of t, assuming that $k'c_0 = 1.00\ \mathrm{s}^{-1}$.

The *degree of polymerization*, x, is defined as the number of monomer units in a polymer molecule. The *number-average degree of polymerization* is denoted by $\langle x\rangle_n$ and is given by

$$\langle x\rangle_n = \frac{c_0}{c} = \frac{1}{1-p} \tag{13.4-8}$$

This value is a mean value with each molecule given equal weight (importance) in the averaging. Equation (13.4-4) can be expressed in terms of $\langle x\rangle_n$:

$$\langle x\rangle_n = 1 + k'c_0t \tag{13.4-9}$$



○ 1,10-Decamethylene glycol at 161°C [S.D. Hamann, D.H. Solomon, and J.D. Swift, J. *Macromol Sci. Chem.*, **A2**, 153 (1968)]

● Diethylene glycol at 109°C [P.J. Flory, *J. Am. Chem. Soc.*, **61**, 3334 (1939)]

Figure 13.11 Polyesterification of Adipic Acid with Two Polyalcohols, Catalyzed with *p*-Toluene Sulfonic Acid. The left axis shows the value of $1/(1-p)$ where p is the fraction of carboxyl groups that have reacted. The right axis is labeled with the percent of original carboxyl groups that have reacted. From H. R. Allcock and F. W. Lampe, *Contemporary Polymer Chemistry*, Prentice Hall, Englewood Cliffs, NJ, 1981, p. 254.

Equation (13.4-9) agrees with experiment fairly well for the later stages of polymerization, although not so well for the early stages. Figure 13.11 shows data for two polyesterification reactions, each beginning with 82% of the carboxyl groups esterified.

Since there is a distribution of degrees of polymerization, there is a distribution of molecular masses. If x is even, the molecular mass of molecules with a given value of x is

$$M_{\mathrm{x}} = \frac{x}{2}M_r + 18\,\mathrm{amu} = xM_0 + 18\,\mathrm{amu} \approx x\,M_0 \qquad (13.4\text{-}10)$$

where M_{r} is the mass of the repeating unit of the polymer in amu and M_0 is equal to $M_{\mathrm{r}}/2$. The term 18 amu is added because each molecule has an OH group at one end and an H atom at the other end that are not part of the repeating unit. Equation (13.4-10) can be modified for odd values of x. For either odd or even x, the final approximate equality is valid for large values of x.

Let N_{x} be the number of polymer molecules with degree of polymerization equal to x and let X_{x} denote the *number fraction* of polymer molecules with this degree of polymerization:

$$X_{\mathrm{x}} = \frac{N_{\mathrm{x}}}{N} \qquad (13.4\text{-}11)$$

where N is the total number of polymer molecules. The *number-average molecular mass* is the mean molecular mass with each molecule given equal importance in the averaging process:

$$\langle \mathrm{M} \rangle_n = \frac{1}{N}\sum_{x=1}^{\infty} N_{\mathrm{x}} M_{\mathrm{x}} = \sum_{x=1}^{\infty} X_{\mathrm{x}} M_{\mathrm{x}} \qquad (13.4\text{-}12)$$

where the sum is over all values of x. We have used an infinite upper limit for the sum for mathematical convenience. This introduces only a negligible error since N_{x} rapidly approaches zero for large values of x. The number-average molecular mass is equal to the total polymer mass divided by the total number of polymer molecules.

A formula for $\langle \mathrm{M} \rangle_n$ can be derived from statistical reasoning.[24] We assume that x is even. The polymer molecule consists of $x-1$ units with esterified carboxyl groups, and one unit with a free carboxyl group. Let the fraction of all carboxyl groups that are free be equal to $1-p$, and the fraction that are esterified be equal to p. The probability of having a given value of x is

$$\text{Probability of } x = p^{x-1}(1-p) \qquad (13.4\text{-}13)$$

The number-average molecular mass can now be written

$$\langle \mathrm{M} \rangle_n = \sum_{x=1}^{\infty} X_{\mathrm{x}} x\, M_0 = M_0(1-p)\sum_{x=1}^{\infty} x\, p^{x-1} \qquad (13.4\text{-}14)$$

where a term equal to 18 amu has been omitted. This sum can be found in tables,[25] giving

$$\langle \mathrm{M} \rangle_n = \frac{M_0(1-p)}{(1-p)^2} = \frac{M_0}{1-p} \qquad (13.4\text{-}15)$$

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[24] H. R. Allcock and F. W. Lampe, *op. cit.* (note 23).

[25] See for example H. B. Dwight, *Tables of Integrals and Other Mathematical Data*, 4th ed., Macmillan, New York, 1961, p. 8.

From Eqs. (13.4-7) and (13.4-15), we can write an equation for the time dependence of $\langle \mathrm{M} \rangle_n$:

$$\langle \mathrm{M} \rangle_n = M_0(1 + c_0 k' t) \tag{13.4-16}$$

where we continue to neglect 18 amu compared with $\langle \mathrm{M} \rangle_n$. For fairly large values of the time,

$$1 + c_0 k' t \approx c_0 k' t \tag{13.4-17}$$

giving

$$\langle \mathrm{M} \rangle_n = M_0 c_0 k' t \tag{13.4-18}$$

This relation can also be obtained using reaction kinetics.[26] The time dependence of the number fraction of any degree of polymerization can be obtained by substituting Eq. (13.4-6) into Eq. (13.4-13).

Exercise 13.17

Obtain an expression for the time dependence of X_{x}.

The *mass fraction* of molecules with degree of polymerization x is

$$W_{\mathrm{x}} = \frac{\text{mass of molecules with degree of polymerization } x}{\text{mass of all molecules}} \tag{13.4-19a}$$

$$= \frac{N_{\mathrm{x}} M_{\mathrm{x}}}{\sum_{x=1}^{\infty} N_{\mathrm{x}} M_{\mathrm{x}}} \tag{13.4-19b}$$

The *mass-average molecular mass* (often called the "weight-average molecular weight") is defined by

$$\langle \mathrm{M} \rangle_w = \sum_{x=1}^{\infty} W_{\mathrm{x}} M_{\mathrm{x}} = \frac{\sum_{x=1}^{\infty} N_{\mathrm{x}} M_{\mathrm{x}}^2}{\sum_{x=1}^{\infty} N_{\mathrm{x}} M_{\mathrm{x}}} \tag{13.4-20}$$

In this average, each molecule is given an importance (weight) in the average proportional to its mass. The required sum can be found in tables,[27] giving

$$\langle \mathrm{M} \rangle_w = (1-p)^2 M_0 \sum_{x=1}^{\infty} x^2 p^{x-1} = M_0 \frac{1+p}{1-p} \tag{13.4-21}$$

The mass-average molecular mass is always equal to or larger than the number-average molecular mass since the heavier molecules are given larger importance than lighter molecules in the mass average. If p is nearly equal to unity, the mass-average molecular mass is approximately twice as large as the number-average molecular mass. The evolution in time of the mass-average molecular mass can be expressed as a function of time, as was done for $\langle \mathrm{M} \rangle_n$ in Eq. (13.4-16). Figure 13.12a shows the distribution of mass in a polyester, according to Eq. (13.4-13) and Figure 13.12b shows the evolution in time of several mass fractions during a condensation polymerization.

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[26] C. Tanford, *op. cit.* (note 23).

[27] H. B. Dwight, *op. cit.* (note 25).

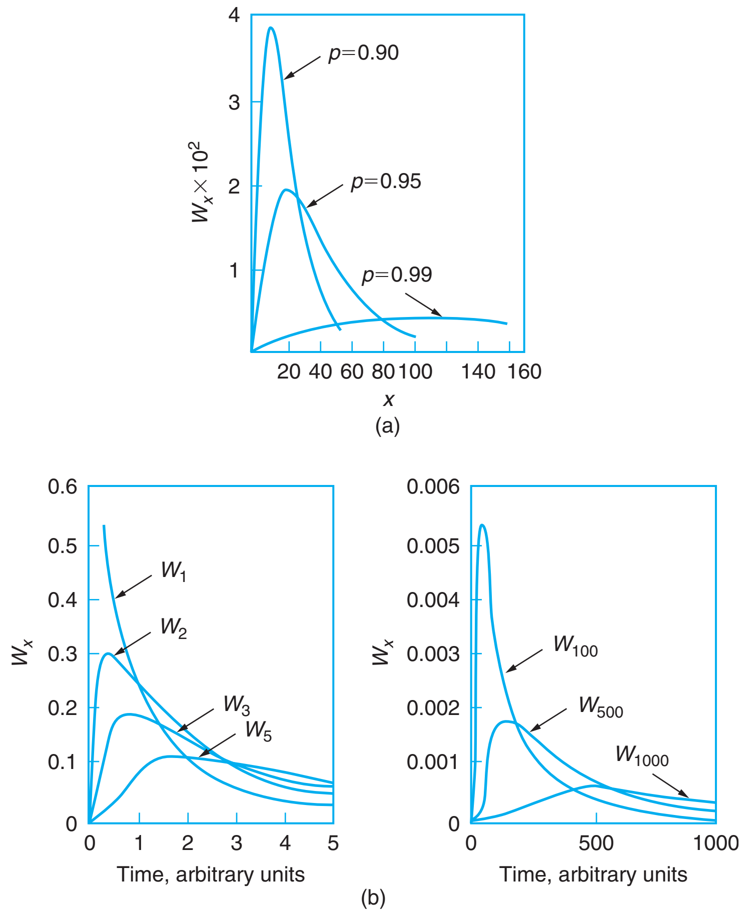

Figure 13.12 A Condensation Polymerization Distribution by Mass. (a) Conversions of 90%, 95%, and 99%. The horizontal axis is labeled with x, the degree of polymerization. The vertical axis is labeled with the mass fraction of molecules with x monomer units. (b) The evolution of mass fractions. Note that all of the mass fractions shown except for W_1 rise and then decline as molecules of larger size are formed. Part (a) from Allcock and Lampe, *op. cit.*, p. 261. Part (b) from T C. Tanford, *Physical Chemistry of Macromolecules*, Wiley, New York, 1961, p. 595.

Exercise 13.18

Show that

$$\langle \mathrm{M} \rangle_w = M_0(1 + 2k' c_0 t) \qquad (13.4\text{-}22)$$

PROBLEMS

Section 13.4: The Reaction Kinetics of Polymer Formation

13.27 Find the number-average and mass-average molecular masses for a sample of a polyvinyl alcohol that has equal numbers of molecules with molecular masses 5000 amu, 10,000 amu, 15,000 amu, 20,000 amu, 25,000 amu, 30,000 amu, and 35,000 amu.

13.28 Find the number-average and mass-average molecular masses for a sample of a polyvinyl alcohol that has molecules with the following percentages and molecular masses:

10.00%	5000 amu
25.00%	15000 amu
60.00%	25000 amu
5.00%	35000 amu

13.29 The hydroxy acid $HO(–CH_2–)_5CO_2H$ forms a polyester by condensation polymerization.

a. Show that the same equations apply that were used for the condensation polymerization of a diacid and a dialcohol.

b. If the mass-average molecular mass is reported to 20,000 amu, find the fraction of carboxyl groups that has been esterified.

c. Find the number-average molecular mass for part b.

d. Find the average degree of polymerization.

13.30 The sum in Eq. (13.4-14) is similar to the geometric progression

$$S = \sum_{n=0}^{\infty} p^n = \frac{1}{1-p}$$

This formula is valid only if $p < 1$. Show that the result in Eq. (13.4-15) and that in Eq. (13.4-21) can be obtained by differentiating the sum with respect to p.

13.31 Carry out the solution of the kinetic equation for an uncatalyzed polyesterification if the reaction is assumed second order in carboxyl groups and first order in hydroxyl groups:

$$\frac{dc}{dt} = k_f c^3$$

13.32 The amino acid 7-aminoheptanoic acid forms a polyamide (nylon) in *m*-cresol solution, with the second-order rate coefficients[28]

temperature/°C	150	187
k/kg mol^{-1} min^{-1}	1.0×10^{-3}	2.74×10^{-2}

a. Find the times required at 150°C to attain a value of p equal to 0.95 and a value of p equal to 0.99.

b. Find the number-average and mass-average molecular masses at $p = 0.99$.

c. Find the activation energy of the reaction and find the time required to reach a value of p equal to 0.95 at 175°C.

13.5 Nonequilibrium Electrochemistry

Chapter 8 presented a discussion of the cell voltage of electrochemical cells at equilibrium. There are many practical applications of electrochemistry, including the commercial reduction of aluminum from its ore and the use of various batteries, but nearly all of them involve nonzero currents. If a nonzero current is being drawn from a galvanic cell or if a nonzero current is being passed through an electrolytic cell, the cell voltage can differ from its equilibrium value. When you are cranking your automobile engine, the voltage in the starting circuit might drop from its equilibrium value of 12 volts to 10 or 11 volts. This deviation arises from *polarization* of the cell, which is caused by nonequilibrium changes at the surface of the electrode and in the solutions near the electrodes. An electrode that passes no current, even for a large potential, is called an *ideal polarized electrode*. An electrode that does not change its potential no matter what current is passing is called a *nonpolarizable electrode* or an *ideal depolarized electrode*. All real electrodes are intermediate between these two nonexistent extremes.

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[28] B. A. Zhubanov *et al.*, *Izv. Akad. Nauk. SSR Ser. Khim.*, **17**, 69 (1967), cited in H. R. Allcock and F. W. Lampe, *op. cit.*, p. 268 (note 23).

Electrolytic Cells Near Equilibrium

Figure 13.13 schematically shows a particular electrolytic cell. The two electrodes are made of platinum, and the electrolyte solution is an aqueous HCl solution. The external power supply drives electrons through the external circuit from left to right. In the solution positive ions move from left to right and negative ions move from right to left. An oxidation half-reaction occurs at the left electrode and a reduction half-reaction occurs at the right electrode.

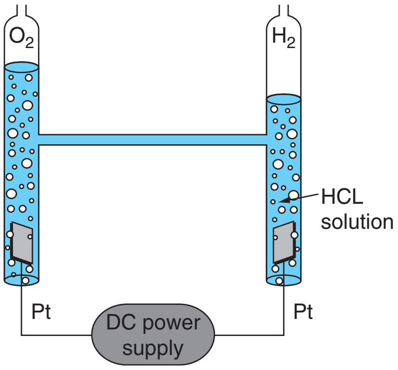

Figure 13.13 An Electrolytic Cell for the Electrolysis of an HCl Solution.

EXAMPLE 13.6

Find the voltage required to produce an infinitesimal electrolysis current at 298.15 K in the cell of Figure 13.13. Determine what products will be produced. Assume that any gaseous products are maintained at pressure $P°$ and that the hydrogen and chloride ions are at unit activity.

Solution

The only possible cathode half-reaction is

$$2\,H^+ + 2e^- \longrightarrow H_2(g) \qquad E° = 0.0000\,V$$

If the hydrogen gas is maintained at the electrode at pressure $P°$, the cathode is a standard hydrogen electrode. There are two conceivable anode half-reactions:

$$2\,H_2O \longrightarrow O_2(g) + 4\,H^+ + 4e^- \qquad E° = -1.229\,V$$
$$2\,Cl^- \longrightarrow Cl_2(g) + 2e^- \qquad E° = -1.3583\,V$$

To produce oxygen at pressure $P°$ with HCl at unit activity, the reversible cell voltage would be -1.229 V. To produce chlorine at pressure $P°$, the reversible cell voltage would have to be -1.3583 V. Water will be oxidized and O_2 will be formed at the anode if a voltage slightly larger than 1.229 V is applied to the cell.

If the products and reactants in Example 13.6 were not at unit activity, the Nernst equation would be used to find the voltage required to produce each possible product.

Exercise 13.19

a. Determine what products will be formed if an aqueous solution of sodium chloride with activity on the molality scale equal to 1.000 is electrolyzed with an infinitesimal current at 298.15 K, and find the voltage required. Assume that any gaseous products are maintained at pressure $P°$. Write the half-reaction equations and the cell reaction equation.

b. Pure sodium chloride can be electrolyzed above its melting temperature of 801°C. Write the half-reaction equations and the cell reaction equation. This is the process used by Sir Humphrey Davy when he first isolated metallic sodium.

Sir Humphrey Davy, 1778–1829, was a great English chemist who discovered several elements, including sodium, potassium, and magnesium. He was also famous for inventing a safety lamp for miners. He hired Michael Faraday as an assistant in 1811, although Faraday had no scientific education at the time.

Electrochemical Cells with Finite Currents. The Electrical Double Layer

We now investigate the molecular processes at the surfaces of electrodes. If a metallic phase such as an electrode is negatively charged, the extra electrons will repel each other and move to the surface of the electrode in order to be as far from each other as possible. Similarly, any excess positive charges will be found at the surface of a positively charged electrode. Ions and neutral molecules can be adsorbed on an electrode surface. Adsorbed ions are divided into two classes. If an ion is adsorbed directly on the surface, it is said to be *specifically adsorbed*. Specifically adsorbed ions are generally adsorbed without a complete "solvation sphere" of attached solvent molecules. Every electrolyte solution contains at least one type of cation and one type of anion, and the cations will generally not be adsorbed to the same extent as the anions, so that adsorbed ions contribute to the charge at the surface. In addition to specifically adsorbed ions, a charged electrode surface will attract an excess of oppositely charged ions in the solution near the electrode. These *nonspecifically adsorbed ions* are fully solvated and will not approach so closely to the surface as specifically adsorbed ions.

The region near an electrode surface thus contains two layers of charge. The electrode surface (including specifically adsorbed ions) has a charge of one sign. This charge attracts a more diffuse layer of ions of the opposite charge, as shown schematically in Figure 13.14a. These two regions are called the *electrical double layer* or sometimes the *diffuse double layer*. The layer of specifically adsorbed ions is called the *compact layer*, the *inner Helmholtz layer*, or the *Stern layer*. The location of the nonspecifically adsorbed ions is sometimes called the *outer Helmholtz plane* or the *Guoy plane*.

Guoy and Chapman developed a theory of the charge distribution in the double layer about 10 years before Debye and Hückel developed their theory of ionic solutions, which is quite similar to it.[29] If one neglects nonelectrostatic contributions to the potential energy of an ion of type i with valence z_i, the concentration of ions of type i in a region of electric potential φ is given by the Boltzmann probability formula, Eq. (9.3-41):

$$c_i = c_{i0}e^{-z_i e\varphi/k_\mathrm{B}T} = c_{i0}e^{-z_i F\varphi/RT} \tag{13.5-1}$$

where c_i is the concentration of ions of type i and where c_{i0} is the concentration at a location where $\varphi = 0$. In the second version of the equation, F is Faraday's constant, equal to $N_\mathrm{Av}e = 96485\ \mathrm{C\ mol^{-1}}$.

Guoy and Chapman combined Eq. (13.4-1) with the Poisson equation of electrostatics and found that if the potential is taken equal to zero at large distances, the electric potential in the diffuse double layer is given as a function of x, the distance from the electrode, by

$$\varphi = \varphi_0 e^{-\kappa x} \tag{13.5-2}$$

where φ_0 is the value of the potential at the surface of the electrode. The parameter κ is given by

$$\kappa = e\left(\frac{2N_\mathrm{Av}\rho_1 I}{\varepsilon k_\mathrm{B}T}\right)^{1/2} \tag{13.5-3}$$

where ε is the permittivity of the solvent, ρ_1 is the density of the solvent, I is the ionic strength as defined in Chapter 7, e is the charge on a proton, k_B is Boltzmann's constant, and T is the absolute temperature. Figure 13.14b shows this potential as a function of distance from the electrode surface for an ionic strength of $0.010\ \mathrm{mol\ kg^{-1}}$ and a temperature of 298.15 K. The *Debye length* is defined equal to $1/\kappa$. It is the distance from the surface of the electrode to the location at which the potential is equal to $1/e$ (about 0.368) of its value at the surface and is a measure of the effective thickness of the diffuse double layer.

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[29] G. Guoy, *J. Phys. (Paris)*, **9**, 457 (1910); D. L Chapman, *Phil. Mag.*, **25**, 475 (1913).

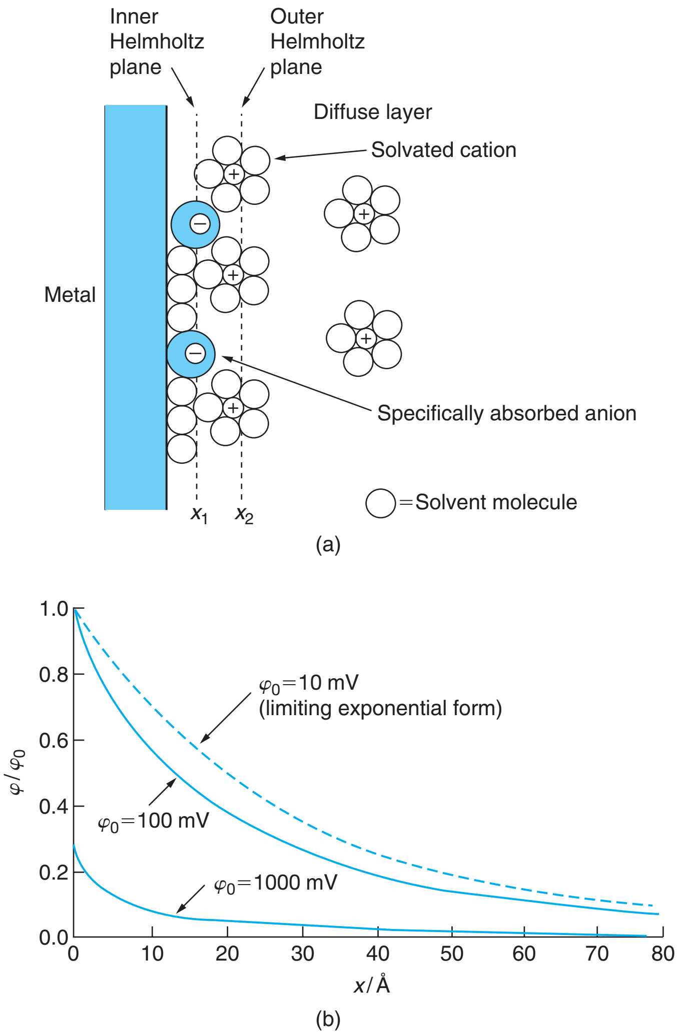

Figure 13.14 The Electrical Double Layer. (a) The structure of the double layer (schematic). From Bard and Faulkner, *op. cit.*, p. 8. (b) The electric potential in the diffuse double layer. From Bard and Faulkner, *op. cit.*, p. 505.

EXAMPLE 13.7

Find the Debye length at 298.15 K for an aqueous solution of HCl with a molality of 0.0200 mol kg^{-1}.

Solution

The permittivity of water at this temperature is 6.954×10^{-10} C^2 N^{-1} m^{-2} and the density of water is 997 kg m^{-3}.

$$\kappa = e\left(\frac{2N_{\mathrm{Av}}\rho_1 I}{\varepsilon k_{\mathrm{B}} T}\right)^{1/2}$$

$$\kappa = (1.602 \times 10^{-19}\ \mathrm{C})\left(\frac{2(6.022 \times 10^{23}\ \mathrm{mol^{-1}})(997\ \mathrm{kg\ m^{-3}})(0.0200\ \mathrm{mol\ kg^{-1}})}{(6.954 \times 10^{-10}\ \mathrm{C^2\ N^{-1}\ m^{-2}})(1.3807 \times 10^{-23}\ \mathrm{J\ K^{-1}})(298.15\ \mathrm{K})}\right)^{1/2}$$

$$= 4.64 \times 10^{8}\ \mathrm{m^{-1}}$$

$$\text{Debye length} = \frac{1}{\kappa} = 2.15 \times 10^{-9}\ \mathrm{m} = 21.5\ \text{Å}$$

The electrical double layer resembles a capacitor, which is a pair of parallel conducting plates separated by a dielectric medium or a vacuum, and which can hold charges of opposite sign on the two plates. Typical values of the capacitance of the electrical double layer range from 10 to 40 μF cm^{-2} (microfarads per square centimeter).[30] The *farad* is defined such that a voltage difference of 1 volt on a capacitor with capacitance 1 farad will produce a charge of 1 coulomb on each plate. It is a rather large unit, so that the microfarad is the practical unit. The *charge density* (charge per unit volume) ρ_c is given by

$$\rho_c = F(z_+c_+ + z_-c_-) \tag{13.5-4}$$

where z_+ and z_- are the valences of the cation and anion, respectively, and c_+ and c_- are the concentrations of the cation and anion, respectively. In a neutral electrolyte solution far from a charged surface, the charge density equals zero. The charge density near a charged surface can be obtained by combining Eqs. (13.5-1), (13.5-2), and (13.5-4).

EXAMPLE 13.8

Write the equation for the charge density in the Guoy–Chapman theory.

$$c_+ = c_{+0}e^{-z_+F\varphi/RT}$$

$$c_- = c_{-0}e^{-z_-F\varphi/RT}$$

$$\varphi = \varphi_0 e^{-\kappa x}$$

$$\rho_c = Fz_+c_{+0}\exp\left(\frac{-z_+F\varphi_0 e^{-\kappa x}}{RT}\right) + Fz_-c_{-0}\exp\left(\frac{-z_-F\varphi_0 e^{-\kappa x}}{RT}\right)$$

Figure 13.15 shows the charge density in an aqueous 1-1 electrolyte solution of molality equal to 0.010 mol kg^{-1} at 298.15 K in the vicinity of a positive electrode with $\varphi_0 = 10$ mV, according to the Guoy–Chapman theory.

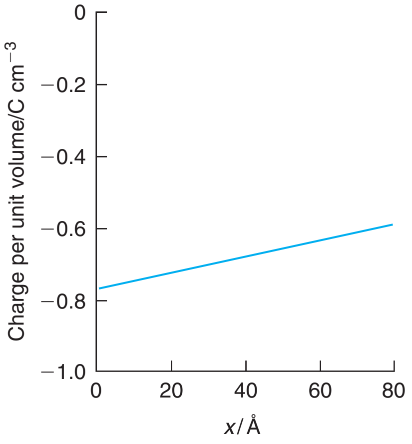

Figure 13.15 The Distribution of Charge in the Diffuse Double Layer According to the Guoy–Chapman Theory.

Rates of Electrode Processes

The chemical reaction at an electrode can be an oxidation (anodic) half-reaction or a reduction (cathodic) half-reaction. Either of these half-reactions if occurring alone

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[30] A. J. Bard and L. R. Faulkner, *Electrochemical Methods—Fundamentals and Applications*, Wiley, New York, 1980, p. 8.

would correspond to a current passing through the electrochemical cell. At equilibrium no current is flowing but the two half-reactions can occur with nonzero rates and produce anodic and cathodic currents that cancel. The *exchange current* is defined as the equilibrium magnitude of each of these currents. The exchange current per unit area is denoted by j_0 and is commonly expressed in $\mathrm{A\,cm^{-2}}$ (amperes per square centimeter).

If the exchange current is large, a relatively small change in either the anodic or cathodic current can produce a sizable net current, so that the electrode can approximate a nonpolarizable electrode. If the exchange current is small, only a small net current is likely to occur, and the electrode can approximate an ideal polarizable electrode. The magnitude of the exchange current depends on the temperature, and is different for different electrode materials and different solution compositions. Typical values range from $5.4 \times 10^{-3}\ \mathrm{A\,cm^{-2}}$ for $0.0200\ \mathrm{mol\,L^{-1}}\ \mathrm{Zn^{2+}}$ against a zinc amalgam with mole fraction 0.010, down to $10^{-10}\ \mathrm{A\,cm^{-2}}$ for the oxygen electrode with a platinum surface in acid solution.[31] The zinc amalgam electrode is said to be a *reversible electrode*, since it is possible to reverse the direction of the net current at this electrode with a small change in potential. The oxygen electrode is called an *irreversible electrode*, since a small change in potential produces a negligible change in net current, because of the small size of the exchange current.

The Overpotential

The *back e.m.f.* is a voltage that opposes the passage of a current through an electrolytic cell. There are three sources of the back e.m.f. The first is the *reversible back e.m.f.* due to the cell reaction. For example, in a Daniell cell with unit activities the reversible back e.m.f. is the equilibrium standard-state cell potential of 1.100 V. For activities other than unit activities, the reversible back e.m.f. can be calculated from the Nernst equation. For an infinitesimal electrolytic current, the reversible back e.m.f. is the only contribution to the back e.m.f. For a finite current, the "IR drop" in the voltage across the electrolyte solution due to its electrical resistance also contributes. In many cases, we will be able to neglect this contribution. The third source of back e.m.f. for a finite current is the *overpotential*, which is due to the polarization of the electrode.

There are two principal contributions to the overpotential.[32] The first contribution is the concentration overpotential, which is due to changes in concentration near the surface of the electrodes due to the passage of the current. The second contribution is the activation overpotential, related to the activation energy of the chemical reaction at the electrode.

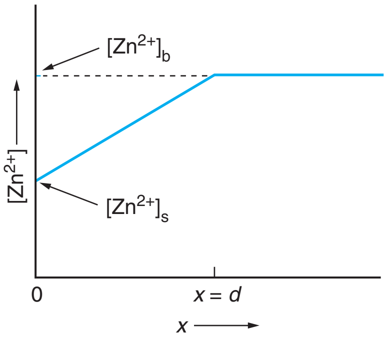

Figure 13.16 The Assumed Concentration Profile in a Boundary Layer Near an Electrode.

The Concentration Overpotential If a Daniell cell is undergoing electrolysis at a nonzero rate, zinc ions are being reduced at the surface of the zinc electrode. If there is no stirring, the zinc ions are replaced from the bulk solution by diffusion. As a simplification, let us assume that the concentration of zinc ions near the zinc electrode varies linearly, as represented in Figure 13.16, where d is the effective thickness of the boundary layer. The value of d depends on the shape of the electrodes, the concentration of the solutes, the value of the diffusion coefficient, and so on. We will not attempt to evaluate it directly, but will express it in terms of a limiting current.

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[31] H. A. Laitinen and W. E. Harris, *Chemical Analysis*, 2nd ed., McGraw-Hill, New York, 1975, p. 233.
[32] *Ibid.*, p. 258ff.

For a planar electrode and for the assumed concentration profile of Figure 13.16, Fick's law of diffusion, Eq. (10.2-4), gives the diffusion flux of zinc ions as

$$J(\mathrm{Zn}^{2+}) = D(\mathrm{Zn}^{2+})\frac{[\mathrm{Zn}^{2+}]_\mathrm{b} - [\mathrm{Zn}^{2+}]_\mathrm{s}}{d} \tag{13.5-5}$$

where $D(\mathrm{Zn}^{2+})$ is the diffusion coefficient of Zn^{2+} ions, where $[\mathrm{Zn}^{2+}]_\mathrm{b}$ is the concentration in the bulk of the solution, and where $[\mathrm{Zn}^{2+}]_\mathrm{s}$ is the concentration at the surface of the electrode. The *current density* j (current per unit area of electrode surface) is

$$j = nFJ(\mathrm{Zn}^{2+}) = nFD(\mathrm{Zn}^{2+})\frac{[\mathrm{Zn}^{2+}]_\mathrm{b} - [\mathrm{Zn}^{2+}]_\mathrm{s}}{d} \tag{13.5-6a}$$

where n is the number of electrons reacting per ion ($n = 2$ in the case of Zn^{2+} ions).

If a large electrolytic current flows, the concentration of zinc ions at the surface will be small because the ions are rapidly reduced at the surface. The current density approaches a limit for large counter e.m.f., in which case the surface concentration approaches zero:

$$j_\mathrm{lim} = \frac{nFD[\mathrm{Zn}^{2+}]_\mathrm{b}}{d} \tag{13.5-6b}$$

If the potential is increased enough, water can be reduced to form hydrogen gas, so the limiting value in Eq. (13.5-7) must be estimated from potentials that are not sufficient to reduce water or any reducible species other than zinc ions.

If there is stirring, the zinc ions are brought to the electrode by convection as well as by diffusion. If convection predominates, the quotient $D(\mathrm{Zn}^{2+})/d$ in Eq. (13.5-7) is replaced by the rate of convection (volume of solution brought to unit area of electrode per second) called m, the *mass transport coefficient*. With a combination of convection and diffusion $D(\mathrm{Zn}^{2+})/d$ is replaced by a weighted sum of $D(\mathrm{Zn}^{2+})/d$ and the rate of convection.

If we regard the boundary layer as a concentration cell, the analogue of Eq. (8.3-7) gives the electric potential difference across the boundary layer. This potential difference is the concentration overpotential, denoted by η_conc:

$$|\eta_\mathrm{conc}| = \frac{RT}{nF}\ln\left(\frac{[\mathrm{Zn}^{2+}]_\mathrm{b}}{[\mathrm{Zn}^{2+}]_\mathrm{s}}\right) \tag{13.5-7}$$

Using Eqs. (13.5-6) and (13.5-7) and assuming that activity coefficients are equal to unity we obtain the relation for the concentration overpotential:

$$|\eta_\mathrm{conc}| = -\frac{RT}{nF}\ln\left(1 - \frac{j}{j_\mathrm{lim}}\right) \tag{13.5-8}$$

Exercise 13.20

Show that Eq. (13.5-8) follows from Eqs. (13.5-6) and (13.5-7).

EXAMPLE 13.9

Evaluate the concentration overpotential at a cadmium amalgam electrode, the diffusion flux of Cd^{2+} ions, and the current per square centimeter for 298.15 K. Assume that $d = 200\ \mu\mathrm{m}$, that the concentration at the electrode is $0.0100\ \mathrm{mol\,L^{-1}}$, and that the concentration in the bulk is $0.0200\ \mathrm{mol\,L^{-1}}$. The diffusion coefficient for Cd^{2+} ions at this temperature equals $8.7 \times 10^{-10}\ \mathrm{m^2\,s^{-1}}$.[a]

Solution

$$|\eta_{\mathrm{conc}}| = \frac{(8.31435\ \mathrm{J\,K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})}{2(96485\ \mathrm{C\,mol^{-1}})} \ln\left(\frac{0.0200\ \mathrm{mol\,L^{-1}}}{0.0100\ \mathrm{mol\,L^{-1}}}\right) = 0.00890\ \mathrm{V}$$

$$J(\mathrm{Cd}^{2+}) = D(\mathrm{Cd}^{2+})\frac{\partial c(\mathrm{Cd}^{2+})}{\partial x} \approx (8.7 \times 10^{-10}\ \mathrm{m^2\ s^{-1}})\frac{0.0100\ \mathrm{mol\,m^{-3}}}{200 \times 10^{-6}\ \mathrm{m}}$$

$$= 4.35 \times 10^{-8}\ \mathrm{mol\,m^{-2}\ s^{-1}}$$

$$j(\mathrm{Cd}^{2+}) = 2FJ(\mathrm{Cd}^{2+}) = 2(96485\ \mathrm{C\,mol^{-1}})(4.35 \times 10^{-8}\ \mathrm{mol\,m^{-2}\ s^{-1}})$$

$$= 8.4 \times 10^{-3}\ \mathrm{A\,m^{-2}} = 8.4 \times 10^{-7}\ \mathrm{A\,cm^{-2}}$$

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[a] A. J. Bard and L. R. Faulkner, *op. cit.*, p. 154.

Equation (13.5-8) gives the concentration overpotential for one electrode. The concentration overpotential of the Daniell cell contains also a contribution from the other electrode, from which newly formed copper ions diffuse into the bulk of the solution. It is sometimes possible to study the behavior of a single electrode by the use of a *reference electrode* and a third electrode, called a *counter electrode*. A common choice for a reference electrode is a silver/silver chloride electrode in a saturated potassium chloride solution. The counter electrode is placed in a container with a porous plug, which forms a liquid junction. The liquid junction potential is presumably fairly small and nearly constant if the KCl solution is much more concentrated than the cell solution. The liquid junction is placed close to the surface of the electrode to be studied (the working electrode), as in Figure 13.17. The potential difference between the reference electrode and the working electrode is measured without allowing a current to pass between the reference electrode and the working electrode, but allowing a controlled current to pass between the working electrode and the counter electrode.

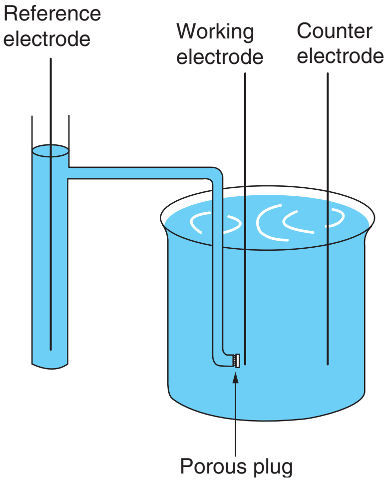

Figure 13.17 An Electrochemical Cell with a Third Electrode.

The Activation Overpotential This part of the overpotential is due to chemical processes at the electrode. For example, consider a cation that can be further oxidized by losing n electrons at an inert electrode such as a platinum electrode. An example of such a half-reaction is

$$\mathrm{Fe}^{2+} \rightleftharpoons \mathrm{Fe}^{3+} + e^- \qquad (13.5\text{-}9)$$

where $n = 1$ in this example. We assume that the progress of the oxidation half-reaction can be represented by a potential energy depending on the distance traveled by an ion toward the electrode as shown in Figure 13.18a. This distance represents a type of *reaction coordinate*. Increase in the value of the reaction coordinate (from left to right in the diagram) represents a complicated process: the ion moves toward the electrode, the electrons detach from the ion, and the electrons move into the electrode. The region near an electrode surface can be a region of very high electric fields. A potential difference of 1 V across an interface region with a thickness of 10 nm corresponds to a field of $1 \times 10^8\ \mathrm{V\ m^{-1}}$.

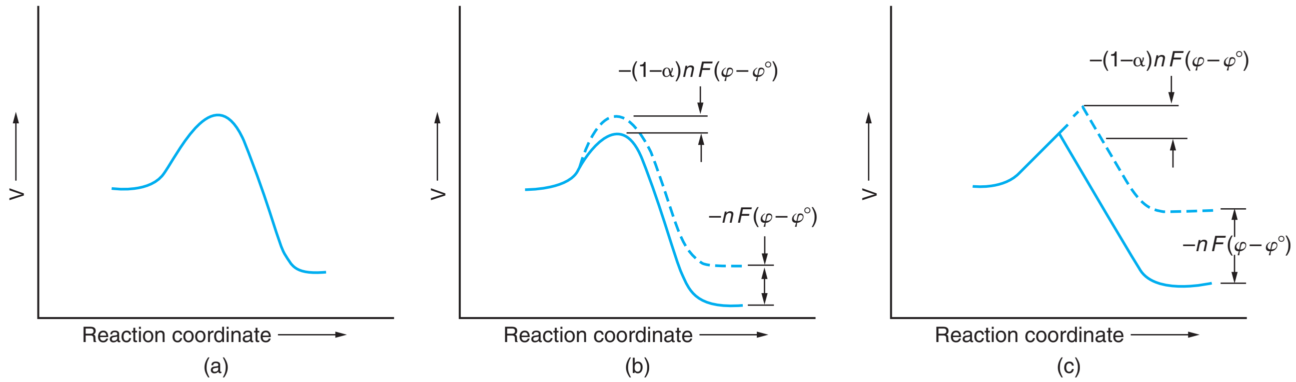

Figure 13.18 The Potential Energy as a Function of a Reaction Coordinate. (a) Without applied potential. (b) With a negative applied potential. (c) Figure to show the effect of the symmetry factor. After Bard and Faulkner, *op. cit.*, p. 94.

The maximum in the potential energy is partly due to the increase of the potential energy of the positive ions as they approach the positive electrode, and partly due to the energy required to remove electrons from the ions. The decrease of potential energy as the reaction proceeds past the maximum in Figure 13.18a is due to the binding of the electrons into the electrode. We regard the state of high potential energy as a transition state and interpret the potential energy to reach the maximum from the left as the activation energy for the oxidation half-reaction, denoted by $E_{\mathrm{a,ox}}$. The potential energy required to reach the maximum from the right is the activation energy for the reverse (reduction) half-reaction, denoted by $E_{\mathrm{a,red}}$. The rate constants of the forward and reverse half-reactions can be represented by the Arrhenius formula of Eq. (12.3-1):

$$k_{\mathrm{ox}} = A_{\mathrm{ox}} e^{-E_{\mathrm{a,ox}}/RT} \tag{13.5-10a}$$

$$k_{\mathrm{red}} = A_{\mathrm{red}} e^{-E_{\mathrm{a,red}}/RT} \tag{13.5-10b}$$

where we assume that the preexponential factors A_{ox} and A_{red} are temperature-independent.

If the system is at equilibrium and if each half-reaction is first order, we can write for unit area of the electrode

$$\begin{aligned} \text{oxidation rate per unit area} &= k_{\mathrm{ox}}[\mathrm{R}]_{\mathrm{eq}} \\ &= k_{\mathrm{red}}[\mathrm{O}]_{\mathrm{eq}} \\ &= \text{reduction rate per unit area} \end{aligned} \tag{13.5-11}$$

where [O] is the concentration of the oxidized species (Fe^{3+} in our example) and [R] is the concentration of the reduced species (Fe^{2+} in our example) at the surface of the electrode. At equilibrium at the standard-state voltage [R] and [O] are equal and $k_{\mathrm{red}} = k_{\mathrm{ox}}$. We denote this value of the rate constants by k_{eq}°:

$$k_{\mathrm{eq}}^{\circ} = A_{\mathrm{ox}} \exp(-E_{\mathrm{a,ox}}^{\circ}/RT) = A_{\mathrm{red}} \exp(-E_{\mathrm{a,red}}^{\circ}/RT) \tag{13.5-12}$$

where the superscript ° means that the values apply in the standard state at equilibrium.

Let us now change the counter e.m.f. in the external circuit, thus changing the electric potential in the electrode from φ° (the value of φ corresponding to $E = E^{\circ}$) to a new value φ. The potential energy of n moles of electrons in the electrode is changed by an amount equal to $-nF(\varphi - \varphi^\circ)$, where n is the number of electrons transferred in the reaction ($n = 1$ in our example). If the maximum in the potential energy curve remains at the same position, the activation energy for the reduction increases by $nF(\varphi - \varphi^\circ)$ while the activation energy of the oxidation remains unchanged. However, the ordinary case is that, as shown schematically in Figure 13.18b, the position of the maximum is lowered, but by a magnitude smaller than $|nF(\varphi - \varphi^\circ)|$.

We define a parameter α such that the position of the minimum is lowered by $(1-\alpha)nF(\varphi - \varphi^\circ)$, lowering the activation energy of the oxidation by the same amount. The activation energy of the reduction is increased by the amount $\alpha nF(\varphi - \varphi^\circ)$. The parameter α is called the *transfer coefficient* or the *symmetry factor*. The name "symmetry factor" is used because its value, which generally lies between 0 and 1, is related to the shape (symmetry) of the curve in Figure 13.18a.

Figure 13.18c shows in an oversimplified way how the shape of the curve affects the value of α. For this illustration we assume that the position of the right side of the curve is determined solely by the electric potential at the electrode, whereas the left side of the curve is determined solely by chemical factors that are unaffected by the potential of the electrode, and assume also that the two sides of the curve meet at a cusp. When the electric potential is increased by an amount $\varphi - \varphi^\circ$, the entire right side is lowered by an amount $nF(\varphi - \varphi^\circ)$. The peak drops by an amount $nF(\varphi - \varphi^\circ)/2$ (corresponding to $\alpha = 1/2$) if the slopes of the two sides are equal in magnitude, and by a different amount if the slopes have different magnitudes. The parameter α is thus a measure of the asymmetry of the curve in the diagram.

Exercise 13.21

Show by sketching graphs similar to Figure 13.18c that $\alpha < 1/2$ if the left side of the curve is steeper than the right, and that $\alpha > 1/2$ if the right side is steeper.

Assuming that the preexponential factors in Eq. (13.5-10) do not depend on the electric potential in the electrode, we write

$$\begin{aligned} k_{\text{ox}} &= A_{\text{ox}}\exp\left[-\frac{E_{\text{a,ox}} - (1-\alpha)nF(\varphi - \varphi^\circ)}{RT}\right] \\ &= k^\circ \exp\left[\frac{(1-\alpha)nF(\varphi - \varphi^\circ)}{RT}\right] \end{aligned} \tag{13.5-13a}$$

Similarly,

$$k_{\text{red}} = k^\circ \exp\left[-\alpha nF(\varphi - \varphi^\circ)/RT\right] \tag{13.5-13b}$$

Let us now investigate the case of equilibrium at a potential not necessarily equal to φ°. The magnitudes of j_a, the anodic current per unit area, and j_c, the cathodic current per unit area of electrode, are given by

$$|j_{\text{a}}| = nFk_{\text{ox}}[\text{R}]_{\text{s}} \tag{13.5-14a}$$

$$|j_{\text{c}}| = nFk_{\text{red}}[\text{O}]_{\text{s}} \tag{13.5-14b}$$

where the concentrations at the surface of the electrode enter in these equations. At equilibrium, the net current is zero and the surface concentrations are equal to the bulk concentrations, so that

$$nFk^{\circ}\exp\left[\frac{(1-\alpha)nF\left(\varphi_{\mathrm{eq}}-\varphi^{\circ}\right)}{RT}\right][\mathrm{R}]_{\mathrm{b}}= nFk^{\circ}\exp\left[-\frac{\alpha nF\left(\varphi_{\mathrm{eq}}-\varphi^{\circ}\right)}{RT}\right][\mathrm{O}]_{\mathrm{b}} \tag{13.5-15}$$

Each side of Eq. (13.5-15) is equal to the exchange current density (the exchange current per unit area). When equal factors on the two sides of this equation are canceled, the symmetry factor α disappears from the equation:

$$\exp\left[\frac{nF\left(\varphi_{\mathrm{eq}}-\varphi^{\circ}\right)}{RT}\right]=\frac{[\mathrm{O}]_{\mathrm{b}}}{[\mathrm{R}]_{\mathrm{b}}} \tag{13.5-16}$$

This equation is equivalent to the Nernst equation, which means that our treatment is consistent with equilibrium electrochemistry.

Exercise 13.22

Carry out the algebraic steps to put Eq. (13.5-16) into the standard form of the Nernst equation.

If both sides of Eq. (13.5-16) are raised to the $-\alpha$ power, we obtain

$$\exp\left[\frac{-\alpha nF\left(\varphi_{\mathrm{eq}}-\varphi^{\circ}\right)}{RT}\right]=\left[\frac{[\mathrm{O}]_{\mathrm{b}}}{[\mathrm{R}]_{\mathrm{b}}}\right]^{-\alpha} \tag{13.5-17}$$

When Eq. (13.5-17) is substituted into Eq. (13.5-15), we obtain an expression for the exchange current density, j_0:

$$j_0 = nFk^{\circ}[\mathrm{R}]_{\mathrm{b}}^{1-\alpha}[\mathrm{O}]_{\mathrm{b}}^{\alpha} \tag{13.5-18}$$

If the voltage is changed from the equilibrium value, the resulting current density is

$$\begin{aligned} j &= j_a - |\,j_c| \\ &= nFk^{\circ}\exp\left[\frac{(1-\alpha)nF(\varphi-\varphi^{\circ})}{RT}\right][\mathrm{R}]_{\mathrm{s}} \\ &\quad - nFk^{\circ}\exp\left[\frac{-\alpha nF(\varphi-\varphi^{\circ})}{RT}\right][\mathrm{O}]_{\mathrm{s}} \end{aligned} \tag{13.5-19}$$

where we count the current as positive if the electrode half-reaction proceeds in the oxidation direction. Equation (13.5-19) gives the dependence of the current on the potential for any value of the potential. We now express this dependence in terms of the overpotential, η, defined by

$$\eta = \varphi - \varphi_{\mathrm{eq}} \tag{13.5-20}$$

We divide the first term on the right-hand side of Eq. (13.5-19) by the left-hand side of Eq. (13.5-15) and divide the second term by the right-hand side of Eq. (13.5-15) and obtain

$$\frac{j}{j_0}=\frac{[\mathrm{R}]_{\mathrm{s}}}{[\mathrm{R}]_{\mathrm{b}}}=\exp\left[\frac{(1-\alpha)nF\eta}{RT}\right]-\frac{[\mathrm{O}]_{\mathrm{s}}}{[\mathrm{O}]_{\mathrm{b}}}\exp\left[\frac{-\alpha nF\eta}{RT}\right] \tag{13.5-21}$$

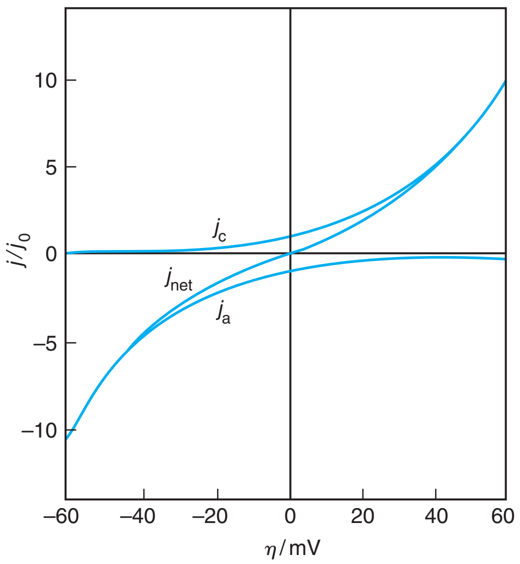

Figure 13.19 The Anodic Current, the Cathodic Current, and the Net Current at an Electrode as a Function of the Overpotential (Schematic).

Exercise 13.23

Carry out the steps of algebra to obtain Eq. (13.5-21).

Equation (13.5-21) is a fundamental equation of electrode kinetics. It indicates that the current is proportional to the exchange current, but that it has a fairly complicated dependence on the overpotential. Figure 13.19 shows the anodic current, the cathodic current, and the net current for a hypothetical electrode reaction. Ohm's law is not obeyed except for small values of the overpotential.

If stirring is so efficient that the bulk and surface concentrations are equal, the concentrations cancel out of Eq. (13.5-21), which is then known as the *Butler–Volmer equation*:

$$\frac{j}{j_0} = \exp\left[\frac{(1-\alpha)nF\eta}{RT}\right] - \exp\left[\frac{-\alpha nF\eta}{RT}\right] \tag{13.5-22}$$

There are two important limiting cases. One is the case of small overpotential, in which case the exponents in Eq. (13.5-21) or Eq. (13.5-22) are small, and the approximation

$$e^x \approx 1 + x$$

can be used. Application of this approximation to the Butler–Volmer equation gives

$$j \approx j_0\left[1 + \frac{(1-\alpha)nF\eta}{RT} - 1 + \frac{\alpha nF\eta}{RT}\right] \approx \frac{j_0 nF\eta}{RT} \tag{13.5-23}$$

so that Ohm's law is obeyed. The factor $RT/(j_0 nF)$ has the dimensions of resistance and is sometimes called the *charge transfer resistance*.

The second limiting case is that of large overpotential. Consider the case that the overpotential is large and negative. The second term on the right-hand side of the

Butler–Volmer equation, Eq. (13.5-22), is much larger than the first term, and

$$|j| \approx j_0 e^{-\alpha nF\eta/RT} \tag{13.5-24}$$

Solving this equation for η gives

$$\eta = \frac{RT}{\alpha nF}\ln(j_0) - \frac{RT}{\alpha nF}\ln(|j|) \tag{13.5-25}$$

Equation (13.5-25) is of the form of the *Tafel equation*, an empirical equation of the form

$$|\eta| = a + b\log_{10}(|j|) \tag{13.5-26}$$

The reduction of hydrogen ions at various metal electrode surfaces has been extensively studied. The mechanism of the electrode reaction can depend on the material of the electrode. One possible mechanism is[33]

$$(1)\quad H^+ + e^- + M \rightleftharpoons M{-}H \tag{13.5-27a}$$

$$(2)\quad 2\,M{-}H \longrightarrow 2\,M + H_2 \tag{13.5-27b}$$

where M denotes the metal of the electrode, and M−H denotes a chemically adsorbed hydrogen atom. Another possible mechanism is[34]

$$(1)\quad H^+ + e^- + M \rightleftharpoons M{-}H \tag{13.5-28a}$$

$$(2)\quad M{-}H + H^+ + e^- \longrightarrow M + H_2 \tag{13.5-28b}$$

In either of these mechanisms, it is possible for different metals that either the first step or the second step is rate-limiting. If the first step of the mechanism of Eq. (13.5-27) is rate-limiting in both directions,

$$(\text{forward rate}) = k_1[H^+]_G(1-\theta) \tag{13.5-29}$$

where $[H^+]_G$ denotes the concentration of hydrogen ions at the Guoy plane (outer Helmholtz plane) and θ denotes the fraction of surface sites occupied by hydrogen atoms. If the electric potential in the bulk of the solution is called zero, then by the Boltzmann probability distribution

$$[H^+]_G = [H^+]_b e^{-F\varphi_1/RT} \tag{13.5-30}$$

where $[H^+]_b$ denotes the concentration of H^+ in the bulk of the solution and where φ_1 is the electric potential at the Guoy plane.

The rate at equilibrium gives the exchange current. Using Eq. (13.5-13a) for the rate constant,

$$j_0 = F(1-\alpha)[H^+]_b \exp\left[\frac{-F\varphi_1}{RT}\right]k^\circ \exp\left[\frac{(1-\alpha)nF(\varphi-\varphi^\circ)}{RT}\right] \tag{13.5-31}$$

With the expression in Eq. (13.5-31) for the exchange current, the Butler–Volmer equation, Eq. (13.5-22), and Eqs. (13.5-23) through (13.5-25) can be used, since it is of the same form for a reduction as for an oxidation half-reaction.

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[33] K. J. Laidler, *J. Chem. Educ.*, **47**, 600 (1970) (note 1).

[34] *Ibid.*

For a current density of 0.01 A cm^{-2} and a hydrogen ion concentration of 1.0 mol L^{-1}, the overpotentials for the reduction of hydrogen ions at several electrodes are found to be[35]

0.035 V	for platinized platinum
0.56 V	for iron
0.76 V	for silver
1.10 V	for mercury

Overpotentials for different reactions at the same electrode will also differ from each other in different ways, and it is even possible to react one substance at a nonzero current when another substance in the solution would preferentially react at an infinitesimal current. An example that is exploited in *polarography* is the reduction of a fairly active metal onto a mercury electrode. The overpotential for production of hydrogen from water on a mercury electrode is so large that almost no hydrogen is evolved at a potential difference sufficient to plate out the metal, even if hydrogen would preferentially be evolved at an infinitesimal current.

PROBLEMS

Section 13.5: Nonequilibrium Electrochemistry

13.33 In the *Hall–Heroult process* for the production of aluminum, aluminum oxide is dissolved in molten cryolite, Na_3AlF_6, which melts at 1000°C, and electrolyzed. The cathode is molten aluminum, and the anode is made of graphite. The anode product is carbon dioxide. Write the half-reaction equations and the cell reaction equation.

13.34 Find the activity of chloride ion necessary so that chlorine instead of oxygen would be evolved when an infinitesimal current flows at 298.15 K in the electrolysis cell of Example 13.6.

13.35 Find the value of the charge transfer resistance at 298.15 K for the reduction of hydrogen ion from a solution of 0.0100 mol L^{-1} on a mercury electrode with an area of 1.00 cm^2. Assume a value of the exchange current density of $j_0 = 2.5 \times 10^{-15}\,\mathrm{A\,cm^{-2}}$.

13.36 For the formation of hydrogen gas from a dilute sulfuric acid solution on a mercury electrode at 25°C, the current density was equal to $4.8 \times 10^{-6}\,\mathrm{A\,cm^{-2}}$ at an overpotential of 0.60 V and was equal to $3.7 \times 10^{-7}\,\mathrm{A\,cm^{-2}}$ at an overpotential of 0.50 V. Find the values of the parameters in the Tafel equation, Eq. (13.5-26).

13.6 Experimental Molecular Study of Chemical Reaction Mechanisms

The "classical" study of chemical reaction rates involves determination of concentrations of reactants or products as a function of time. Such information cannot lead directly to knowledge of a reaction mechanism. However, there are techniques that deliver molecular information about a reaction mechanism.

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[35] W. C. Gardiner, Jr., *Rates and Mechanisms of Chemical Reactions*, W. A. Benjamin, Inc., New York, 1969, p. 197.

Detection of Reactive Intermediates

If a reactive intermediate included in a proposed mechanism can be detected in the experimental system, that mechanism becomes more plausible, and if the intermediate's concentration can be determined as a function of time, individual rate constants for elementary steps can sometimes be evaluated. The most direct technique for detecting reactive intermediates is spectroscopy, since spectrophotometers with very rapid response times can be constructed. An early example of spectroscopic detection of a reactive intermediate was a study of the decomposition of N_2O_5.[36] According to the mechanism of Example 12.13, the first step is the formation of NO_2 and NO_3 from N_2O_5. Schott and Davidson carried out shock tube studies, using the reaction vessel as a spectrophotometer cell. They monitored the absorption of light at 546 nm and 652 nm, at which wavelengths NO_3 absorbs much more strongly than NO_2; at 366 nm, at which wavelength NO_2 absorbs more strongly than does NO_3; and at 436 nm, at which wavelength NO_2 and NO_3 absorb nearly equally. They were able to determine the concentration of NO_3 as a function of time and to calculate values for the elementary rate constants in the mechanism of Example 12.13. They found that the preexponential factor in the Arrhenius expression for k_2 is equal to $1.66 \times 10^8\,\mathrm{L\,mol^{-1}\,s^{-1}}$ and that the activation energy for k_2 is approximately equal to $16\,\mathrm{kJ\,mol^{-1}}$ over the temperature range from 300 K to 820 K.

Exercise 13.24

Find the value of k_2 at 300 K and at 800 K.

Another technique for the detection of reactive intermediates is *mass spectrometry*. In a mass spectrometer molecules are converted into positive ions, often undergoing fragmentation in the process. The resulting ions are accelerated by an electrical field, attaining a speed depending on their charge/mass ratio. They are then passed through electrical and magnetic fields (or other analyzing devices) and separated, so that the number of ions with each charge/mass ratio can be determined. The identity and structure of a substance can sometimes be deduced from its molecular mass and from its fragmentation pattern. To detect reactive intermediates, one carries out a gas-phase reaction in a vessel that adjoins the ionization chamber of a mass spectrometer. A small aperture allows the mixture of reacting gases to pass into the ionization chamber of the mass spectrometer. The low pressure in both chambers lowers the collision rate of reactive intermediates, prolonging their lifetimes. The mass spectrum of a reactive intermediate can sometimes be found in the mass spectrum of the reacting mixture.

It is also possible to infer the presence of certain kinds of reactive intermediates from their chemical effects. In the *mirror technique* a reacting gas is passed through a tube with a metallic mirror deposited on its inner surface. If free radicals are present they can combine with the metal to form volatile products that can be trapped at low temperature and analyzed. For example, a lead mirror will combine with methyl radicals to form tetramethyl lead, $Pb(CH_3)_4$, a stable substance that can be condensed in a cold

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[36] G. Schott and N. Davidson, *J. Am. Chem. Soc.*, **80**, 1841 (1958). See also H. Sun and F. Heinz, *J. Phys. Chem.*, **B101**, 705 (1997).

trap.[37] Molecular oxygen also reacts with free radicals, and if addition of oxygen to a reacting system inhibits the rate of reaction it is likely that some kind of a free radical intermediate is present in the reaction mechanism.

Another technique that can be used to detect the presence of free radical intermediates is based on the fact that almost any free radical catalyzes the conversion of *ortho*-H_2 to *para*-H_2 and vice versa. In *ortho*-H_2 the nuclear spins are parallel, and in *para*-H_2 the nuclear spins are antiparallel. At room temperature equilibrium H_2 consists of 75% *ortho*-H_2 and 25% *para*-H_2, whereas at low temperatures the equilibrium mixture is nearly 100% *para*-H_2. If *para*-H_2 prepared at low temperature is brought in contact with free radicals, the rate of conversion to the equilibrium mixture is a measure of the amount of free radicals present. However, these techniques for the detection of free radical intermediates do not distinguish one free radical intermediate from another.

Another technique is the use of *isotopic substitution*. For example, the decomposition of acetaldehyde

$$CH_3CHO \longrightarrow CH_4 + CO \tag{13.6-1}$$

is thought to proceed by the mechanism

$$(1) \quad CH_3CHO \longrightarrow CH_3 + CHO \tag{13.6-2a}$$

$$(2) \quad CH_3 + CH_3CHO \longrightarrow CH_4 + CH_3CO \tag{13.6-2b}$$

$$(3) \quad CH_3CO \longrightarrow CH_3 + CO \tag{13.6-2c}$$

A mixture of CH_3CHO and CD_3CDO was reacted, where D stands for deuterium (^2H).[38] The product mixture was found to contain the statistically expected mixture of randomly isotopically substituted methanes, which increased the plausibility of this mechanism, since a mechanism without free radicals such as CH_3 would not have mixed the isotopes randomly.

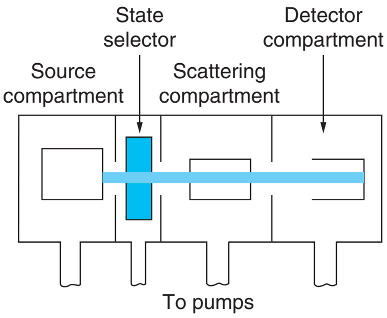

Figure 13.20 An Apparatus for Generating a Molecular Beam (Schematic).

Molecular Beam Reactions

In this technique the reaction is carried out by forming beams of reactants in an otherwise evacuated chamber. Figure 13.20 shows schematically an apparatus for generating a molecular beam. The material is vaporized in an oven and the molecules exit from a small aperture into an evacuated chamber. The molecules pass through a second barrier with a small aperture into a chamber that is evacuated to even lower pressure. This chamber can contain a velocity selector, which passes only those molecules in a narrow range of speeds. Figure 13.21 shows schematically one type of velocity selector, called a *time-of-flight (TOF) selector*. The rotating disks have slots and molecules can pass through the apparatus only if they reach each disk when one of its slots is in the beam position. Varying the speed of rotation of the disks allows different speeds to be selected. The molecules then pass into a third chamber in which the beam molecules can react with a second substance.

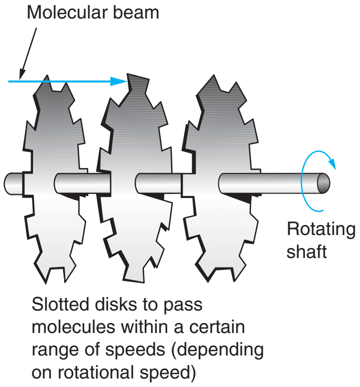

Figure 13.21 A Velocity-Selecting Apparatus (Schematic).

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[37] S. W. Benson, *op. cit.*, p. 101 (note 6) gives a table of free radicals and metals that had been studied as of the 1950s.

[38] S. W. Benson, *op. cit.*, p. 108 (note 6).

EXAMPLE 13.10

If the distance between the two disks in Figure 13.21 is 2.00 cm and if the difference in orientation of the slots in the two disks is 15.0 degrees (0.262 radian), find the rotational speed necessary to pass molecules with a speed of 950 m s^{-1}.

Solution

$$\text{time of flight} = \frac{0.0200\ \text{m}}{950\ \text{m s}^{-1}} = 2.105 \times 10^{-5}\ \text{s}$$

$$\omega = \frac{0.262\ \text{radian}}{2.105 \times 10^{-5}\ \text{s}} = 1.24 \times 10^{4}\ \text{radians s}^{-1}$$

$$(1.24 \times 10^{4}\ \text{radians s}^{-1})\frac{1\ \text{rev}}{2\pi\ \text{radians}} = 1.98 \times 10^{3}\ \text{rev s}^{-1}$$

$$(1.98 \times 10^{3}\ \text{rev s}^{-1})\left(\frac{60\ \text{s}}{1\ \text{min}}\right) = 1.19 \times 10^{5}\ \text{rev min}^{-1}$$

Chemical reactions can be carried out with two crossed molecular beams. Figure 13.22 shows an apparatus for the reaction of chlorine atoms with molecules

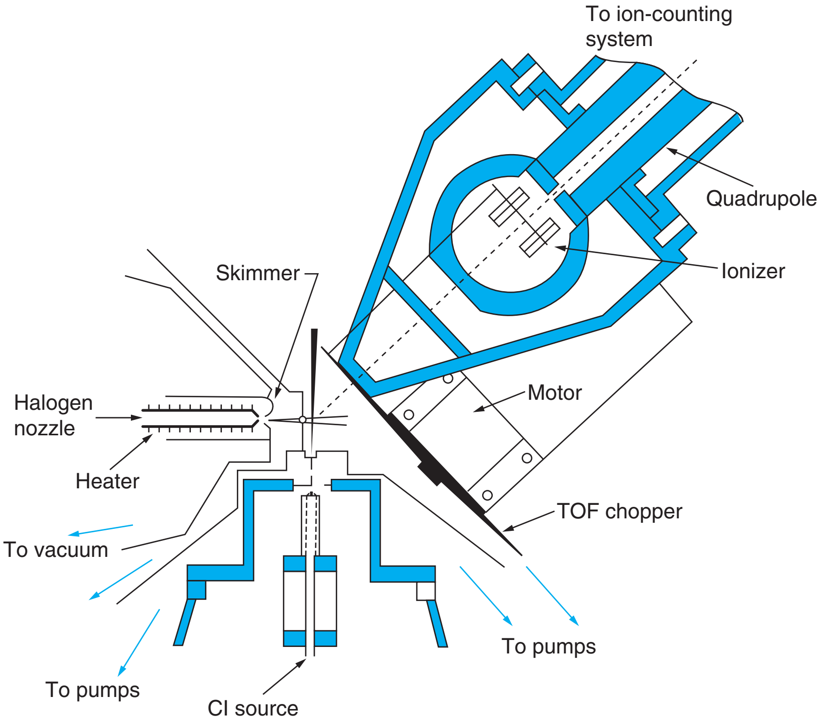

Figure 13.22 A Crossed-Molecular Beam Apparatus (Schematic). From R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity*, Oxford University Press, New York, 1987, p. 234.

of the other halogens. The reactant molecules pass into a mass spectrometer that can be moved to different angles so that the angular distribution of the products can be studied. The TOF selector allows for determination of the velocity distribution of the products, giving information on the distribution of energy between translational and internal degrees of freedom. Other types of detectors are used. For example, a surface ionization detector can detect alkali metal atoms.[39]

It is also possible to carry out a reaction by bringing a beam of molecules into a stationary gaseous sample. The reaction cross section can be measured by the attenuation of the beam. The reaction cross section generally depends on the states of the reactants and products and on the collision energy. An ordinary chemical reaction is a sum of such reactions, since various states of the reactant and product molecules are represented in a system of many molecules. The "ideal" molecular beam kinetics experiment would give the reaction cross section for different values of the collision energy and for different states of the reactants, the angular distribution of products, the velocity distribution of the product molecules, and the distribution of electronic, vibrational, and rotational states of the products. No single experiment has given all of these pieces of information, but each of them has been obtained in at least one kind of experiment. Some techniques used in molecular beam experiments are:[40]

1. *Chemiluminescence*. In this method, radiation emitted by excited products is spectroscopically analyzed as it is emitted. The intensities of radiation due to various transitions can be used to determine the population distribution for product states. Modern techniques also allow time-resolved spectra to be observed (intensity as a function of time as well as of wavelength). Measurements in the picosecond region are becoming common and femtosecond measurements are being carried out.
2. *Chemical lasers*. Some reactions produce product molecules with an inverted population distribution. That is, the population of some state of higher energy is larger than that of some state of lower energy. In this case, a *chemical laser* is possible, in which incident radiation can cause stimulated emission, and in which radiation of the same wavelength is emitted. For example, the flash photolysis of trifluoroiodomethane in the presence of hydrogen and a buffer gas can produce excited HF molecules with a population inversion:

$$(1) \quad CF_3I \xrightarrow{\text{uv flash}} F + CF_2I \tag{13.6-3a}$$

$$(2) \quad F + H_2 \longrightarrow H + HF^* \tag{13.6-3b}$$

$$(3) \quad HF^* \xrightarrow{\text{stimulated emission}} HF + h\nu \tag{13.6-3c}$$

   Incident radiation of the proper frequency can cause emission of radiation from the excited HF molecules. Figure 13.23 shows the laser emission as a function of time for a number of transitions in this system.
3. *Laser pump and laser probe*. In this technique one laser is trained on a beam of reactant molecules, essentially using photons as one of the reagents. A second laser is trained on the beam in the product region, raising product molecules to excited states, from which they fluoresce. Spectroscopic analysis of the fluorescent radiation gives information about the distribution of products and their states.

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[39] G. G. Hammes, *Principles of Chemical Kinetics*, Academic Press, New York, 1978, p. 113ff.

[40] G. G. Hammes, *op. cit.*, p. 210ff (note 39).

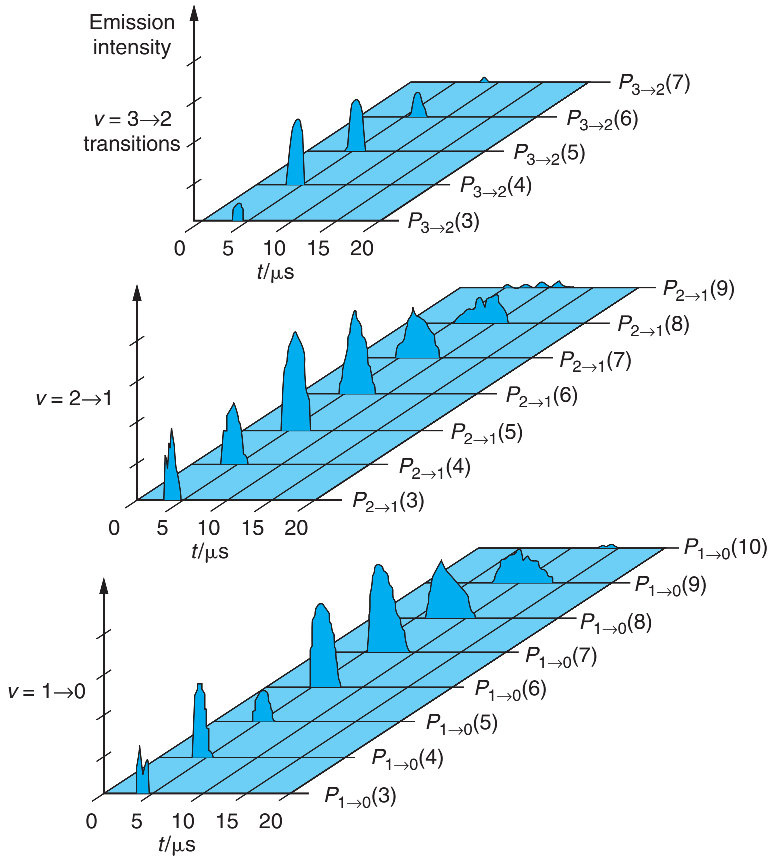

Figure 13.23 Intensity of Laser Pulses as a Function of Time for Excited HF Molecules. In each plot, the vertical axis represents the intensity of a laser pulse emitted by HF formed in a flash-initiated reaction. The horizontal axis represents time measured in microseconds. Each curve is labeled with both the initial and the final values of the vibrational quantum number v. The number in parentheses is the final value of J, the rotational quantum number (the initial value of J is smaller than this value by unity). From R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity*, Oxford University Press, New York, 1987, p. 213.

The second reaction in the mechanism of Eq. (13.6-3) has been thoroughly studied:[41]

$$F + H_2 \longrightarrow H + HF \tag{13.6-4}$$

The molar energy change of the reaction from ground state to ground state is $\Delta E_0 = -122\ \text{kJ mol}^{-1}$. The molar activation energy ΔE_0 is equal to $6.7\ \text{kJ mol}^{-1}$. The smallness of the activation energy correlates with an activated complex that is similar in structure to the reactants, in agreement with *Hammond's postulate*, which states that "the more exoergic the reaction, the more the transition state will resemble the reagents."

Levine and Bernstein reviewed the experimental and theoretical study of this reaction up to the time of publication of their book. The first investigation was a chemical

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[41] R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity*, Oxford University Press, New York, 1987, pp. 306ff, 396ff.

laser study, in which it was verified that there is a population inversion in the products, with the $v = 2$ vibrational state more highly populated than the other states, so that laser action can occur from the $v = 2$ state to the $v = 1$ state or the $v = 0$ state. The next investigation was a crossed molecular beam study, in which the angular distribution of products was determined, and in which it was found that most of the products were "back-scattered" (scattered generally in the direction from which the reactants had come).

Next came a classical trajectory calculation, in which the large back-scattering was also found to occur. After this, an *ab initio* calculation of the potential energy surface was carried out. Next came a quantum-mechanical calculation, in which it was found that "resonances" or "quasi-bound states" occurred at the transition state, which means that the activated complex existed for a longer period of time than expected, as it would if there were a "basin" in the potential energy surface at the transition state. This phenomenon was explained by the fact that the potential energy surface has a saddle that is fairly broad in the direction of the symmetric stretch, lowering the energy of the activated complex and causing its relative persistence.

Finally, a detailed chemiluminescence study gave the distribution of product states, showing the most back-scattering in the lower four vibrational states, but a significant forward scattering in the $v = 4$ vibrational state, and determining that on the average, 66% of the energy of reaction goes into vibrational energy, 8% into rotational energy, and the remainder into translational energy. The calculations did not agree well with the new experimental results.

Since the publication of the book by Levine and Bernstein, detailed quantum-mechanical calculations of state-to-state reaction probabilities have been carried out.[42] Several different potential energy surfaces were used in these calculations. Better agreement with experiment was attained, but only states of zero angular momentum were included. Further research is focused on finding better potential energy surfaces. One calculation gave a barrier height of 0.089 eV, corresponding to 8.6 kJ mol^{-1}.[43] Gimenez et al. carried out a detailed comparison between their three-dimensional quantum mechanical calculations, and found good agreement with experiment.[44] Aoiz and coworkers carried out a quasiclassical trajectory study and found significant discrepancies between previous experimental results and the theory.[45] Persky and Kornweitz published a critical review of the experimental data on this reaction.[46] They recommend the following experimental values for the Arrhenius parameters for the reaction between 190 K and 376 K:

$$A = (1.1 \pm 0.1) \times 10^{-10}\ \mathrm{cm^3\ molecule^{-1}\ s^{-1}}$$

$$E_a = 3.7 \pm 0.4\ \mathrm{kJ\ mol^{-1}}$$

The $F + H_2$ reaction is one of the most thoroughly studied of all chemical reactions, but study of it continues as both calculations and experiments become more sophisticated.

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[42] C. Yu, Y. Sun, D. J. Kouri, P. Halvick, D. G. Truhlar, and D. W. Schwenke, *J. Chem. Phys.*, **90**, 7608 (1989); C. Yu, D. J. Kouri, M. Zhaoo, D. G. Truhlar, and D. W. Schwenke, *Chem. Phys. Lett.*, **157**, 491 (1989).

[43] G. E. Scuseria, *J. Chem. Phys.*, **95**, 7426 (1991).

[44] X. Gimenez, J. M. Lucas, A. Aguilar, and A. Lagana, *J. Phys. Chem.*, **97**, 8578 (1993).

[45] F. J. Aoiz, L. Banares, V. J. Herrero, V. S. Rabanos, K. Stark, and H.-J. Werner, *J. Chem. Phys.*, **102**, 9248 (1995).

[46] A. Persky and H. Kornweitz, *Int. J. Chem. Kinetics*, **29**, 67 (1997).

PROBLEMS

Section 13.6: Experimental Molecular Study of Chemical Reaction Mechanisms

13.37 For a velocity selector such as depicted in Figure 13.21, find the molecular speed selected if the distance between the rotating disks is 2.00 cm, the difference in orientation of the two disks is 15.0 degrees, and the rotational speed is 82100 revolutions per minute.

13.38 For the data in the previous problem, find the range of speeds selected if the slots in the disks have a width of 2.00 degrees.

13.39 For the data in the two previous problems, find the width of slots necessary to give a range of speeds equal to 20.0 m s^{-1}.

13.40 Find the value of the forward rate constant of the reaction of Eq. (13.6-4) for 298 K and for 373 K. Express your results in $\text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$ and in $\text{L mol}^{-1}\ \text{s}^{-1}$.

Summary of the Chapter

Catalysis involves an alternative mechanism in which the catalyst is involved. Catalysis is divided into three classes: heterogeneous catalysis, homogeneous catalysis, and enzyme catalysis. Heterogeneous catalysis at the surfaces of solids involves adsorption of the reactants. We discussed the Langmuir theory of adsorption and applied it to heterogeneous catalysis. Homogeneous catalysis involves mechanisms with steps that occur in a single phase, and example reactions were analyzed.

The accepted theory of biological catalysis asserts that an enzyme possesses an active site into which the reactant molecule fits in such a way that it is more reactive in the active site than out of it. We obtained the rate law for the simplest mechanism, due to Michaelis and Menten.

We discussed several special topics in reaction mechanisms: Autocatalytic reactions and oscillatory reactions were discussed, as was the reaction kinetics of polymer formation and the kinetics of nonequilibrium electrochemistry.

We discussed various techniques for direct detection of reaction intermediates. These techniques included direct observation of the reaction intermediates and study of their effects. A survey of work on the gas-phase chemical reaction was presented:

$$\text{F} + \text{H}_2 \longrightarrow \text{H} + \text{HF}$$

Although this reaction has been extensively studied on the molecular level, both experimentally and theoretically, it is still the subject of ongoing research and cannot be said to be completely understood.

ADDITIONAL PROBLEMS

13.41 Label each statement as either true or false. If a statement is true only under special circumstances, label it as false.

a. A catalyst can change the equilibrium constant of a reaction.

b. A reaction can be catalyzed heterogeneously if only one of the reactants is adsorbed.

c. An inhibitor for an enzyme-catalyzed reaction must compete with a reactant for an active site.

d. If a catalyst catalyzes a forward reaction, it must also catalyze the reverse reaction.

e. One way to verify a reaction mechanism is to observe the presence of reactive intermediates.

13.42 **a.** Write a computer program to integrate the three simultaneous differential equations for the Lotka–Volterra mechanism of Equation (13.3-11) using Euler's method.[47] Assume that the concentration of A is kept fixed. Make your value of Δt small enough for adequate accuracy. Run the program for several different sets of values of the initial concentrations and the rate constants. Try to determine how the behavior depends on these values.

b. Determine the period of the oscillation for one or more of your sets of initial conditions.

c. Using the Runge–Kutta method,[48] write a computer program to integrate the differential equations of part a. Run the program for some of the same sets of values as used in part a to test the accuracy of the Euler method.

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[47] R. G. Mortimer, *Mathematics for Physical Chemistry*, 3rd ed., Academic Press, San Diego, 2005, p. 260ff.

[48] R. G. Mortimer, *loc. cit.*, p. 261; R. L. Burden and J. D. Faires, *Numerical Analysis*, 4th ed., Brooks/Cole, Pacific Grove, CA, 2001.

3

The Molecular Nature of Matter

14

Classical Mechanics and the Old Quantum Theory

PRINCIPAL FACTS AND IDEAS

1. The molecular nature of matter is studied through quantum mechanics.
2. Classical mechanics is the historical precursor of quantum mechanics. In this theory the state of a system is specified by giving values of coordinates and velocities.
3. Classical mechanics accurately describes the motions of objects of large mass that are moving at speeds much slower than the speed of light.
4. Classical mechanics ascribes exact trajectories to particles.
5. The classical wave equation describes the vibrations of strings and light waves.
6. The old quantum theory includes Planck's black-body radiation theory, Einstein's theory of the photoelectric effect, and Bohr's theory of the hydrogen atom.
7. The old quantum theories contained quantization as hypotheses.
8. The old quantum theories have been superseded by quantum mechanics.

14.1 Introduction

Part 1 of this textbook presents the study of the macroscopic properties of material systems of many molecules, based on thermodynamics. This part of the textbook presents the study of individual atoms and molecules. This study is based on quantum mechanics. Classical mechanics pre-dated quantum mechanics, and this chapter presents both classical mechanics and the so-called Old Quantum Theory, which consists of several theories contrived to explain the failure in the late 1800s of classical mechanics to describe or explain certain molecular phenomena.

Sir Isaac Newton, 1642–1727, was a great British mathematician and physicist who was also one of the inventors of calculus.

Classical mechanics was invented by Sir Isaac Newton to describe and predict the motions of objects such as the planets as they move about the sun. Although classical mechanics was a great success when applied to objects much larger than atoms, it was a complete failure when applied to atoms and molecules. It was superseded by quantum mechanics, which has enjoyed great success in explaining and predicting atomic and molecular properties. However, quantum mechanics was built upon classical mechanics, and someone has said that if classical mechanics had not been discovered prior to quantum mechanics, it would have had to be invented in order to construct quantum mechanics.

There are some important differences between classical mechanics and quantum mechanics. Classical mechanics, like thermodynamics, is based on experimentally grounded laws, while quantum mechanics is based on postulates, which means unproved assumptions that can be accepted only if their consequences agree with experiments. However, thermodynamics, classical mechanics, and quantum mechanics are all mathematical theories. Galileo once wrote “The book of nature is written in the language of mathematics.” We will review some of the mathematics that we use as we encounter it, and there are a few mathematics topics presented in the appendixes. There are also several books that cover the application of mathematics to physical chemistry.[1]

Mathematical functions play an important role in thermodynamics, classical mechanics, and quantum mechanics. A *mathematical function* is a rule that delivers a value of a *dependent variable* when the values of one or more *independent variables* are specified. We can choose the values of the independent variables, but once we have done that, the function delivers the value of the dependent variable. In both thermodynamics and classical mechanics, mathematical functions are used to represent measurable properties of a system, providing values of such properties when values of independent variables are specified. For example, if our system is a macroscopic sample of a gas at equilibrium, the value of n, the amount of the gas, the value of T, the temperature, and the value of V, the volume of the gas, can be used to specify the state of the system. Once values for these variables are specified, the pressure, P, and other macroscopic variables are dependent variables that are determined by the state of the system. We say that P is a *state function*. The situation is somewhat similar in classical mechanics. For example, the kinetic energy or the angular momentum of a system is a state function of the coordinates and momentum components of all particles in the system. We will find in quantum mechanics that the principal use of mathematical functions is to represent quantitites that are not physically measurable.

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[1] See for example Robert G. Mortimer, *Mathematics for Physical Chemistry*, 3rd ed., Academic Press, San Diego, CA, U.S.A., 2005; James R. Barrante, *Applied Mathematics for Physical Chemistry*, 3rd ed., Pearson Prentice-Hall, Upper Saddle River, NJ, 2004; Donald A. McQuarrie, *Mathematical Methods for Scientists and Engineers*, University Science Books, Sausalito, CA, 2003.

14.2

Classical Mechanics

According to classical mechanics, the state of a system is specified by giving the position and velocity of every particle in the system. Consider a single particle without any internal structure so that it cannot rotate or vibrate. If it can move in three dimensions we can specify its position by the three Cartesian coordinates x, y, and z. These three coordinates are equivalent to a *position vector* that reaches from the origin of coordinates to the location of the particle. Any quantity that has direction as well as magnitude is a vector. We denote a vector by a letter in boldface type and we denote this position vector by **r**. It can also be denoted by a letter with an arrow above it, as in $\overrightarrow{r}$, by a letter with a wavy underscore, as in $\underset{\sim}{r}$. The Cartesian coordinates x, y, and z are called the *Cartesian components* of the position vector **r**. A vector can also be denoted by listing its three Cartesian components inside parentheses, as in (x, y, z). Any quantity that has both magnitude and direction is a vector. A quantity that has no particular direction but can be positive, negative, or zero, is called a *scalar*. Appendix B contains an elementary introduction to vectors, and additional information can be found in the references of note number 1.

The velocity of the particle is the time derivative of its position vector and is a vector **v** with the Cartesian components v_x, v_y, and v_z:

$$v_x = \frac{dx}{dt} \qquad v_y = \frac{dy}{dt} \qquad v_z = \frac{dz}{dt} \tag{14.2-1a}$$

These three equations can be represented by a single vector equation

$$\mathbf{v} = \frac{d\mathbf{r}}{dt} \tag{14.2-1b}$$

The *speed* of a particle is the magnitude of the velocity, given by

$$v = |\mathbf{v}| = \sqrt{v_x^2 + v_y^2 + v_z^2} \tag{14.2-2}$$

which is a three-dimensional version of the theorem of Pythagoras. The kinetic energy of the particle is defined by

$$\mathscr{K} = \tfrac{1}{2}mv^2 = \tfrac{1}{2}mv^2(v_x^2 + v_y^2 + v_z^2) \tag{14.2-3}$$

where m is the mass of the particle. The kinetic energy is an example of a function of the variables that specify the state of the particle. A function of these variables is called a *state function*.

Units of Measurement

In using a formula such as that of Eq. (14.2-3), one must use consistent units or risk getting the wrong answer. The set of units that chemists and physicists now use is the *international system of units*, or *SI units*. The letters SI stand for *Système Internationale*, the French name for the set of units. In this system there are seven base units. The unit of length is the *meter* (m). The unit of mass is the *kilogram* (kg). The unit of time is the *second* (s). The unit of temperature is the *kelvin* (K). The unit of electric current is the *ampere* (A). The unit of luminous intensity is the *candela* (cd). The unit for the amount of a substance is the *mole* (mol).

In addition to the base units, there are a number of derived units. The *newton* (N) is the SI unit of force:

$$1\,\mathrm{N} = 1\,\mathrm{kg\,m\,s^{-2}} \quad \text{(definition)} \tag{14.2-4}$$

The pascal is named for Blaise Pascal, 1623–1662, a famous French philosopher, theologian, and mathematician.

The *pascal* (Pa) is the SI unit of pressure (force per unit area):

$$1\,\mathrm{Pa} = 1\,\mathrm{N\,m^{-2}} = 1\,\mathrm{kg\,m^{-1}\,s^{-2}} \quad \text{(definition)} \tag{14.2-5}$$

The joule is named for James Prescott Joule, 1818–1889, a great English physicist who pioneered in the study of thermodynamics while managing his family's brewery.

The SI unit of energy is the *joule* (J):

$$1\,\mathrm{J} = 1\,\mathrm{N\,m} = 1\,\mathrm{kg\,m^2\,s^{-2}} \quad \text{(definition)} \tag{14.2-6}$$

Newton's Laws of Motion

According to classical mechanics the motions of particles are governed by Newton's three laws, which we accept as summaries and generalizations of experimental fact. *Newton's first law* is called the *law of inertia*: *A stationary particle tends to remain stationary unless acted on by a force, and a moving particle tends to continue moving with unchanged velocity unless acted on by a force*. The first law is a special case of *Newton's second law*, which is called the *law of acceleration* and is expressed by the equation

$$\boxed{\mathbf{F} = m\mathbf{a} = m\frac{d\mathbf{v}}{dt} = m\frac{d^2\mathbf{r}}{dt^2}} \tag{14.2-7}$$

where t represents the time. In this equation the vector $\mathbf{F}$ is the force acting upon an object of mass m, $\mathbf{r}$ is its position vector, $\mathbf{v}$ is its velocity, which is the rate of change of its position, and $\mathbf{a}$ is its acceleration, which is the rate of change of the velocity. The x component of the acceleration is

$$a_x = \frac{dv_x}{dt} = \frac{d^2x}{dt^2} \tag{14.2-8}$$

with similar equations for the y and z components. Equation (14.2-7) is equivalent to three scalar equations.

$$F_x = ma_x = m\frac{dv_x}{dt} = m\frac{d^2x}{dt^2} \tag{14.2-9a}$$

$$F_y = ma_y = m\frac{dv_y}{dt} = m\frac{d^2y}{dt^2} \tag{14.2-9b}$$

$$F_z = ma_z = m\frac{dv_z}{dt} = m\frac{d^2z}{dt^2} \tag{14.2-9c}$$

Newton's third law is called the *law of action and reaction*. It asserts that if $\mathbf{F}_{21}$ is the force exerted on object 2 by object 1, and if $\mathbf{F}_{12}$ is the force exerted on object 1 by object 2, then

$$\mathbf{F}_{21} = -\mathbf{F}_{12} \quad \text{(Newton's third law)} \tag{14.2-10}$$

We tend to take Newton's third law for granted, but if you stop and think for a moment, it is quite interesting. If you stand on a floor and jump into the air, you put a force on the floor. The floor, which hardly moves at all, throws you into the air because of Newton's third law.

If a force on a particle depends only on its position, the force can be derived from a *potential energy*. For the z component of such a force

$$F_z = -\left(\frac{\partial \mathscr{V}}{\partial z}\right)_{x,y} \tag{14.2-11}$$

where the potential energy is denoted by $\mathscr{V}$. Similar equations apply for the x and y directions. See Appendix E for further information. The derivative in Eq. (14.2-11) is a *partial derivative*, which means that if you have a formula representing $\mathscr{V}$, you differentiate with respect to z in the usual way, treating any other independent variables (x and y in this case) as though they were constants.

The total energy of a particle subject to a potential energy is the sum of its kinetic energy $\mathscr{K}$ and its potential energy $\mathscr{V}$:

$$E = \mathscr{K} + \mathscr{V} = \frac{1}{2}mv^2 + \mathscr{V} \tag{14.2-12}$$

The total energy of an object subject to a potential energy obeys the *law of conservation of energy*, which states that the total energy of the object is constant in time.

The Harmonic Oscillator

In order to show how Newton's laws determine the behavior of a particle, we apply them to a harmonic oscillator, which is a model system designed to represent a mass attached to a stationary object by a spring, as shown in Figure 14.1. A *model system* is designed to imitate a real system, but is defined to have simpler properties so that it can

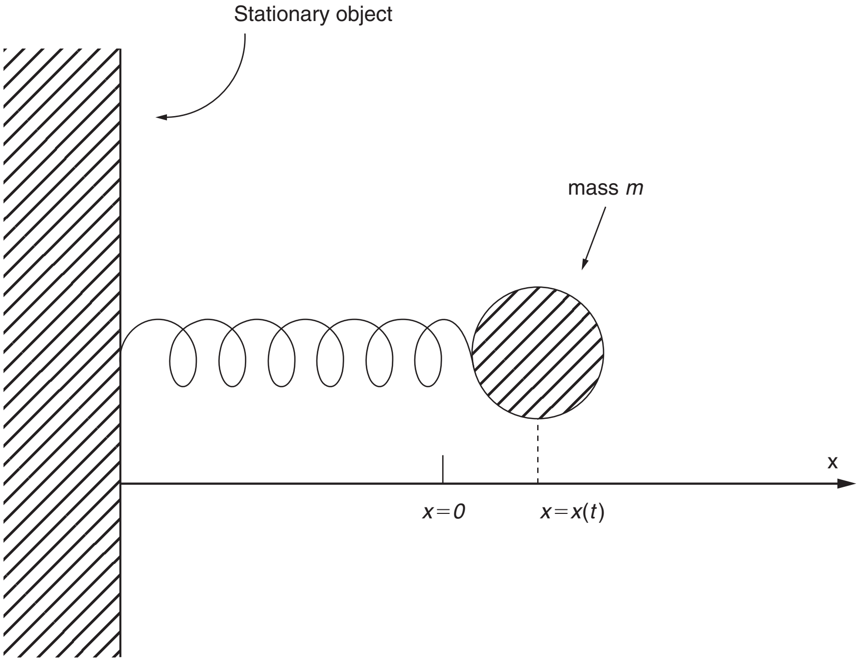


Figure 14.1 A System Represented by a Harmonic Oscillator.

be analyzed more easily. Let the horizontal coordinate x of the mass equal zero at its equilibrium position and assign it to be positive if the spring is stretched and negative if the spring is compressed. If the magnitude of x is not too large the force on the mass due to the spring is given by *Hooke's law*:

Hooke's law is named for Robert Hooke, 1635–1703, one of Newton's contemporaries and rivals.

$$F_x = -kx \tag{14.2-13}$$

where k is called the *force constant*. Hooke's law fails if a spring is stretched beyond its elastic limit or if it is sufficiently compressed that its coils touch each other.

The harmonic oscillator has the following properties: (1) the x coordinate is not limited to any finite range; (2) Hooke's law is obeyed exactly for all values of x; (3) the mass of the spring is negligible; (4) there is no friction.

Newton's second law, Eq. (14.2-7), provides the *equation of motion* of the harmonic oscillator:

$$-kx = m\frac{d^2x}{dt^2} \tag{14.2-14}$$

This is a *differential equation*. It is called *linear* because the dependent variable x enters only to the first power and is called *second order* because its highest-order derivative is the second derivative. The solution to a differential equation is a function that gives the dependent variable (x in this case) as a function of the independent variable (t in this case). There can be more than one solution function for a given differential equation. The *general solution* of a differential equation is a family of functions that includes nearly every solution of the equation.

Since both the sine and the cosine are proportional to the negative of their second derivatives, a general solution for Eq. (14.2-14) can be written by inspection:

$$x(t) = A\sin(\sqrt{k/mt}) + B\cos(\sqrt{k/mt}) \tag{14.2-15}$$

where A and B are constants. This solution conforms to the fact that the general solution of a linear second-order differential equation is represented by a formula that contains two arbitrary constants. The expression for the velocity is obtained by differentiation:

$$v_x(t) = \frac{dx}{dt} = \sqrt{k/m}\,[A\cos(\sqrt{k/mt}) - B\sin(\sqrt{k/mt})] \tag{14.2-16}$$

The solution to Eq. (14.2-14) can be obtained in a more systematic way. A general linear differential equation with constant coefficients can be written

$$0 = c_0x + c_1\frac{dx}{dt} + c_2\frac{d^2x}{dt^2} + \cdots \tag{14.2-17}$$

where the c's represent constants. It is a fact that a solution to a linear differential equation with constant coefficients can be written as

$$x(t) = e^{\lambda t} \tag{14.2-18}$$

where λ is a parameter that is determined by the coefficients. This solution is called a *trial solution* because we try it in the equation. Substitution of this trial solution into Eq. (14.2-14) gives

$$-ke^{\lambda t} = m\frac{d^2e^{\lambda t}}{dt^2} = m\lambda^2e^{\lambda t} \tag{14.2-19}$$

division by $e^{\lambda t}$ gives the *characteristic equation*

$$\lambda^2 = -\frac{k}{m} \tag{14.2-20}$$

There are two solutions to this equation:

$$\lambda_1 = i\sqrt{\frac{k}{m}} \tag{14.2-21a}$$

$$\lambda_2 = -i\sqrt{\frac{k}{m}} \tag{14.2-21b}$$

where i is the *imaginary unit*, defined to equal $\sqrt{-1}$. Each of these values of λ gives a solution to the equation, so we have two solutions to the differential equation. A *linear combination* (sum of functions with constant coefficients) of the two solutions is also a solution to the equation.

Exercise 14.1

The linear combination

$$c_1 e^{\lambda_1 t} + c_2 e^{\lambda_2 t} = c_1 e^{i\sqrt{k/mt}} + c_2 e^{-i\sqrt{k/mt}} \tag{14.2-22}$$

where c_1 and c_2 are constants is a general solution to Eq. (14.2-14), since it contains two arbitrary constants. Use the *identity* (an equation that holds for any value of α)

$$e^{i\alpha} = \cos(\alpha) + i\sin(\alpha) \tag{14.2-23}$$

to show that this solution is identical to the solution in Eq. (14.2-15). Obtain the relation between c_1, c_2, A, and B.

To make the general solution in Eq. (14.2-15) apply to a particular case we must assign values to A and B. We use *initial conditions* to do this. One choice for the initial conditions is to specify values of the position and velocity at the initial time. Let us consider the case that

$$x(0) = x_0 \tag{14.2-24a}$$

$$v_x(0) = 0 \tag{14.2-24b}$$

where x_0 is a specified constant. Since $\cos(0) = 1$ and $\sin(0) = 0$, the first condition requires that $B = x_0$ and the second condition requires that $A = 0$. The specific solution that applies to our initial conditions is now

$$x(t) = x_0\cos(\sqrt{k/mt}) \tag{14.2-25}$$

$$v_x(t) = -\sqrt{k/m}\, x_0\sin(\sqrt{k/mt}) \tag{14.2-26}$$

The constant x_0 is the largest magnitude that x attains and is called the *amplitude* of the oscillation. You can see that x and v_x are now determined for all values of the time, both positive and negative. This is a characteristic of classical equations of motion. We say that classical mechanics is *deterministic*, which means that the classical equations of motion determine the position and velocity of any particle for all time if the initial conditions are precisely specified.

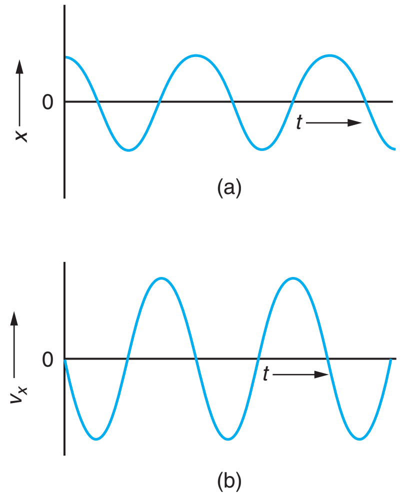


Figure 14.2 The Behavior of a Harmonic Oscillator. (a) The position as a function of time according to classical mechanics. (b) The velocity as a function of time according to classical mechanics.

Exercise 14.2

Show that the functions in Eq. (14.2-25) and Eq. (14.2-26) correspond to the given initial conditions.

Figure 14.2a shows the position of the harmonic oscillator as a function of time, and Figure 14.2b shows the velocity as a function of time. This motion is called *uniform harmonic motion*. It is a *periodic motion*, repeating the same pattern over and over again as time passes. The length of time required for the oscillator to go from a given state to the next repetition of that state is called the *period* of the oscillation and is denoted by τ. It is the length of time required for the argument of the cosine function in Eq. (14.2-25) and the sine function in Eq. (14.2-26) to change by 2π:

$$\sqrt{\frac{k}{m}}\tau = 2\pi \tag{14.2-27}$$

or

$$\tau = 2\pi\sqrt{\frac{m}{k}} \tag{14.2-28}$$

The *frequency* ν is the number of oscillations per second and equals the reciprocal of the period:

$$\boxed{\nu = \frac{1}{\tau} = \frac{1}{2\pi}\sqrt{\frac{k}{m}}} \tag{14.2-29}$$

The frequency is larger if the force constant is larger, and smaller if the mass is larger. The unit of frequency is the reciprocal second, called the hertz (Hz).

EXAMPLE 14.1

A single covalent bond is similar to a spring with a force constant near 500 N m^{-1}. Estimate the frequency of oscillation of a hydrogen atom at one end of such a spring with the other end held fixed.

Solution

$$\nu = \frac{1}{2\pi}\sqrt{\frac{500\,\mathrm{N\,m^{-1}}}{1.674\times 10^{-27}\,\mathrm{kg}}} = 8.7\times 10^{13}\,\mathrm{Hz}$$

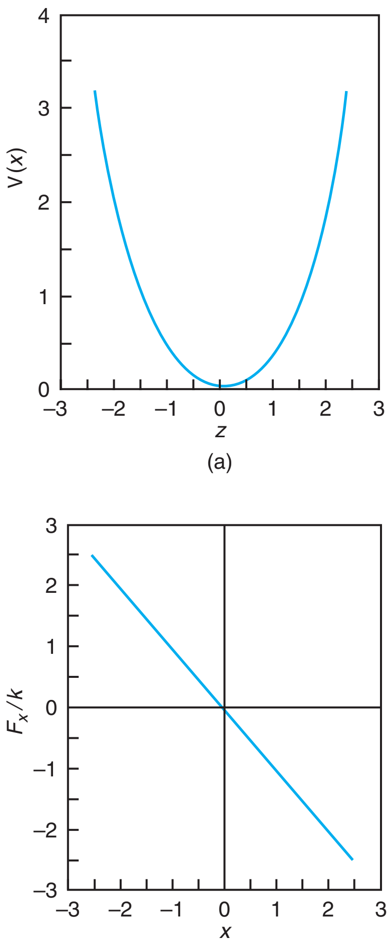
This frequency is similar to that of a molecular vibration.

The kinetic energy $\mathscr{K}$ of our harmonic oscillator is

$$\mathscr{K} = \frac{1}{2}mv_x^2 \tag{14.2-30}$$

From Eq. (14.2-26) the kinetic energy is given as a function of time by

$$\mathscr{K} = \frac{1}{2}mv_x^2 = \frac{1}{2}m\frac{k}{m}x_0^2\left[\sin\left(\sqrt{\frac{k}{m}}t\right)\right]^2 = \frac{k}{2}x_0^2\sin^2\left(\sqrt{\frac{k}{m}}t\right) \tag{14.2-31}$$



(a)

(b)

Figure 14.3 Mechanical Variables of a Harmonic Oscillator. (a) The potential energy. (b) The force on the oscillator.

Since a force is given as a derivative of a potential energy, a constant can be added to a potential energy without changing the force or any other physical property.

A time-independent force is equal to the negative derivative of a potential energy. The potential energy corresponding to the force of Eq. (14.2-13) is

$$\mathscr{V}(x) = \frac{1}{2}kx^2 + \mathscr{V}_0 \tag{14.2-32}$$

where $\mathscr{V}_0$ is a constant. Since the derivative of a constant is zero, we can always add any constant to a potential energy without any physical effect. We choose to set $\mathscr{V}_0$ equal to zero. Figure 14.3a shows the potential energy for the harmonic oscillator as a function of x, and Figure 14.3b shows the force due to this potential energy. For our initial conditions, the potential energy is given as a function of time by

$$\mathscr{V} = \frac{k}{2}x_0^2\cos^2\left(\sqrt{\frac{k}{m}}t\right) \tag{14.2-33}$$

The total energy, E, is the sum of the kinetic and potential energies:

$$E = \mathscr{K} + \mathscr{V} = \frac{1}{2}kx_0^2\left[\sin^2\left(\sqrt{\frac{k}{m}}t\right) + \cos^2\left(\sqrt{\frac{k}{m}}t\right)\right] = \frac{1}{2}kx_0^2 \tag{14.2-34}$$

The final equality follows from the trigonometric identity:

$$\sin^2(\alpha) + \cos^2(\alpha) = 1 \tag{14.2-35}$$

The total energy does not change during the oscillation, corresponding to *conservation of energy*. A conserved quantity is one that remains constant, and is called a *constant of the motion*. The total energy of the harmonic oscillator is a constant of the motion.

The largest value of x is called the *turning point*, because this is the point at which the oscillator changes its direction of motion. At the turning point the kinetic energy vanishes and the total energy equals the potential energy. If we denote the value of x at the turning point by x_t,

$$E = \mathscr{V}(x_t) = \frac{1}{2}kx_t^2 \tag{14.2-36}$$

Therefore

$$x_t = \sqrt{\frac{2E}{k}} \tag{14.2-37}$$

For our initial conditions, $x_t = x_0$, so that

$$E = \frac{1}{2}kx_0^2 \tag{14.2-38}$$

as in Eq. (14.2-34).

A different version of the harmonic oscillator can be used as a model for a vibrating diatomic molecule. This model oscillator consists of two movable objects connected by a spring, as depicted in Figure 14.4. As shown in Appendix E our formulas hold for this model if we let x represent the distance between the two objects and replace the mass m by the *reduced mass* μ:

$$\mu = \frac{m_1m_2}{m_1 + m_2} \quad \text{(definition of the reduced mass)} \tag{14.2-39}$$

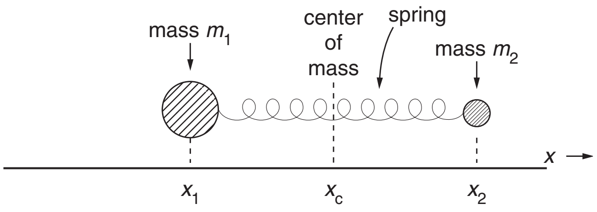


Figure 14.4 A Second System Represented by a Harmonic Oscillator.

where m_1 and m_2 are the masses of the two objects. The motion of the two-particle oscillator is mathematically the same as the motion of a fictitious particle of mass μ at the end of the same spring with the other end of the spring held fixed. For this model the frequency of oscillation is given by

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{14.2-40}$$

where k is the force constant.

Exercise 14.3

The frequency of vibration of a hydrogen molecule equals $1.3194 \times 10^{14}\ \mathrm{s^{-1}}$. Find the value of the force constant of chemical bond in the H_2 molecule.

PROBLEMS

Section 14.2: Classical Mechanics

14.1 The vibrational frequency of a $^{12}C^{16}O$ molecule is $6.5405 \times 10^{13}\ \mathrm{s^{-1}}$. The atomic masses are: ^{12}C: 12.00000 amu; ^{13}C: 13.00335 amu; ^{16}O: 15.994915 amu; ^{17}O: 16.99913 amu.

- **a.** Find the value of the force constant.
- **b.** Find the vibrational frequency of a $^{13}C^{16}O$ molecule, assuming that the force constant is unchanged.
- **c.** Find the vibrational frequency of a $^{12}C^{17}O$ molecule assuming that the force constant is unchanged.

14.2 Assume that a $^{12}C^{16}O$ molecule is adsorbed on a platinum surface in such a way that the carbon atom is held stationary but the oxygen atom vibrates. Find the vibrational frequency of the oxygen atom. Assume that the force constant of the bond is the same as that of the free CO molecule, determined in Problem 14.1.

14.3 The frequency of vibration of a $^{1}H^{35}Cl$ molecule is $8.966 \times 10^{13}\ \mathrm{s^{-1}}$.

- **a.** What would the frequency be if the chlorine atom were infinitely massive?
- **b.** What would the frequency be if the hydrogen atom were infinitely massive?

14.4 The frequency of vibration of an H_2 molecule is equal to $1.31945 \times 10^{14}\ \mathrm{s^{-1}}$. The atomic mass of H is 1.007825 amu and that of ^2H is 2.014102 amu. Assume that the force constant of the vibration is unchanged by isotopic substitution.

- **a.** Find the frequency of vibration of an HD molecule, where $D = {}^2H$.
- **b.** Find the frequency of vibration of a D_2 molecule.

14.5 Assume that a hydrogen atom is bonded to a large crystal with a chemical bond that is equivalent to a spring having a force constant equal to $600.0\ \mathrm{N\ m^{-1}}$. Assume that the hydrogen atom oscillates harmonically but the atom at the other end of the bond is stationary. Find the frequency of the oscillation.

14.6 Assume that a particle of mass m moves only in the z direction and is subject to a constant force given by $F_z = -mg$. Solve its equation of motion, finding v_z and z as functions of time for arbitrary values of $z(0)$ and $v_z(0)$, the values at time zero.

14.7 The frequency of oscillation of several diatomic molecules is as follows:

a. HF $1.2406 \times 10^{14}\ \mathrm{s}^{-1}$

b. HCl $8.9665 \times 10^{13}\ \mathrm{s}^{-1}$

c. HBr $7.9414 \times 10^{13}\ \mathrm{s}^{-1}$

d. Br2 $9.7528 \times 10^{12}\ \mathrm{s}^{-1}$

Find the force constant for the bond in each molecule. Comment on your results, since all of these molecules have single bonds.

14.8 **a.** Show that a vertical spring with a mass m suspended from it is lengthened by an amount equal to mg/k where g is the acceleration due to gravity, and k is the spring constant.

b. If z is the displacement of the mass from its equilibrium position, show that the potential energy is given by

$$\mathscr{V} = \mathscr{V}_0 + \frac{kz'^2}{2} + \text{constant}$$

where $\mathscr{V}_0$ is the potential energy of the spring at its equilibrium length without the mass attached to it, and where z' is the displacement of the mass from its new equilibrium position.

c. Show that the frequency of oscillation is the same as in the horizontal position. An object of mass 0.250 kg is suspended from a spring with $k = 5.55\ \mathrm{N m^{-1}}$. Find the distance by which the spring is lengthened, the period, and the frequency.

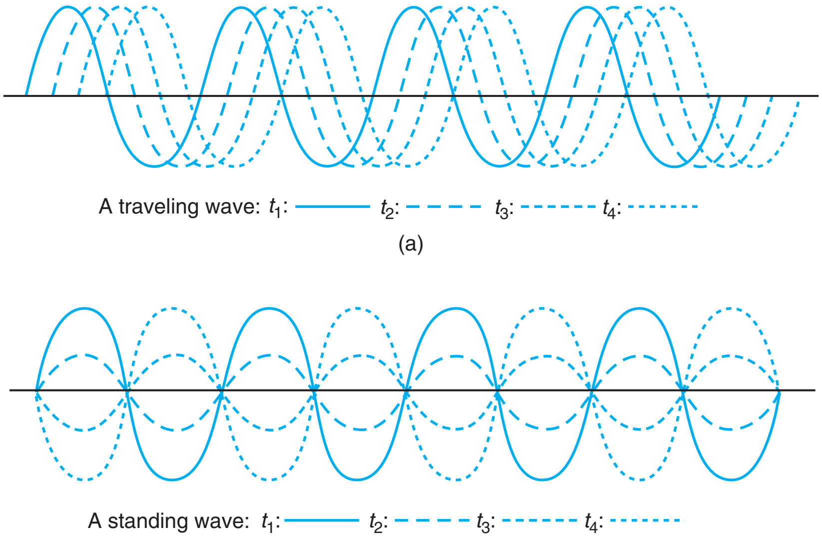
14.3 Classical Waves

A wave is an oscillating displacement that depends on position and time. Waves that are described by classical mechanics include sound waves, waves on the surface of a body of water, and vibrations of strings in musical instruments. In a water wave the displacement is the distance to a point on the surface from its equilibrium position, and in a sound wave the displacement is the difference between the pressure and its equilibrium value. A region of positive displacement is called a *crest*, and a region of negative displacement is called a *trough*. A location where the displacement of a wave equals zero is called a *node*. The distance from one crest to the next is called the *wavelength* λ. The *period* τ of a wave is the time for the first return of the oscillating object to an initial state. The *frequency* ν is the reciprocal of the period, or the number of oscillations per second.

There are two principal types of waves. A *traveling wave* propagates (moves along) like waves on the surface of a body of water. A *standing wave* such as the vibration of a string in a musical instrument does not propagate, but has stationary nodes. Figure 14.5 represents some features of traveling and standing waves. The traveling wave in Figure 14.5a moves to the right without changing shape, whereas the standing wave in Figure 14.5b oscillates between stationary nodes.

One important property of waves is *interference*. When two waves of the same type come to the same location, their displacements add. If two crests or two troughs coincide, a displacement of larger magnitude results. This addition is called *constructive interference*. If a crest of one wave and a trough of another wave coincide, they will partially or completely cancel each other. This cancellation is called *destructive interference*.

A property that arises from interference is *diffraction*. If a water wave encounters a post, there will be a reflected wave with circular crests that moves out in all directions from the post. The reflected waves from a row of equally spaced posts can



(a)

(b)

Figure 14.5 Traveling and Standing Waves. (a) A traveling wave at times $t_1 < t_2 < t_3 < t_4$. (b) A standing wave at times $t_1 < t_2 < t_3 < t_4$.

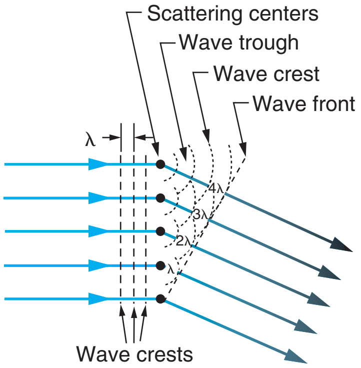


Figure 14.6 The Diffraction of a Wave by a Row of Scattering Centers. The direction of the diffracted wave depends on the wavelength.

interfere to produce a diffracted wave with straight crests, which can travel in a direction different from that of the incident wave. Light waves and other waves exhibit the same phenomenon.

A *plane wave* is a traveling wave in three dimensions in which a crest of the wave occupies a plane at right angles to the direction of propagation. Figure 14.6 illustrates *diffraction* of a plane wave by a set of equally spaced scattering centers. The broken lines in Figure 14.6 represent the crests of a plane wave moving from left to right. The arcs represent the crests of diffracted waves moving outward from the scattering centers. At a large distance from the scattering centers these crests interfere to produce a plane wave moving in a different direction from the original direction of propagation. The wave nature of light was established experimentally when interference and diffraction of light were observed.

The Flexible String

In order to illustrate the mathematics of classical waves, we now analyze the vibrations of a flexible string, which is a model system designed to resemble a real vibrating string. It is defined to have the following properties:

1. The string is uniform. All parts have the same mass per unit length, denoted by ρ.
2. There is a tension force of magnitude $\mathscr{T}$ pulling at each end of the string.
3. The string is perfectly flexible.
4. There is no friction.
5. The string undergoes only small displacements, so that the total length of the string remains nearly constant and the magnitude of the tension force $\mathscr{T}$ is nearly constant.

The state of the string at time t is specified by giving the displacement and velocity at each point of the string.

$$z = z(x, t) \tag{14.3-1}$$

$$v_z = v_z(x, t) = \frac{\partial z}{\partial t} \tag{14.3-2}$$

The displacement and velocity are functions of x as well as functions of t. The derivative $\partial z/\partial t$ is a partial derivative, taken with a fixed value of x. The classical equation of motion of the flexible string is derived in Appendix E from Newton's second law. From Eq. (E-10) the wave equation is

$$\frac{\partial^2 z}{\partial x^2} = \frac{\rho}{\mathscr{T}}\frac{\partial^2 z}{\partial t^2} = \frac{1}{c^2}\frac{\partial^2 z}{\partial t^2} \tag{14.3-3}$$

where we let

$$c^2 = \mathscr{T}/\rho \tag{14.3-4}$$

Since Eq. (14.3-3) contains partial derivatives, it is called a *partial differential equation*. Its solution gives z as a function of x and t.

Let the string be fixed at $x = 0$ and $x = L$ so that nodes occur at these locations. We assume that at time $t = 0$ the string is displaced into some shape in the x–z plane and released to vibrate freely in this plane. We obtain a solution of Eq. (14.3-3) by *separation of variables*. We assume a *trial solution* that is a product of a function of x and a function of t:

$$z(x, t) = \varphi(x)\eta(t) \tag{14.3-5}$$

We substitute the trial solution into the differential equation and perform algebraic operations that produce an equation with terms that are functions of only one independent variable. We substitute the trial function of Eq. (14.3-5) into Eq. (14.3-3):

$$\eta\frac{d^2\varphi}{dx^2} = \frac{1}{c^2}\varphi\frac{d^2\eta}{dt^2} \tag{14.3-6}$$

These derivatives are ordinary derivatives since η and φ are functions of one variable. We divide Eq. (14.3-6) by $\varphi\eta$ to complete the separation of variables:

$$\frac{1}{\varphi(x)}\frac{d^2\varphi}{dx^2} = \frac{1}{c^2\eta(t)}\frac{d^2\eta}{dt^2} \tag{14.3-7}$$

Each term now depends on only one independent variable.

Since x and t are independent variables, it is possible to keep t fixed while we allow x to range. The right-hand side of Eq. (14.3-7) is then equal to a constant (the separation constant), so the term containing x must be a constant function of x. Similarly, the term containing t must be a constant function of t and must be equal to the separation constant:

$$\frac{1}{\varphi(x)}\frac{d^2\varphi}{dx^2} = \text{constant} = -\kappa^2 \tag{14.3-8}$$

$$\frac{1}{c^2\eta(t)}\frac{d^2\eta}{dt^2} = -\kappa^2 \tag{14.3-9}$$

The separation constant must be negative to give an oscillatory solution. We denote this constant by $-\kappa^2$ so that κ will be a real quantity.

Exercise 14.4

If the separation constant is assumed to be positive, we have the equation

$$\frac{1}{\varphi(x)}\frac{d^2\varphi}{dx^2} = \text{constant} = a^2$$

where a is a real constant.

a. Show that the following function is a solution to this equation:

$$\varphi = Le^{ax} + Me^{-ax}$$

where L and M are constants. This is not a periodic function.

b. Show that

$$\eta = Pe^{act} + Qe^{-act}$$

which is not an oscillating function.

Multiplying Eq. (14.3-8) by φ and Eq. (14.3-9) by $c^2\eta$ gives

$$\frac{d^2\varphi}{dx^2} = -\kappa^2\varphi(x) \tag{14.3-10}$$

$$\frac{d^2\eta}{dt^2} = -\kappa^2c^2\eta(t) \tag{14.3-11}$$

These equations have the same form as Eq. (14.2-14) with different symbols. We transcribe the solution to that equation with appropriate replacements of symbols:

$$\varphi(x) = B\cos(\kappa x) + D\sin(\kappa x) \tag{14.3-12}$$

$$\eta(t) = F\cos(\kappa ct) + G\sin(\kappa ct) \tag{14.3-13}$$

where B, D, F, and G are constants. The product of the coordinate factor φ and the time factor η is a function that represents the displacement of the string as a function of position and time. We call $z(x, t)$ a *wave function*. Our present wave function is not necessarily a general solution to the original wave equation, since solutions can exist that are not the product of two factors.

Exercise 14.5

Show that the product of the factors in Eq. (14.3-12) and (14.3-13) satisfies Eq. (14.3-3).

The wave function $z(x, t)$ does not yet apply to our case that z vanishes at $x = 0$ and at $x = L$. We call this condition a *boundary condition* since it pertains to the ends of the string. If $z(x, t)$ vanishes at these points, the coordinate factor $\varphi(x)$ must also vanish at these points, since it contains all of the x dependence of z. The condition that $\varphi(0) = 0$ requires that $B = 0$, since $\sin(0) = 0$ and $\cos(0) = 1$. The sine function vanishes if its argument is an integral multiple of $\pi(90°)$ so that the condition $\varphi(L) = 0$ requires that

$$\kappa L = n\pi \tag{14.3-14}$$

where n is an integer. We can write a different coordinate factor for each value of n:

$$\varphi(x) = \varphi_n(x) = D\sin\left(\frac{n\pi x}{L}\right) \tag{14.3-15}$$

The coordinate factor φ has been determined partly by the differential equation and partly by the boundary conditions.

The values of the constants D, F, and G are now chosen to match our initial conditions. A second-order differential equation requires two initial conditions. We choose as the first initial condition that the string is passing through its equilibrium position ($z = 0$ for all x) at time $t = 0$. This requires that $F = 0$, since $\sin(0) = 0$ and $\cos(0) = 1$. The time factor η is now determined by Eq. (14.3-14) and our initial conditions. The wave function can now be written as

$$\begin{aligned} z(x, t) = z_n(x, t) = \varphi_n(x)\eta_n(t) &= DG\sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi ct}{L}\right) \\ &= A\sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi ct}{L}\right) \end{aligned} \tag{14.3-16}$$

Where we replace the constant product DG by a single symbol, A.

We now choose the second initial condition to be that the maximum value of z is equal to z_0:

$$z(x, t) = z_n(x, t) = z_0\sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi ct}{L}\right) \tag{14.3-17}$$

This is a set of solutions, one for each value of n. Each solution corresponds to a different standing wave. The differential equation, the boundary conditions, and the initial conditions have completely determined the set of wave functions.

The velocity is given by

$$v_z = \frac{\partial z}{\partial t} = z_0\left(\frac{n\pi c}{L}\right)\sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{n\pi ct}{L}\right) \tag{14.3-18}$$

The velocity at $t = 0$ is

$$v_z(0) = z_0\left(\frac{n\pi c}{L}\right)\sin\left(\frac{n\pi x}{L}\right) \tag{14.3-19}$$

Our second initial condition has specified the initial velocity. Instead of specifying the maximum amplitude we could have specified that the initial velocity is given by this function.

Exercise 14.6

a. Show by substitution that Eq. (14.3-16) satisfies Eq. (14.3-3).
b. What is the effect on the wave function of replacing n by its negative?
c. What is the relationship between the value of n and the number of nodes?

The wavelength λ for our standing wave is the distance such that the argument of the sine function in Eq. (14.3-15) changes by 2π. This gives

$$\lambda = \frac{2L}{n} \tag{14.3-20}$$

The wavelength is *quantized*. That is, it can take on a certain value for each value of n, but no values between these allowed values. There is a relation between κ and λ:

$$\lambda = \frac{2L}{n} = \frac{2\pi}{\kappa} \tag{14.3-21}$$

The relation between λ and κ is independent of the value of n.

The period τ of our standing wave is the time required for the argument of the time factor $\sin(n\pi ct/L)$ to change by 2π, so that

$$2\pi = \frac{n\pi c\tau}{L} \quad \text{or} \quad \tau = \frac{2L}{nc} \tag{14.3-22}$$

The frequency ν is the number of oscillations per unit time and equals the reciprocal of the period:

$$\boxed{\nu = \frac{nc}{2L} = \frac{n}{2L}\sqrt{\frac{\mathscr{T}}{\rho}}} \tag{14.3-23}$$

The frequency is quantized. It is directly proportional to the integer n, inversely proportional to the length of the string, directly proportional to the square root of the tension force, and inversely proportional to the square root of the mass per unit length.

The strings of real musical instruments obey our formulas to a good approximation. In musical acoustics, the standing wave with $n = 1$ is called the *fundamental* or the *first harmonic*, the standing wave with $n = 2$ is called the *first overtone* or the *second harmonic*, and so on. Figure 14.7 represents the coordinate factor φ for several values of n. Each graph in the figure represents the position of the string at a time when the time factor η equals unity. For other times, the string oscillates between the position given by this graph and its negative.

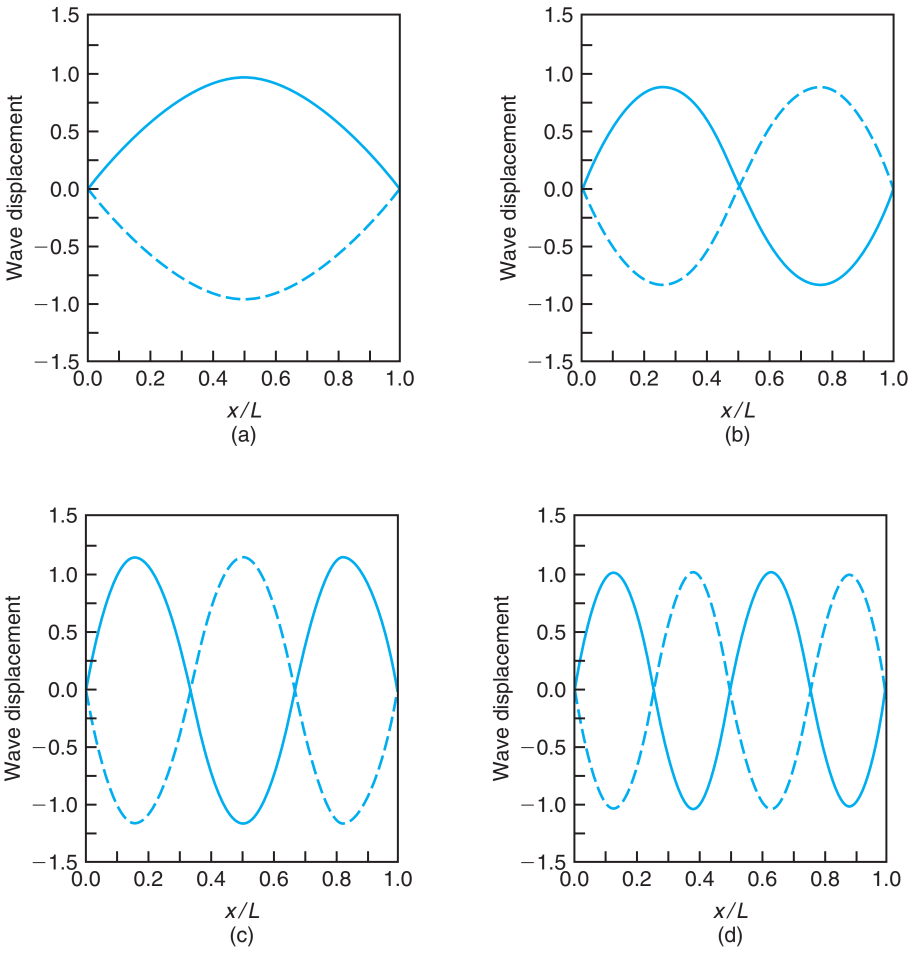


Figure 14.7 Standing Waves in a Flexible String. (a) The wave function for $n = 1$. (b) The wave function for $n = 2$. (c) The wave function for $n = 3$. (d) The wave function for $n = 4$.

A string does not usually move as described by a single harmonic. A *linear combination* of harmonics can satisfy the wave equation:

$$z(x, t) = \sum_{n=1}^{\infty} a_n(t) \sin\left(\frac{n\pi x}{L}\right) \tag{14.3-24}$$

The fact that a linear combination of solutions can be a solution to the wave equation is called the *principle of superposition*. When a string in a musical instrument is struck or bowed, it moves according to some linear combination of harmonics. A violin sounds different from a piano because of the difference in the strengths of various harmonics.

The Fourier series is named for Jean Baptiste Joseph Fourier, 1768–1830, a famous French mathematician and physicist.

The linear combination shown in Eq. (14.3-24) is called a *Fourier sine series*. Fourier cosine series also exist, which are linear combinations of cosine functions. The *Fourier coefficients* $a_1, a_2, \ldots$ must depend on t to satisfy the wave equation. With the initial condition that the string is passing through its equilibrium position at

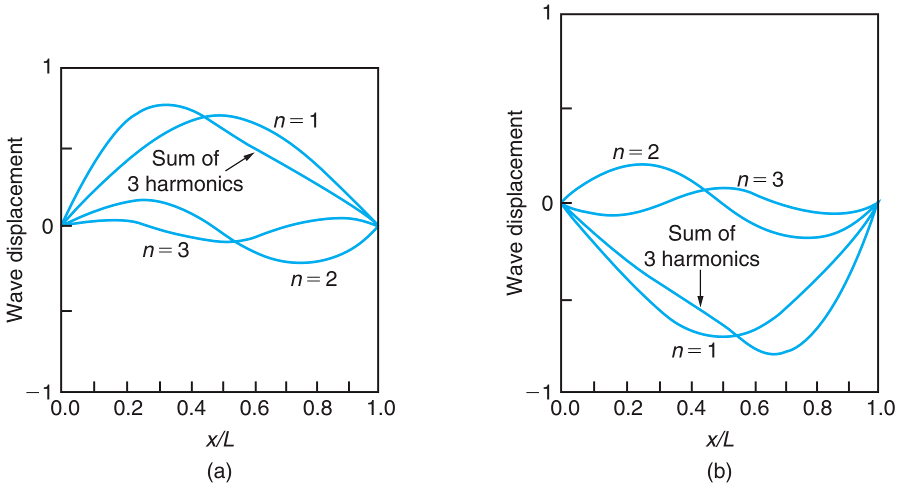


Figure 14.8 The Superposition of Three Harmonics of a Flexible String. (a) At time $t = L/4c$. (b) At time $t = 3L/4c$.

$t = 0$, the following linear combination is a solution of the wave equation

$$z(x,t) = \sum_{n=1}^{\infty} A_n \sin\left(\frac{n\pi x}{L}\right) \sin\left(\frac{n\pi ct}{L}\right) \tag{14.3-25}$$

where $A_1, A_2, \ldots$ are constants.

Exercise 14.7

Show by substitution that the series in Eq. (14.3-25) satisfies Eq. (14.3-3).

The different harmonics exhibit constructive interference and destructive interference that continually change, because the different harmonics have different frequencies. Figure 14.8 shows a linear combination of three harmonics with $A_1 = 1$, $A_2 = 0.2$, and $A_3 = 0.1$. Figure 14.8a shows the sum at time $t = L/(4c)$, and Figure 14.8b shows the sum at $t = 3L/(4c)$.

Traveling Waves

In a string of finite length with stationary ends, only standing waves can occur. Traveling waves can occur in a very long string. A wave function that satisfies Eq. (14.3-3) and corresponds to a traveling wave is

$$z(x,t) = A\sin(\kappa x - \kappa ct) \tag{14.3-26}$$

Exercise 14.8

Show by substitution that the function in Eq. (14.3-26) satisfies Eq. (14.3-3).

We can find the speed of a traveling wave by following the motion of one of the nodes. At time $t = 0$ there is a node in the wave function of Eq. (14.3-26) at $x = 0$. At time t this node will be located at the point where $x - ct = 0$. Thus

$$x(\text{node}) = ct \tag{14.3-27}$$

The node is moving toward the positive end of the x axis with a speed equal to c. From Eq. (14.3-4) the speed is determined by the tension force T and the mass per unit length ρ:

$$c = \sqrt{\frac{\mathscr{T}}{\rho}} \tag{14.3-28}$$

Exercise 14.9

What change would have to be made in the mass per unit length to quadruple the speed of propagation? What change would have to made in the tension force to double the speed of propagation?

If the function of Eq. (14.3-26) is replaced by

$$z(x, t) = A\sin(\kappa x + \kappa ct) \tag{14.3-29}$$

the wave travels toward the negative end of the x axis with speed c. This function satisfies the same wave equation as the function shown in Eq. (14.3-26) and the speed is the same.

Exercise 14.10

a. Show that the function of Eq. (14.3-29) satisfies Eq. (14.3-3).
b. Show that the speed of the wave is equal to c and that the wave moves to the left.

In one wavelength, the argument of the φ function changes by 2π if t is fixed, so that the same relationship occurs as in Eq. (14.3-21) for a standing wave:

$$\boxed{\kappa = \frac{2\pi}{\lambda}} \tag{14.3-30}$$

The relationship between the frequency and the wavelength can be obtained by observing that in time t, the length of the wave "train" that passes a fixed point is

$$\text{Length} = ct \tag{14.3-31}$$

where c is the speed. The number of wavelengths in this wave train is equal to

$$\text{Number} = \frac{ct}{\lambda} \tag{14.3-32}$$

In time t, the number of oscillations is equal to

$$\text{Number} = \nu t \tag{14.3-33}$$

so that $\nu t = ct/\lambda$, or

$$\boxed{\nu = \frac{c}{\lambda}} \tag{14.3-34}$$

Equation (14.3-34) is the general relation between wavelength and frequency for a traveling wave. This important equation holds for all kinds of waves, including sound waves and electromagnetic waves. If we replace λ by $2L/n$ and c by $\sqrt{\mathscr{T}/\rho}$ we obtain

$$\nu = \frac{n}{2L}\sqrt{\frac{\mathscr{T}}{\rho}} \tag{14.3-35}$$

which is identical to Eq. (14.3-23), the formula for the frequency of a standing wave.

Using Eqs. (14.3-30) and (14.3-34), we can now write

$$z(x,t) = A\sin\left(\frac{2\pi x}{\lambda} - 2\pi\nu t\right) \tag{14.3-36}$$

Exercise 14.11

In addition to waves in strings, other oscillations such as sound waves obey wave equations. The speed of sound in air at sea level and 20°C is 343 $\mathrm{m\,s^{-1}}$. Find the wavelength of a sound wave with a frequency of 440 $\mathrm{s^{-1}}$, or 440 Hertz. (This frequency is the frequency of "A" above middle "C" in the musical scale.)

Two traveling waves moving in opposite directions can interfere to produce a standing wave. The two traveling waves

$$z_R(x,t) = A\sin(\kappa x - \kappa ct) \tag{14.3-37a}$$

and

$$z_L(x,t) = A\sin(\kappa x + \kappa ct) \tag{14.3-37b}$$

interfere to give

$$z(x,t) = z_R(x,t) + z_L(x,t) = A[\sin(\kappa x + \kappa ct) + \sin(\kappa x - \kappa ct)] \tag{14.3-38}$$

which by the use of trigonometric identities is the same as the standing wave

$$z(x,t) = 2A\sin(\kappa x)\cos(\kappa ct) \tag{14.3-39}$$

Exercise 14.12

Use trigonometric identities to obtain Eq. (14.3-39) from Eq. (14.3-38).

The Wave Theory of Electromagnetic Radiation

James Clerk Maxwell, 1831–1879, was a British physicist who made fundamental contributions to electrodynamics, gas kinetic theory, and thermodynamics.

In 1865, Maxwell developed a mathematical theory of electromagnetism. According to this theory the electric field $\mathscr{E}$ and the magnetic field $\mathscr{H}$ can oscillate like waves, constituting electromagnetic radiation. Examples of electromagnetic radiation are

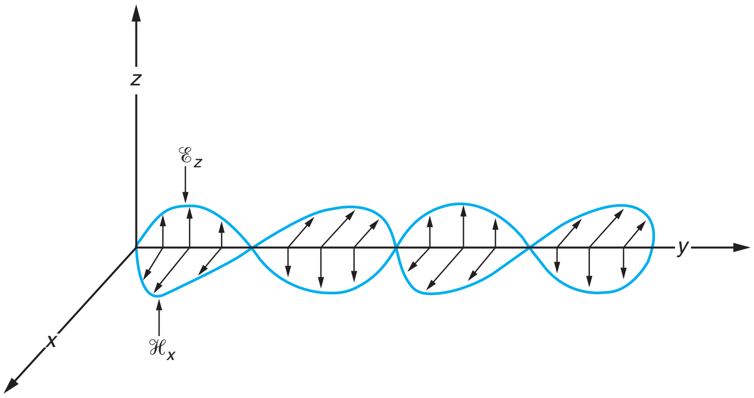


Figure 14.9 The Electric and Magnetic Fields in an Electromagnetic Wave.

visible light, infrared radiation, ultraviolet radiation, X-rays, radio waves, microwaves, and so on, which differ from each other only in having different wavelengths and frequencies.

Electromagnetic radiation obeys wave equations similar to other wave equations except that there are two oscillating quantities, the electric field $\mathscr{E}$ and the magnetic field $\mathscr{H}$. The equations are introduced briefly in Appendix F. These equations lead to standing waves and traveling waves similar to waves in a string. The electric field cannot oscillate without the magnetic field and vice versa, so the electromagnetic wave behaves like a single wave. Figure 14.9 depicts a plane polarized wave traveling in the y direction, with the electric field $\mathscr{E}$ oscillating in the z direction and with the magnetic field $\mathscr{H}$ oscillating in the x direction. As time passes, this traveling wave moves to the right without changing its shape or wavelength. Appendix F contains additional information about electromagnetic waves.

It was originally thought that all space was filled by a substance called the "luminiferous ether," which was supposedly the medium that oscillated when electromagnetic waves propagated. This medium would have to be very rigid for the speed of light to be as large as it is, but it could not impede the motions of objects moving through it. The existence of such a medium was disproved when Michelson and Morley found that the speed of light was independent of the motion of the observer. This experimental fact was the origin of Einstein's special theory of relativity, and we now know that electromagnetic waves do not require a material medium in which to oscillate.

Albert Abraham Michelson, 1852–1931, a German-American physicist, and Edward Morley, 1838–1923, an American chemist, collaborated on these measurements in 1887 at Case Western Reserve University.

Electric and magnetic fields exert forces on charged particles so that molecules and atoms can absorb electromagnetic radiation. The converse is also true. According to Maxwell's theory, oscillating electric charges emit electromagnetic radiation.

PROBLEMS

Section 14.3: Classical Waves

14.9 If a violin string has a fundamental frequency of 264 s^{-1}, find the frequency of each of the first three overtones.

14.10 The speed of sound in air at 25°C is 346.2 $\mathrm{m\,s^{-1}}$. Find the wavelength of the sound wave with frequency 264 s^{-1} at this temperature.

14.11 **a.** In a closed organ pipe, the wavelength of the fundamental wave corresponds to twice the length of the pipe. Find the length of the pipe that is needed at 25°C for "A" above "middle C," which has frequency equal to 440 s^{-1}. Assume that the speed of sound in air is 346.2 $\mathrm{m\,s^{-1}}$ at 25°C. What do you think will happen to the pitch if the temperature increases?

What would you have to do to produce the correct pitch at a different temperature?

b. In a musical instrument such as a clarinet with an open-ended "pipe," the fundamental wave has a wavelength approximately equal to four times the length of the pipe. Find the length of the pipe for A above middle C at 25°C.

c. The overtones for the instruments of parts a and b have different patterns, since each overtone wave for an open pipe has a node at the closed end of a pipe and a maximum at the open end. Find the frequency at 25°C of the first overtone for an organ pipe and for a clarinet for A above middle C.

14.12 The speed of sound in sea water at 25°C is 1531 $\mathrm{m\,s^{-1}}$. If a SONAR system on a submarine uses a frequency of 500 $\mathrm{s^{-1}}$ find the wavelength of the sound waves.

14.13 Assume that the fundamental and the first overtone are simultaneously excited in a flexible string such that

$$z(y,t) = A_1 \sin(\pi y/L)\sin(\pi ct/L) + A_2 \sin(2\pi y/L)\sin(2\pi ct/L)$$

where

$$A_1 = 4A_2$$

Construct a graph representing the shape of the string at time $t = 0$, at time $t = L/(4c)$, and at time $t = 3L/(4c)$. Comment on the differences in the shapes.

14.14 Show that the relationship $\nu = c/\lambda$ for a traveling wave also holds for the standing wave in Eq. (14.3-39).

14.15 **a.** A violin string has a mass per unit length of 3.0 $\mathrm{g\,m^{-1}}$. Find the tension force necessary to produce a fundamental frequency of 440 $\mathrm{s^{-1}}$ if the length of the string is 50.0 cm.

b. If the string were infinitely long with the same tension force, what would be the speed of a traveling wave of wavelength 1.00 m?

14.16 For liquid water at 25°C, the permittivity depends on frequency, and for fairly low frequency is equal to $6.954 \times 10^{-10}\ \mathrm{C^2\,N^{-1}\,m^{-2}}$. The refractive index is defined as the ratio:

$$\text{refractive index} = n = c_{\text{vacuum}}/c_{\text{medium}}$$

The refractive index of water is equal to 1.33 for visible light. Find the speed of light in water and the permittivity for frequencies corresponding to visible light. To four significant digits, the permeability is the same as that of a vacuum for these frequencies.

14.17 The wavelength of yellow light given off in air by sodium in flame tests is 589.2 nm.

a. Find the frequency of this light. The index of refraction of air is 1.00027.

b. Find the wavelength of this light in carbon disulfide at 20°C. The index of refraction of carbon disulfide at 20°C is equal to 1.62546.

14.4 The Old Quantum Theory

The Atomic Nature of Matter

John Dalton, 1766–1844, was an English schoolmaster and chemist. After becoming famous, he continued to teach young pupils elementary subjects.

Joseph John Thomson, 1856–1940, was a British physicist who received the 1906 Nobel Prize in physics for his discovery of the electron and his measurement of its charge-to-mass ratio.

All of ordinary matter is made up of atoms. Although the idea of atoms was introduced by the Greek philosopher Democritus, it became part of chemistry only after 1803, when Dalton proposed his atomic theory. This theory asserts that each element has its own characteristic type of atoms, and that atoms combine as units to produce compounds. Dalton's theory did not include any information about the structure of atoms and how they could bind to other atoms to make molecules. Dalton even proposed that atoms might have little hooks that could snag similar hooks on other molecules.

In the 1870s Thomson showed that the "cathode rays" emitted by negatively charged metals in a vacuum consisted of negatively charged particles, now known as electrons. Thomson pictured an atom as containing stationary electrons imbedded in a positive matrix, like raisins in an English plum pudding. However, Rutherford discovered in 1911 that an atom contains a very small positive nucleus, so that the electrons must orbit the nucleus. The charge on the electron was measured by Millikan in a series of experiments carried out between 1908 and 1917. Moseley discovered the concept of

Ernest Rutherford, 1st Baron Rutherford of Nelson, 1871–1937, was a British physicist originally from New Zealand who won the 1908 Nobel Prize in chemistry for his discovery of the atomic nucleus, and who coined the terms alpha, beta, and gamma radiation.

Henry Gwyn-Jeffreys Moseley, 1887–1915, was a British physicist who was also a lieutenant in the British Army and was killed in action in Turkey in 1915.

Robert Andrews Millikan, 1868–1953, was an American physicist who received the 1923 Nobel Prize in physics for determining the charge on the electron.

atomic number in 1913, showing that each element was characterized by the charge on its nucleus.

The atomic nucleus can be regarded as being made up of protons and neutrons. Protons and neutrons now appear to be made up of quarks, and the "superstring" theory proposes that quarks, electrons, and other fundamental particles consist of vibrations of tiny strings.[2] For most chemical purposes, it is sufficient to regard an atom as consisting of a positive nucleus and a number of negative electrons.

Planck's Theory of Black-body Radiation

If an object has a temperature near 1000°C, it glows visibly red, no matter what material it is made of. At higher temperatures it glows orange, yellow, white, or even blue if the temperature is high enough. It is found experimentally that at any temperature an object with a lower reflectivity glows more intensely. A *black body*, a model system that reflects no radiation at any wavelength, has the maximum emissivity at every wavelength.

The best laboratory approximation to a black body is not an object, but a small hole in the side of a hollow box. Any light falling on the hole from outside will be absorbed as it is reflected around in the box. Measurements on the light emitted through the hole when the box is heated show that the amount of light emitted and its spectral distribution depend only on the temperature of the walls of the box. Figure 14.10 shows the *spectral radiant emittance* η of a black body as a function of wavelength for several absolute temperatures. This quantity is defined such that $\eta(\lambda)d\lambda$ is the energy per unit time per unit area emitted in the wavelengths lying between λ and $\lambda + d\lambda$. The visible part of the electromagnetic spectrum, which ranges from about 400 nm to 700 nm, is labeled in the figure.

The maximum in the curve shifts to shorter wavelengths as the temperature is raised. At 5800 K the maximum in the curve is near 500 nm, in the green portion of the visible region. Black-body radiation of this temperature appears to be "white" light, similar to sunlight. Below 2000 K only the red part of the visible spectrum (around 600 to 700 nm) is significantly represented. Near room temperature almost all of the radiation is in the infrared region. It is this infrared radiation from the surface of the earth that is involved in the greenhouse effect in the earth's atmosphere.

The *total radiant emittance* (the spectral radiant emittance summed over all wavelengths) is equal to the area under the curve. The *Stefan–Boltzmann law* is an empirical law that relates the total radiant emittance to the absolute temperature of the black body:

$$(\textit{total radiant emittance}) = \sigma T^4 \tag{14.4-1a}$$

The Stefan–Boltzmann constant σ has the experimental value

$$\sigma = 5.67051 \times 10^{-8}\,\mathrm{J\,m^{-2}\,s^{-1}\,K^{-4}} = 5.67051 \times 10^{-8}\,\mathrm{W\,m^{-2}\,K^{-4}} \tag{14.4-1b}$$

where the joule (J) is the unit of energy and the watt (W, equal to joules per second) is the unit of power.

Rayleigh and Jeans constructed a classical theory of black-body radiation. They defined as their system the set of standing electromagnetic waves that could exist inside a box made of electrically conductive material. An electric field cannot penetrate a perfect conductor (one with zero resistance), because a finite electric field would produce an infinite current. Electromagnetic waves must have nodes at perfectly conducting

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[2] See for example, B. Greene, *The Elegant Universe*, Vintage Books, New York, 2000.

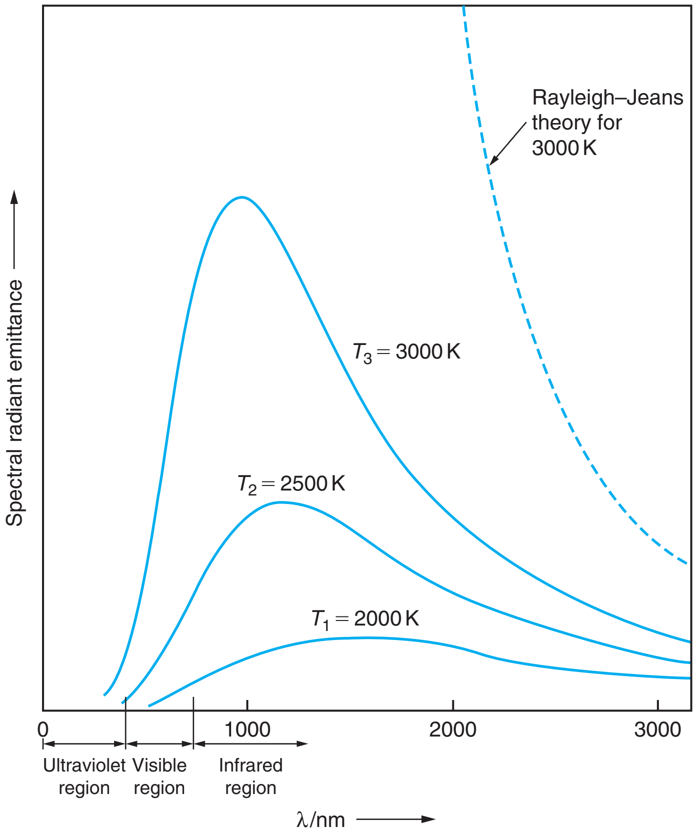

Figure 14.10 The Quantized Energies of an Oscillator as Postulated by Planck. The horizontal line segments are plotted at the heights of the assumed energy values, 0, $h\nu$, $3h\nu$, $4h\nu$, $5h\nu$, $6h\nu$, $7h\nu$, etc.

walls, so that a conducting box can contain standing electromagnetic waves with nodes at the walls. For a rectangular box, Rayleigh and Jeans counted the possible standing waves of various wavelengths that could exist with nodes at the walls and computed the average energy of each standing wave as a function of temperature using standard methods of classical physics. Their result was

$$\eta(\lambda)\,d\lambda = \frac{2\pi c k_{\mathrm{B}} T}{\lambda^4} d\lambda \qquad (14.4\text{-}2)$$

where c is the speed of light, T is the absolute temperature, and k_{B} is Boltzmann's constant:

$$k_{\mathrm{B}} = \frac{R}{N_{\mathrm{Av}}} = 1.38066 \times 10^{-23}\,\mathrm{J\,K^{-1}}$$

where R is the ideal gas constant and N_{Av} is Avogadro's constant.

John William Strutt, 3rd Baron Rayleigh, 1842–1919, was the 1904 Nobel Prize winner in physics, and Sir James Jeans, 1877–1946, was a British astronomer and physicist.

Although the formula of Rayleigh and Jeans agrees with experiment for large values of the wavelength, it predicts that the spectral radiant emittance becomes large without bound in the limit of short wavelength, which contradicts experimental results. This result is due to the fact that more and more standing waves can fit into a box if the wavelength is made shorter and shorter. The failure of the Rayleigh–Jeans theory to agree with experiment was called the "ultraviolet catastrophe."

Max Planck, 1858–1947, received the Nobel Prize in physics in 1918 for this theory, although at first most physicists were reluctant to believe that it was correct.

In 1900 Max Planck devised a new theory of black-body radiation that agreed with experimental results. This theory is the first part of what we call the "old quantum theory." The following statements are a simplified version of the assumptions that led to his result:[3]

1. The walls of the box contain oscillating electric charges. Each oscillator has a characteristic fixed frequency of oscillation, but many oscillators are present and many frequencies are represented.
2. The standing waves in the box are equilibrated with the oscillators so that the average energy of standing waves of a given frequency equals the average energy of the wall oscillators of the same frequency.
3. The energy of an oscillator is *quantized*. That is, it is capable of assuming only one of the values from the set:

$$E = 0, h\nu, 2h\nu, 3h\nu, 4h\nu, \ldots, nh\nu, \ldots \tag{14.4-3}$$

where ν is the frequency of the oscillator and where h is a new constant, now known as *Planck's constant*. The quantity n, which can take on any non-negative integral value, is called a *quantum number*. Figure 14.11 schematically shows this energy quantization. Quantization has been compared to standing on a ladder. A person can stand on any rung of a ladder, but nowhere between the rungs. The energy can take on any of the values in Eq. (14.4-3), but cannot take on any value between these values.

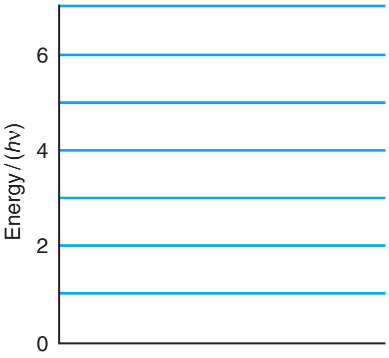

Figure 14.11 The Quantized Energies of an Oscillator as Postulated by Planck. The horizontal line segments are plotted at the heights of the assumed energy values, 0, $h\nu$, $3h\nu$, $4h\nu$, $5h\nu$, $6h\nu$, $7h\nu$, etc.

4. The probability of a state of energy E is given by the *Boltzmann probability distribution*:

$$(\text{probability of a state of energy } E) \propto e^{-E/k_{\mathrm{B}}T} \tag{14.4-4}$$

where the symbol $\propto$ stands for "is proportional to," where T is the absolute temperature, and where k_{B} is Boltzmann's constant. We discuss the Boltzmann probability distribution in Parts 2 and 4 of this textbook, but simply state it as an assumption of Planck at this point.

Planck's theory removed the ultraviolet catastrophe because short wavelengths correspond to large frequencies and large energy spacings. The excited states therefore have very small populations. The result of Planck's theory is that

$$\boxed{\eta(\lambda)d\lambda = \frac{2\pi hc^2}{\lambda^5(e^{hc/\lambda k_{\mathrm{B}}T} - 1)}d\lambda} \tag{14.4-5}$$

Planck was able to achieve agreement with experimental data by choosing a value of h approximately equal to the presently accepted value, 6.62608×10^{-34} J s. Planck's formula agrees with the Stefan–Boltzmann law and with *Wien's law*, which states that the wavelength at the maximum in the spectral radiant emittance curve is inversely proportional to the absolute temperature.

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[3] M. Jammer, *The Conceptual Development of Quantum Mechanics*, McGraw-Hill, New York, 1966, p. 10ff.

EXAMPLE 14.2

Show that the wavelength of maximum spectral radiant emittance is inversely proportional to the absolute temperature and find the proportionality constant.

Solution

To find the maximum, we set the derivative of the function of Eq. (14.4-5) equal to zero:

$$\frac{d\eta}{d\lambda} = 2\pi hc^2 \frac{(hc/\lambda k_B)Te^{hc/\lambda k_B T} - 5(e^{hc/\lambda k_B T} - 1)}{\lambda^6[e^{hc/\lambda k_B T} - 1]} = 0$$

This expression can vanish only if the numerator vanishes, which is equivalent to

$$\frac{hc}{\lambda_{\max} k_B T} = 5\left(1 - e^{-hc/\lambda_{\max} k_B T}\right)$$

or, if we let $x = hc/\lambda_{\max} k_B T$, then

$$x = 5\left(1 - e^{-x}\right)$$

This equation must be solved by numerical approximation. The result is that $x = 4.965$, so that

$$\lambda_{\max} = \frac{1}{4.965}\frac{hc}{k_B T} = \frac{2.898 \times 10^{-3}\,\mathrm{mK}}{T} \tag{14.4-6}$$

This result agrees with Wien's law and with the experimental value of the proportionality constant.

EXAMPLE 14.3

Use the definite integral

$$\int_0^\infty \frac{x^3}{e^x - 1}dx = \frac{\pi^4}{15} \tag{14.4-7}$$

to derive the Stefan–Boltzmann law, Eq. (14.4-1). Calculate the theoretical value of the Stefan–Boltzmann constant.

Solution

The total energy flux is

$$\int_0^\infty \eta(\lambda)\,d\lambda = \int_0^\infty \frac{2\pi hc^2}{\lambda^5(e^{hc/\lambda k_B T} - 1)}d\lambda$$

We make the variable change

$$x = \frac{hc}{\lambda k_B T}$$

so that

$$\int_0^\infty \frac{2\pi hc^2}{\lambda^5(e^{hc/\lambda k_B T} - 1)}d\lambda = 2\pi hc^2\left(\frac{k_B T}{hc}\right)^5\left(\frac{hc}{k_B T}\right)\int_0^\infty \frac{x^3}{e^x - 1}dx$$

$$= 2\pi hc^2\left(\frac{k_{\mathrm{B}}T}{hc}\right)^4\frac{\pi^4}{15} = \frac{2\pi^5k^4}{15h^3c^2}T^4 = \sigma T^4$$

$$\sigma = \frac{2\pi^5(1.3807\times 10^{-23}\,\mathrm{J\,K^{-1}})^4}{15(6.6261\times 10^{-34}\,\mathrm{J\,s})^3(2.9979\times 10^8\,\mathrm{m\,s^{-1}})^2}$$

$$= 5.671\times 10^{-8}\,\mathrm{J\,m^{-2}\,s^{-1}\,K^{-4}}$$

This value agrees well with the experimental value, $5.669\times 10^{-8}\ \mathrm{J\ m^{-2}\ s^{-1}\ K^{-4}}$.

Exercise 14.13

Find the temperature that corresponds to the wavelength of maximum spectral emittance at 650.0 nm, in the red part of the visible spectrum.

Exercise 14.14

Show that in the limit as $\lambda \to \infty$, Eq. (14.4-5) agrees with Eq. (14.4-2).

Einstein's Theory of the Photoelectric Effect

When a metal plate in a vacuum is illuminated, it emits electrons if the wavelength of the incident light is at least as small as a *threshold wavelength* that depends on the identity of the metal. This phenomenon is known as the *photoelectric effect*. Early investigators were surprised to find that the maximum energy of the ejected electrons depended only on the wavelength of the light and not on its intensity. There was no explanation for this behavior until 1905, when Einstein published his theory of the photoelectric effect, which we regard as the second theory of the "old quantum theory." This theory is based on the hypothesis that the energy in a beam of light consists of discrete "quanta," and that each quantum has an energy

Albert Einstein, 1879–1955, was a German-Swiss-American physicist who received the 1921 Nobel Prize in physics for this work. He was the greatest physicist of the 20th century and made fundamental contributions in many areas of theoretical physics.

$$\boxed{E = h\nu = \frac{hc}{\lambda}} \tag{14.4-8}$$

where h is Planck's constant, ν is the frequency of the radiation, λ is its wavelength, and c is the speed of light. Equation (14.4-8) is known as the *Planck–Einstein relation*. The quanta of light are called *photons*.

The name "photon" was coined by the American chemist G. N. Lewis, 1875–1946, who became famous for his invention of the "octet rule" of chemical bonding and his careful statement of the third law of thermodynamics.

The energy of an electron ejected from the metal is equal to the energy of the photon minus the energy required to detach the electron from the metal. The *work function* W is the minimum energy required to detach an electron from a given substance. The maximum electron kinetic energy is

$$E_{\mathrm{max}} = h\nu - W = \frac{hc}{\lambda} - W \tag{14.4-9}$$

In 1916, Robert A. Millikan (the same person who measured the electron's charge) made accurate measurements of the photoelectric effect that agreed well with Eq. (14.4-9).

The Wave–Particle Duality of Light

Since light exhibits a particle-like nature in some experiments and wave-like properties in other experiments, we say that it exhibits a *wave–particle duality*. We cannot give a simple answer to the question: “What is light really like?” We use the wave description when it explains a particular experiment, and use the particle description when it explains another experiment.

EXAMPLE 14.4

The work function of nickel equals 5.0 eV. Find (a) the threshold wavelength for nickel and (b) the maximum electron speed for a wavelength of 195 nm.

Solution

a.

$$W = h\nu_{\text{threshold}} = \frac{hc}{\lambda_{\text{threshold}}}$$

$$\lambda_{\text{threshold}} = \frac{hc}{W} = \frac{(6.6261 \times 10^{-34}\,\text{J s})(2.9979 \times 10^{8}\,\text{m s}^{-1})}{(5.0\,\text{eV})(1.6022 \times 10^{-19}\,\text{J eV}^{-1})}$$

$$= 2.5 \times 10^{-7}\,\text{m} = 250\,\text{nm}$$

b.

$$\frac{1}{2}mv_{\text{max}}^2 = \frac{hc}{\lambda} - \frac{hc}{\lambda_{\text{threshold}}} = \frac{hc}{\lambda} - W$$

$$= \frac{(6.6261 \times 10^{-34}\,\text{J s})(2.9979 \times 10^{8}\,\text{m s}^{-1})}{1.95 \times 10^{-7}\,\text{m}}$$

$$- (5.0\,\text{eV})(1.6022 \times 10^{-19}\,\text{J eV}^{-1})$$

$$= 2.18 \times 10^{-19}\,\text{J}$$

$$v_{\text{max}}^2 = \left(\frac{2(2.18 \times 10^{-19}\,\text{J})}{9.11 \times 10^{-31}\,\text{kg}}\right) = 4.78 \times 10^{11}\,\text{m}^2\,\text{s}^{-2}$$

$$v_{\text{max}} = \sqrt{4.78 \times 10^{11}\,\text{m}^2\,\text{s}^{-2}} = 6.91 \times 10^{5}\,\text{m s}^{-1}$$

Bohr’s Theory of the Hydrogen Atom

Excited hydrogen atoms emit light when excited by an electric spark. However, only certain wavelengths are emitted. Four wavelengths are present in the visible region and other wavelengths occur in the ultraviolet and in the infrared. When viewed in a spectroscope, each wavelength produces an image of the slit of the instrument. These images resemble line segments and are called *spectral lines*. The set of separated lines is called a *line spectrum*. Rydberg was able to represent the wavelengths of all of the spectral lines of hydrogen atoms with a single empirical formula:

$$\frac{1}{\lambda} = \mathscr{R}_{\text{H}}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{14.4-10}$$

where n_1 and n_2 are two positive integers and $\mathscr{R}_{\mathrm{H}}$ is a constant known as *Rydberg's constant*, equal to $1.09677581 \times 10^7\ \mathrm{m}^{-1}$ if the wavelengths are measured in a vacuum. Classical physics was unable to explain this relationship.

Johannes Robert Rydberg, 1854–1919, was professor of physics at the University of Lund in Sweden, where he received both his bachelor's and doctor's degrees in mathematics and where he spent his entire career. He was originally an instructor in mathematics but moved into mathematical physics.

Rutherford's discovery of the atomic nucleus showed that the negative electrons must be orbiting around the nucleus. However, an orbiting electron would be accelerated and according to the electrodynamics of Maxwell should emit electromagnetic radiation. It would lose energy and fall onto the nucleus and collapse the atom, emitting various wavelengths of light as it fell. Classical physics was unable to explain either the line spectrum of the hydrogen atom or the continuing existence of the atom.

In 1913 Bohr published a theory of the hydrogen atom, based on unproved assumptions. We regard his theory as the third part of the "old quantum theory." A simplified version of Bohr's assumptions is:

1. The hydrogen atom consists of a positive nucleus of charge e and an electron of charge $-e$ moving around it in a circular orbit. The charge e had been determined by Millikan to have the value 1.6022×10^{-19} C.
2. The angular momentum (see Appendix E) of the electron is quantized: Its magnitude can take on one of the values $h/2\pi, 2h/2\pi, 3h/2\pi, 4h/2\pi, \ldots, nh/2\pi$, where h is Planck's constant and where n is an integer (a quantum number). Figure 14.12 schematically shows the quantization of the angular momentum.
3. Maxwell's equations do not apply. Radiation is emitted or absorbed only when a transition is made from one quantized value of the angular momentum to another.
4. The wavelength of emitted or absorbed light is given by the Planck–Einstein relation, Eq. (14.4-8), with the energy of the photon equal to the difference in energy of the initial and final states of the atom.
5. In all other regards, classical mechanics is valid.

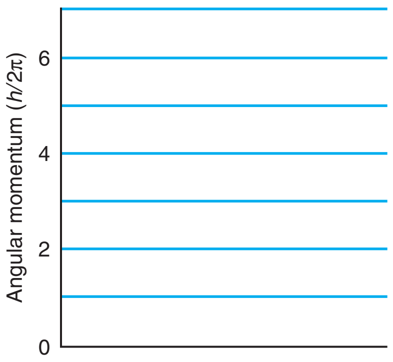

Figure 14.12 The Quantized Angular Momentum Values of Electronic Motion in a Hydrogen Atom as Postulated by Bohr.

Niels Henrik David Bohr, 1885–1962, was a Danish physicist who received the Nobel Prize in physics in 1922 for this work. He was also responsible for much of the accepted physical interpretation of quantum mechanics and for the quantum mechanical explanation of the form of the periodic table of the elements.

We now derive the consequences of Bohr's assumptions. The nucleus is much more massive than the electron and the electron moves about it almost as if the nucleus were stationary. (See Problem 14.29.) We now proceed as though the nucleus was infinitely massive and therefore completely stationary. To maintain a circular orbit about the nucleus, there must be a centripetal force on the electron:

$$F_r = -m_e v^2/r \tag{14.4-11}$$

where v is the speed of the electron, m_e is its mass, and r is the radius of the orbit (see Eq. (E-17) of Appendix E).

EXAMPLE 14.5

Find the centripetal force on an object of mass 1.50 kg if you swing it on a rope so that the radius of the orbit is 2.00 m and the time required for one orbit is 2.00 s.

Solution

$$v = \frac{2\pi(2.00\ \mathrm{m})}{2.00\ \mathrm{s}} = 6.28\ \mathrm{m\,s^{-1}}$$

$$|F| = \frac{m_e v^2}{r} = \frac{(1.50\ \mathrm{kg})(6.28\ \mathrm{m\,s^{-1}})^2}{2.00\ \mathrm{m}} = 29.6\ \mathrm{N}$$

This force is about twice as large as the gravitational force on the mass, 14.7 N.

Coulomb's law is named for Charles Augustin de Coulomb, 1736–1806, the French physicist who discovered this law.

The centripetal force is provided by the electrostatic attraction of the positive nucleus for the negative electron. Coulomb's law for the force between a charge Q_1 and another charge Q_2 separated by a vacuum is

$$F_{12} = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r_{12}} \tag{14.4-12}$$

where ε_0 is the *permittivity* of the vacuum, equal to $8.8545 \times 10^{-12}\,\mathrm{C^2\,N^{-1}\,m^{-2}}$, and where r_{12} is the distance between the charges. If the two charges are of opposite sign, the force is negative, corresponding to attraction. We equate the centripetal force and the electrostatic force:

$$\frac{m_e v^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2} \tag{14.4-13}$$

The angular momentum of the electron in a circular orbit is a vector denoted by **L** and is given by Eq. (E-19) of Appendix E. It is quantized, according to assumption 2, taking on the possible magnitudes

$$L = r m_e v = \frac{nh}{2\pi} \tag{14.4-14}$$

where the *quantum number n* is a positive integer. Equation (14.4-14) is solved for the speed v and the result is substituted into Eq. (14.4-13). The resulting equation is solved for the radius of the orbit to give

$$\boxed{r = \frac{h^2 4\pi\varepsilon_0}{4\pi^2 m_e^2} n^2 = a_0 n^2} \tag{14.4-15}$$

where a_0 is equal to 5.29198×10^{-11} m (52.9198 pm or 0.529198 Å) and is called the *Bohr radius*. This value corresponds to an infinitely massive nucleus. The radius of the orbit is quantized and is proportional to the square of the quantum number n. Figure 14.13 depicts the first few Bohr orbits.

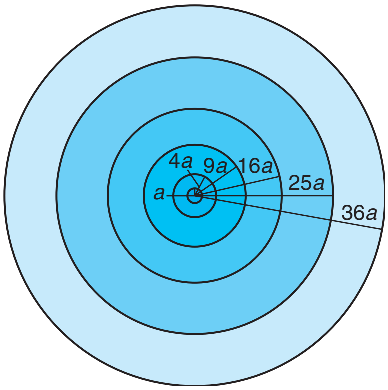

Figure 14.13 The Quantized Bohr Orbits.

Exercise 14.15

a. Obtain Eq. (14.4-15) from Eqs. (14.4-13) and (14.4-14).
b. Using the accepted values of the physical constants, verify the value of the Bohr radius.

The potential energy that corresponds to the Coulomb force of Eq. (14.4-11) is

$$\mathcal{V} = \frac{Q_1 Q_2}{4\pi\varepsilon_0 r_{12}} \tag{14.4-16}$$

The potential energy for an electron of charge $-e$ at a distance r from a nucleus of charge e is

$$\mathcal{V} = -\frac{e^2}{4\pi\varepsilon_0 r} \tag{14.4-17}$$

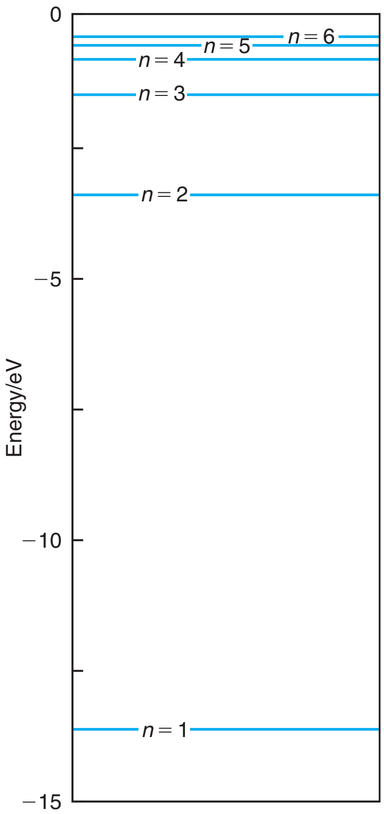

Figure 14.14 The Quantized Electron Energies According to the Bohr Theory. The energy values are all negative, since an energy value of zero corresponds to enough barely energy to remove the electron from the atom.

where we assign the value of $\mathscr{V}$ to approach zero as $r \to \infty$. (Remember that we can always pick the state at which we assign $\mathscr{V}$ to equal zero.) The kinetic energy is given by

$$\mathscr{K} = \frac{1}{2}m_e v^2 = \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 r} = \frac{1}{2}|\mathscr{V}| \tag{14.4-18}$$

where Eq. (14.4-13) has been used to replace v^2. The kinetic energy is equal to half of the magnitude of the potential energy. This is one of the consequences of the *virial theorem* of mechanics and holds for any system acted upon only by electrostatic forces.[4]

The energy of the hydrogen atom is given by the formula:

$$\boxed{E = E_n = \mathscr{K} + \mathscr{V} = -\frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 r} = -\frac{2\pi^2 m_e e^4}{(4\pi\varepsilon_0)^2 h^2 n^2}} \tag{14.4-19a}$$

where we have used Eq. (14.4-15) for the value of r. The energy is quantized and is determined by the value of the quantum number, n. Figure 14.14 depicts the first few energy levels. With the accepted values of the physical constants, we can write

$$E_n = -\frac{2.1797 \times 10^{-18}\,\mathrm{J}}{n^2} = -\frac{13.605\,\mathrm{eV}}{n^2} \tag{14.4-19b}$$

where the electron-volt (eV) is the energy required to move an electron through a potential difference of 1 volt:

$$1\,\mathrm{eV} = 1.60218 \times 10^{-19}\,\mathrm{J}$$

Bohr postulated that a photon is emitted or absorbed only when the electron makes a transition from one energy level to another. The energy of an emitted or absorbed photon is equal to the difference between two quantized energies of the atom:

$$E_{(\mathrm{photon})} = -\Delta E_{\mathrm{atom}} = -(E_{n_2} - E_{n_1}) = \frac{2\pi^2 m_e e^4}{(4\pi\varepsilon_0)^2 h^2}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{14.4-20}$$

where n_2 is the quantum number of the final state and n_1 is the quantum number of the initial state of the atom. Figure 14.15 depicts the first few transitions corresponding to emission of photons. Using the Planck–Einstein relation for the energy of the photon, Eq. (14.4-8), we obtain

$$\frac{1}{\lambda} = \frac{E_{n1} - E_{n2}}{hc} = \frac{2\pi^2 m_e e^4}{(4\pi\varepsilon_0)^2 h^3 c}\left(\frac{1}{n_2^2} - \frac{1}{n_1^2}\right) \tag{14.4-21}$$

This is the formula of Rydberg, Eq. (14.4-10), with the constant given by

$$\mathscr{R}_\infty = \frac{2\pi^2 m_e e^4}{(4\pi\varepsilon_0)^2 h^3 c} = 1.097373 \times 10^7\,\mathrm{m}^{-1} \tag{14.4-22}$$

The subscript ∞ is used to indicate that this value corresponds to an infinitely heavy nucleus.

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[4] I. N. Levine, *Quantum Chemistry*, 4th ed., Prentice-Hall, Englewood Cliffs, NJ, 1991, p. 434ff.

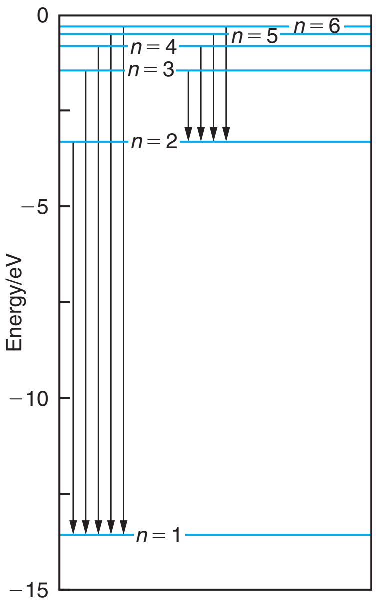

Figure 14.15 The Transitions between Energies of the Hydrogen Atom According to the Bohr Theory.

Exercise 14.16

a. Substitute the values of the constants into the expression of Eq. (14.4-21) to verify the value of $\mathscr{R}_\infty$.

b. Calculate the wavelength and frequency of the light emitted when n changes from 4 to 2. What color does this correspond to?

c. When radiation passes through air instead of a vacuum, wavelengths are increased by a factor equal to the refractive index of air, equal to 1.00027 for visible wavelengths. Find the value of Rydberg's constant for radiation passing through air.

The first set of transitions shown in Figure 14.15, in which the lower-energy state (n_2 state) is the $n = 1$ state, corresponds to the series of spectral lines in the ultraviolet that is known as the Lyman series. The second set of transitions, in which $n_2 = 2$, is the Balmer series. The first four lines of the Balmer series are in the visible region and the others are in the ultraviolet. The next series, in which $n_2 = 3$, is the Paschen series. It lies in the infrared. It is not shown in the figure.

The Bohr theory gives the correct energy expression for the hydrogen atom. Like the other theories of the old quantum theory, it is based on unproved assumptions, not all of which have turned out to be correct. Bohr was unable to extend the theory to apply to the helium atom or any other atom, and it became obvious that the theory was inadequate. However, it and the other theories of the old quantum theory provided the incentive for others to find a more satisfactory theory.

PROBLEMS

Section 14.4: The Old Quantum Theory

14.18 **a.** Find the temperature of a black body with a maximum in its spectral radiant emittance curve at a wavelength of 480 nm.

b. Assume that the surface temperature of the sun is 5800 K and that it radiates like a black body. Find the wavelength of maximum spectral radiant emittance. What color of visible light does this correspond to?

c. Construct a graph of the spectral radiant emittance of a black body with a temperature of 5800 K from a wavelength of 200 nm to a wavelength of 2000 nm. This includes the visible region, which is roughly from 400 nm to 750 nm.

14.19 Interstellar space is filled with isotropic radiation that corresponds to black-body radiation with a temperature of 2.736 K. Find the wavelength of maximum spectral radiant emittance of black-body radiation at this temperature and construct a graph of the spectral radiant emittance as a function of wavelength for this temperature.

14.20 The work function of sodium metal is 2.28 eV, where $1\ \text{eV} = 1.6022 \times 10^{-19}$ J.

a. Find the threshold frequency and wavelength for sodium.

b. Find the frequency and wavelength of light capable of ejecting electrons from sodium metal with a speed of $4.00 \times 10^4\ \text{m s}^{-1}$.

14.21 The work function of platinum is equal to 6.30 eV.

a. Find the threshold frequency and wavelength for sodium.

b. If ultraviolet light of wavelength 253.7 nm irradiates a platinum surface, find the maximum kinetic energy of electrons that can be ejected from the surface.

14.22 Find the value of the centripetal force on an electron in the $n = 1$ orbit of the Bohr theory.

14.23 **a.** Calculate the speed of an electron in the $n = 4$ Bohr orbit and in the $n = 400$ Bohr orbit of a hydrogen atom.

b. Express these speeds as fractions of the speed of light.

14.24 **a.** Derive an expression for the period of the electronic motion in the Bohr theory (the time required for an electron to make one circuit around a Bohr orbit) as a function of n.

b. Find the value of the period and the frequency (the reciprocal of the period) for $n = 1$ and for $n = 1{,}000{,}000$.

14.25 Find the radius of the $n = 1.00 \times 10^6$ orbit of the electron in the hydrogen atom according to the Bohr theory.

14.26 The Balmer series of hydrogen atom spectral lines corresponds to transitions from higher values of n to $n = 2$ in the Bohr energy expression. Find the wavelengths in vacuum of all lines in the Balmer series that lie in the visible region.

14.27 Find the wavelengths of the first six lines in the hydrogen atom spectrum corresponding to transitions to $n = 1$ (the Lyman series). In what region of the electromagnetic spectrum do these lines lie?

14.28 Find the wavelengths of the first six lines in the hydrogen atom spectrum corresponding to transitions to $n = 3$. In what region of the electromagnetic spectrum do these lines lie?

14.29 In order to visualize the approximation that the nucleus is considered stationary while the electron moves around it, assume that a hydrogen atom is moving through space at a speed of 2500 m s^{-1}, roughly the average speed predicted by gas kinetic theory for a hydrogen atom at room temperature. Calculate how many times the electron in the $n = 1$ Bohr orbit goes around the nucleus in the time required for the atom to move a distance equal to the Bohr radius.

14.30 We can correct for the assumption that the nucleus of a hydrogen atom is stationary by replacing the mass of the electron by the reduced mass of the electron and nucleus defined by

$$\mu = \frac{m_n m_e}{m_n + m_e}$$

where m_n is the mass of the nucleus. See Appendix E for details.

a. Find the reduced mass of the nucleus and electron.

b. Find the value of the Bohr radius with this correction.

c. Find the expression for the energy of a hydrogen atom in joules and in electron volts with this correction.

d. Find the value of Rydberg's constant with this correction.

14.31 A positronium atom is a hydrogen-like atom with a nucleus consisting of a positron (an antiparticle with charge e and mass equal to that of the electron).

a. Find the value of the reduced mass of the two particles in a positronium atom and find the ratio of this reduced mass to the mass of an electron.

b. Find the value of the Bohr radius for positronium.

c. Find the energy of the $n = 1$ state of positronium, and find the ratio of this energy to that of a hydrogen atom.

d. Find the radius of the circle in which each particle moves around the center of mass for the $n = 1$ state according to the Bohr theory.

14.32 **a.** Find the reduced mass of the two particles in a deuterium atom (^{2}H). The mass of a deuterium atom in amu is listed in the appendix.

b. Find the energy of a deuterium atom in the 1s state and find the ratio of this energy to that of a hydrogen atom.

c. Find the energy of a He$^+$ ion in the 1s state and find the ratio of this energy to that of a hydrogen atom.

14.33 The gravitational potential energy between two objects is equal to

$$\mathcal{V}_g = G\frac{m_1 m_2}{r_{12}}$$

where G is the gravitational constant, equal to 6.673×10^{-11} m^3 kg^{-1} s^{-2} and where m_1 and m_2 are the masses of the two objects. Since this has the same dependence on r_{12} as does the Coulomb potential energy, the Bohr theory can be transcribed to apply to a hydrogen atom held together by gravity instead of electrostatic attraction.

a. Pretend that the charges on a proton and electron can be somewhat "turned off." Find the Bohr radius for a hydrogen atom with only the gravitational attraction between the proton and the electron, assuming the actual proton and electron masses.

b. Find the energy of the $n = 1$, $n = 2$, and $n = 3$ states of such an atom. Express your answer in joules and in electron volts.

Summary of the Chapter

According to classical mechanics, the state of a single particle is specified by its position and velocity. Newton's three laws are the basis of classical mechanics, and determine how the position and velocity of a particle depend on time. If the position and velocity of all particles of a system are specified for some initial time, the positions and velocities are determined for all times.

Newton's second law, $\mathbf{F} = m\mathbf{a}$, provides an equation of motion for a system that obeys classical mechanics. The solution of the classical equation of motion for the harmonic oscillator provides formulas for the position and velocity that correspond to uniform harmonic motion. The solution of the classical equation of motion for a flexible string prescribes the position and velocity of each point of the string as a function of time. These solutions are deterministic, which means that if the initial conditions are precisely specified, the motion is determined for all times.

The "old quantum theory" consists of theories with arbitrary assumptions of quantization that were devised to explain phenomena that classical physics could not explain. The old quantum theory includes the black-body radiation theory of Planck, the photoelectric effect theory of Einstein, and the hydrogen atom theory of Bohr.

ADDITIONAL PROBLEMS

14.34 The classical equation of motion of a particle of mass m falling in a vacuum near the surface of the earth is

$$m\frac{d^2z}{dt^2} = -mg$$

where m is the mass of the particle and g is the acceleration due to gravity, equal to $9.80\ \mathrm{m\,s^{-2}}$.

a. Solve this equation to obtain a general solution. How does your solution depend on m?

b. Obtain the solution for the case that $z = 0$ at $t = 0$ and $v_z = 0$ at $t = 0$.

c. Is this a conservative system? That is, is the total energy a constant of the motion?

14.35 Identify each statement as either true or false. If a statement is true only under special circumstances, label it as false.

a. A classical equation of motion gives the positions and velocities of all particles of a system for all times if the initial positions and velocities are specified.

b. The energy of a harmonic oscillator is quantized according to classical mechanics.

c. The solution to the equation of motion of a harmonic oscillator can be a linear combination of solutions.

d. The Bohr theory of the hydrogen atom is a hybrid theory, maintaining elements of classical mechanics along with quantization.

e. Planck's constant appears in all three of the theories of the old quantum theory.

14.36 Consider the earth and the sun to be described by the Bohr theory of the hydrogen atom, with the centripetal force provided by gravity instead of electrostatic attraction. The mass of the earth is 5.983×10^{24} kg, and the mass of the sun is larger by a factor of 332,958. The gravitational constant, G, is equal to $6.673 \times 10^{-11}\ \mathrm{m^3\,kg^{-1}\,s^{-2}}$.

a. Find the value of the Bohr radius.

b. The mean radius of the earth's orbit is 1.495×10^8 km. Find the value of the quantum number n for the earth's orbit.

c. Find the value of the angular momentum for this orbit.

15

The Principles of Quantum Mechanics. I. De Broglie Waves and the Schrödinger Equation

PRINCIPAL FACTS AND IDEAS

1. The “matter waves” of de Broglie led to quantum mechanics.
2. The Schrödinger equation describes the waves that correspond to states of systems.
3. The Schrödinger equation has a time-dependent version and a time-independent version.
4. The time-independent Schrödinger equation can be solved for some simple systems and produces quantization as a natural part of the solution.

15.1 De Broglie Waves

Prince Louis Victor de Broglie, 1892–1977, won the Nobel Prize in physics in 1929 for this work.

Niels Bohr received the 1922 Nobel Prize in physics for his hydrogen atom theory, based on an assumption of quantization of angular momentum. In 1923 a graduate student at the University of Paris named Prince Louis de Broglie was trying to find a physical justification for Bohr's hypothesis of quantization. In classical physics, one thing that is quantized is the wavelength of a standing wave. De Broglie sought a way to relate this to Bohr's theory and came up with the idea that a moving particle such as an electron is accompanied by a "fictitious wave."[1]

According to Einstein's theory of relativity, a particle of energy E has a mass m such that

$$E = mc^2 \tag{15.1-1}$$

where c is the speed of light. If we apply this to a photon and use the Planck–Einstein relation, Eq. (14.4-8), for the energy and if we replace mc by the momentum p, Eq. (15.1-1) becomes

$$\frac{hc}{\lambda} = pc \quad \text{or} \quad \lambda = \frac{h}{p} \tag{15.1-2}$$

where λ is the wavelength of the photon and h is Planck's constant. De Broglie deduced that the velocity of the wave accompanying a particle was the same as the velocity of the particle if Eq. (15.1-2) is applied to a particle of mass m.

$$\boxed{\lambda = \frac{h}{p} = \frac{h}{mv}} \tag{15.1-3}$$

We omit de Broglie's argument, which is more complicated than simply saying that Eq. (15.1-3) is analogous to Eq. (15.1-2).

The quantization assumption of Bohr's theory arises naturally from Eq. (15.1-3) if one assumes that the circumference of a circular electron orbit in a hydrogen atom is equal to an integral number of wavelengths. This assumption means that the wave repeats itself with the same phase (with crests in the same positions) on each trip around the orbit, as depicted in Figure 15.1a. The situation depicted in Figure 15.1b is assumed not to occur. For a circular orbit

$$2\pi r = n\lambda = \frac{nh}{mv} \tag{15.1-4}$$

This equation is the same as Eq. (14.4-14), the hypothesis of Bohr:

$$mvr = nh/2\pi \tag{15.1-5}$$

De Broglie had shown that it was not necessary to assume quantization in the hydrogen atom as a hypothesis if one assumes the matter-wave relation of Eq. (15.1-3) for the motion of the electron. This proposal of *matter waves* was revolutionary. When

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[1] M. Jammer, *The Conceptual Development of Quantum Mechanics*, McGraw-Hill, New York, 1966, p. 243ff.

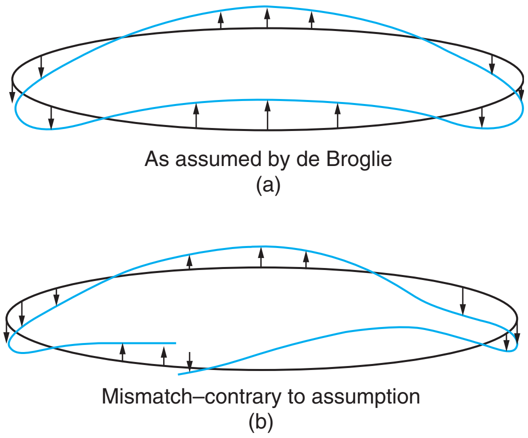

Figure 15.1 De Broglie Waves around a Closed Orbit. (a) An integral number of wavelengths on the circumference. (b) Not an integral number of wavelengths on the circumference.

de Broglie presented his doctoral dissertation containing this proposal, the examining committee accepted the dissertation but refused to believe that it corresponded to physical reality. The wave nature of ordinary objects is not observable because of the small wavelengths that occur.

EXAMPLE 15.1

Calculate the de Broglie wavelength of a baseball of mass 5.1 oz thrown at 95 miles per hour.

Solution

$$\lambda = \frac{6.6261\times 10^{-34}\,\mathrm{J\,s}}{(5.1\,\mathrm{oz})(95\,\mathrm{mi\,h^{-1}})}\left(\frac{16\,\mathrm{oz}}{1\,\mathrm{lb}}\right)\left(\frac{1\,\mathrm{lb}}{0.4536\,\mathrm{kg}}\right)\left(\frac{3600\,\mathrm{s}}{1\,\mathrm{h}}\right)\left(\frac{1\,\mathrm{mi}}{1609\,\mathrm{m}}\right) = 1.1\times 10^{-34}\,\mathrm{m}$$

The smallness of this value suggests why matter waves are not observed for baseballs.

The mass of electrons is so small that de Broglie suggested at his final oral examination that electron diffraction by crystals could verify his theory. In 1927, Davisson and Germer[2] accidentally grew a single crystal while heating a piece of nickel. When they irradiated this nickel crystal with a beam of electrons, they observed diffraction effects, verifying the existence of de Broglie's matter waves.

Exercise 15.1

Find the speed of electrons with a de Broglie wavelength equal to 2.15×10^{-10} m, the lattice spacing in a nickel crystal.

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[2] C. J. Davisson and L. H. Germer, *Phys. Rev.*, **30**, 705 (1927).

The notion of a fictitious wave moving along with a particle has been abandoned. We now speak of a wave–particle duality for particles, similar to the wave–particle duality of photons. The wave-like properties inherently belong to the object and not to an accompanying wave. This wave–particle duality is illustrated by the results of a hypothetical experiment.[3] A beam of electrons, all with the same speed, is allowed to stream in a vacuum toward a partition with two slits in it, as depicted in Figure 15.2a. At some distance on the other side of the partition is a screen coated with a material such as zinc sulfide, which glows when an electron strikes it.

A glowing pattern of bands is observed on the screen when a beam of electrons passes through the slits. This pattern is schematically depicted in Figure 15.2b. The intensity of the glow is plotted as a function of position on the screen. If the difference in the path lengths from the two slits to a given point on the screen equals an integral number of wavelengths, there is constructive interference and a glowing band. Between the bands, there is destructive interference and little or no glow. The beam of electrons clearly behaves like waves that pass through both slits.

If the intensity of the source is decreased so that electrons pass through the slits one at a time, there is a tiny localized flash at the point where each electron arrives. If the flashes are summed over a long time, exactly the same pattern of diffraction bands appears as with an intense beam of electrons, even though the electrons pass through the slits one at a time. If one slit is covered while the electrons continue to pass through the second slit, there is no diffraction pattern; a single band appears on the screen. If the first slit is uncovered and the second slit is covered another single band is observed. The sum of these two single bands shows no interference effect, as shown schematically in Figure 15.2c. Wave-like interference properties are observed only when both slits are open, even when one electron at a time passes through the slits. It appears that each electron passes through both slits in a delocalized wave-like fashion.

PROBLEMS

Section 15.1: De Broglie Waves

15.1 Calculate the de Broglie wavelength of an argon atom moving with a speed equal to the root-mean-square speed of argon atoms at 300 K, given by gas kinetic theory as $v_{\text{rms}} = \sqrt{3k_{\text{B}}T/m}$ where k_{B} is Boltzmann's constant, 1.3807×10^{-23} J K^{-1}, T is the absolute temperature, and m is the mass of the atom.

15.2 In the "solar wind" there are protons entering the earth's atmosphere that have such large speeds that one proton has sufficient kinetic energy to lift a kilogram mass 1.0 foot at the earth's surface.

- **a.** Calculate the speed of such a proton.
- **b.** Calculate the de Broglie wavelength of such a proton.
- **c.** If the energy of the proton were converted totally into a single photon, what would be the wavelength and frequency of the photon?

15.3 Thermal neutrons are neutrons with a distribution of speeds nearly like the equilibrium distribution for gas molecules. In Chapter 9 the most probable speed of gas molecules of mass m is given as $\sqrt{2k_{\text{B}}T/m}$. Find the de Broglie wavelength of a neutron moving at the most probable speed for 300 K. Would thermal neutrons be useful for diffraction experiments to determine crystal lattice spacings?

15.4 Find the de Broglie wavelength of a 1500 kg automobile moving at 65 miles per hour.

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[3] R. P. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics*, Vol. 3, Addison-Wesley, Reading, MA, 1965, Ch. 1.

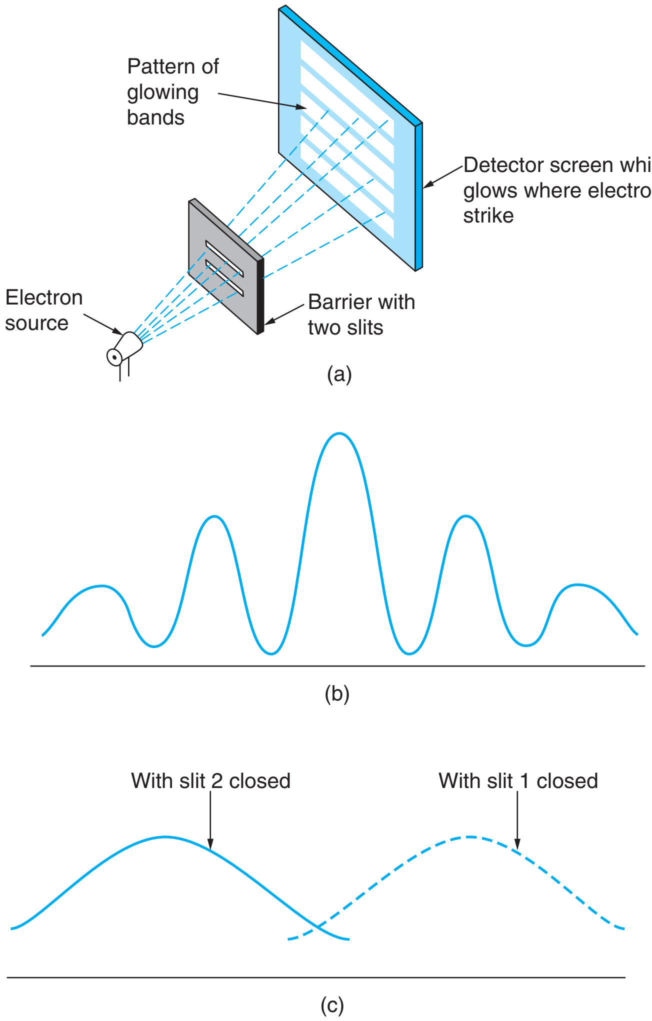

Figure 15.2 A Hypothetical Experiment with Electrons Passing through Two Slits. (a) The Apparatus. (b) The intensity of the glow due to electrons arriving at the screen in figure (a) with both slits open. (c) The intensity of the glow due to electrons arriving at the screen in (a) with one slit open at a time.

15.2 The Schrödinger Equation

Erwin Schrödinger, 1887–1961, was an Austrian physicist who shared the 1933 Nobel Prize in physics with P. A. M. Dirac, who pioneered the development of relativistic quantum mechanics.

If electrons and other particles act like waves, they should obey a wave equation. In 1926, Erwin Schrödinger published a series of four articles containing a wave equation for de Broglie waves, which we now call the Schrödinger equation. The first three articles presented the time-independent version of the wave equation and applied it to the hydrogen atom, rotation and vibration of diatomic molecules, and the effect of an external electric field on energy levels. The time-dependent version of the equation was reported in the fourth article.[4]

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[4] The time-independent equations were presented in *Ann. Physik*, **79**, 361 (1926), **79**, 489 (1926), and **80**, 437 (1926), and the time-dependent equation was presented in *Ann. Physik*, **81**, 109 (1926).

Nonrigorous Derivation of the Time-Independent Schrödinger Equation

In the formal theory of quantum mechanics, the Schrödinger wave equation is taken as a postulate (fundamental hypothesis). In order to demonstrate a relationship with the classical wave equation, we obtain the time-independent Schrödinger equation nonrigorously for the case of a particle that moves parallel to the x axis. For a standing wave along the x axis, the classical coordinate wave equation of Eq. (14.3-10) is

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{\lambda^2}\psi = 0 \tag{15.2-1}$$

where we have used Eq. (14.3-21) to replace the constant κ in terms of the wavelength λ and where we use the letter ψ instead of φ for the coordinate factor. Use of the de Broglie relation, Eq. (15.1-3), to replace λ gives

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{h^2}m^2v^2\psi = 0 \tag{15.2-2}$$

We eliminate the speed v from our equation by using the relation

$$E = \mathscr{K} + \mathscr{V} = \frac{1}{2}mv^2 + \mathscr{V}(x) \tag{15.2-3a}$$

which is the same as

$$m^2v^2 = 2m[E - \mathscr{V}(x)] \tag{15.2-3b}$$

where $\mathscr{K}$ is the kinetic energy, $\mathscr{V}$ is the potential energy, and E is the total energy. Use of Eq. (15.2-3b) in Eq. (15.2-2) gives the *time-independent Schrödinger equation* for de Broglie waves moving parallel to the x axis:

$$\frac{h^2}{8\pi^2 m}\frac{d^2\psi}{dx^2} + \mathscr{V}(x)\psi = E\psi \tag{15.2-4}$$

We introduce the symbol $\hbar$ ("h-bar"):

$$\hbar = \frac{h}{2\pi} \tag{15.2-5}$$

and rewrite the equation:

$$\boxed{-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \mathscr{V}(x)\psi = E\psi} \tag{15.2-6}$$

This equation is made to apply to a specific case by specifying the appropriate potential energy function.

Exercise 15.2

Carry out the algebra to obtain Eq. (15.2-6) from Eq. (15.2-2).

The left-hand side of Eq. (15.2-6) is commonly abbreviated by defining

$$\widehat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \mathscr{V}(x) \tag{15.2-7}$$

so that we abbreviate the Schrödinger equation in the form:

$$\boxed{\widehat{H}\psi = E\psi} \tag{15.2-8}$$

The symbol $\widehat{H}$ is a *mathematical operator*, because it stands for the carrying out of mathematical operations on the function ψ. It is called the *Hamiltonian operator*.

The Time-Dependent Schrödinger Equation

The time-dependent Schrödinger equation is taken as one of the *postulates* (fundamental assumptions) of quantum theory:

$$\boxed{\widehat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t}} \tag{15.2-9}$$

where i is the imaginary unit, defined to equal the square root of -1:

$$i = \sqrt{-1} \tag{15.2-10}$$

and where the $\widehat{H}$ operator is the same as in the time-independent equation. The function Ψ is the *time-dependent wave function* and represents the displacement of a de Broglie wave as a function of position and time. In this chapter and the next we will use a capital psi (Ψ) for a time-dependent wave function and a lower-case psi (ψ) for a coordinate factor (coordinate wave function).

There is no way to obtain the time-dependent Schrödinger equation from a classical wave equation. The classical wave equation of a vibrating string, Eq. (14.3-3), is second order in time. It requires two initial conditions (an initial position and an initial velocity) to make a general solution apply to a specific case. The uncertainty principle of quantum mechanics (to be discussed later) implies that positions and velocities cannot be specified simultaneously with arbitrary accuracy. For this reason only one initial condition is possible, which requires the Schrödinger equation to be first order in time. The fact that the equation is first order in time also requires that the imaginary unit i must occur in the equation in order for oscillatory solutions to exist.

The time-independent Schrödinger equation can be obtained from the time-dependent equation by separation of variables. For motion in the x direction, we assume the trial function

$$\Psi(x, t) = \psi(x)\eta(t) \tag{15.2-11}$$

We substitute (15.2-11) into Eq. (15.2-9) and divide by $\psi(x)\eta(t)$, obtaining

$$\frac{1}{\psi}\widehat{H}\psi = \frac{i\hbar}{\eta}\frac{d\eta}{dt} \tag{15.2-12}$$

The variables x and t are now separated. Since x and t are independent variables, each can be held fixed while the other varies. Each side of the equation must be a constant function of its argument and must be equal to the same constant, which we denote by E:

$$\frac{1}{\psi}\widehat{H}\psi = E \tag{15.2-13}$$

and

$$\frac{i\hbar}{\eta}\frac{d\eta}{dt} = E \tag{15.2-14}$$

Multiplication of the first equation by ψ and of the second equation by $\eta/i\hbar$ gives

$$\widehat{H}\psi = E\psi \tag{15.2-15}$$

and

$$\frac{d\eta}{dt} = \frac{E}{i\hbar}\eta = -\frac{iE}{\hbar}\eta \tag{15.2-16}$$

Equation (15.2-15) is the same as the time-independent Schrödinger equation, Eq. (15.2-8), so ψ is the coordinate wave function that satisfies that equation and E is the constant energy of the system.

Equation (15.2-16) has the solution

$$\eta(t) = Ce^{-iEt/\hbar} \tag{15.2-17}$$

where C is a constant. Since the Eq. (15.2-16) is satisfied for any value of C its value is unimportant. We let $C = 1$ and write the complete wave function as

$$\Psi(x,t) = \psi(x)e^{-iEt/\hbar} \tag{15.2-18}$$

We will see that a solution to the time-independent Schrödinger equation provides both a coordinate wave function ψ and an energy value E. We can immediately write a solution to the time-dependent equation by multiplying a coordinate wave function by the time factor $e^{-iEt/\hbar}$. This type of solution, with the coordinate and time dependence in separate factors, corresponds to a standing wave, because any nodes are stationary. There are also solutions of the time-dependent Schrödinger equation that are not products of a coordinate factor and a time factor. These solutions can correspond to traveling waves.

The coordinate wave function can in many cases be chosen to be a real function. The function η is always complex, and can be written as a real part plus an imaginary part by use of a mathematical identity (see Appendix B):

$$\eta(t) = e^{-iEt/\hbar} = \cos(-Et/\hbar) + i\sin(-Et/\hbar) = \cos(Et/\hbar) - i\sin(Et/\hbar) \tag{15.2-19}$$

In the final version of Eq. (15.2-19) we have used the fact that the cosine is an even function and the sine is an odd function. An *even function* has the property that $f(-x) = f(x)$, and an *odd function* has the property that $f(-x) = -f(x)$. Equation (15.2-19) makes it clear that we have an oscillatory solution. If the factor i had been omitted from the time-dependent Schrödinger equation, the time-dependent factor in the solution would have been

$$\eta(t) = e^{-Et/h} \quad \text{(not usable)} \tag{15.2-20}$$

which is clearly not oscillatory. The real part and the imaginary part oscillate with the same frequency, but out of phase (with their maximum values at different times). The real and imaginary parts of the complete wave function have stationary nodes in the same locations, since they combine with the same coordinate factor.

If we write Eq. (15.2-19) in the form

$$\eta(t) = \cos(2\pi Et/h) - i\sin(2\pi Et/h) \tag{15.2-21}$$

we can recognize the period as

$$\tau = \frac{h}{E} \tag{15.2-22}$$

and the frequency as

$$\nu = \frac{E}{h} \tag{15.2-23}$$

Notice the similarity of this relationship with the Planck–Einstein formula for the energy of a photon, Eq. (14.4-8):

$$E(\text{photon}) = h\nu \tag{15.2-24}$$

The Schrödinger Equation in Three Dimensions

For a single particle moving in three dimensions, the Hamiltonian operator is

$$\widehat{H} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \mathscr{V}(x, y, z) = -\frac{\hbar^2}{2m}\nabla^2 + \mathscr{V}(x, y, z) \tag{15.2-25}$$

The operator ∇^2 is called the *Laplacian operator*, introduced in Eq. (B-45) of Appendix B. In Cartesian coordinates

$$\nabla^2 = \partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2 \tag{15.2-26}$$

In Chapter 17 we will express the Hamiltonian operator in terms of spherical polar coordinates.

If a system consists of n particles moving in three dimensions, its Hamiltonian operator is

$$\widehat{H} = -\sum_{j=1}^{n} \frac{\hbar^2}{2m_j} \nabla_j^2 + \mathscr{V}(q) \tag{15.2-27}$$

where ∇_j^2 is the Laplacian operator for the coordinates of particle number j. The potential energy $\mathscr{V}$ is a function of all of the coordinates, which are abbreviated by the symbol q.

Once the Hamiltonian operator is obtained, the time-dependent Schrödinger equation is abbreviated as in Eq. (15.2-9):

$$\widehat{H}\Psi = i\hbar \frac{\partial \Psi}{\partial t} \tag{15.2-28}$$

where Ψ depends on all of the coordinates and on t. If we assume the trial solution

$$\Psi = \psi(x_1, y_1, z_1, \ldots, x_n, y_n, z_n)\eta(t) \tag{15.2-29}$$

then the time-independent Schrödinger equation can be extracted from the time-dependent equation in exactly the same way as in Eqs. (15.2-11) through (15.2-15).

Eigenvalue Equations

The time-independent Schrödinger equation belongs to a class of equations called *eigenvalue equations*. The word "eigenvalue" is a partial translation of the German word *Eigenwert*. A full translation is "characteristic value." An eigenvalue equation has on one side an operator operating on a function, and on the other side a constant called the *eigenvalue* multiplying the same function, which is called the *eigenfunction*. If $\widehat{A}$ is a mathematical operator, its eigenvalue equation is

$$\widehat{A} f_n = a_n f_n \tag{15.2-30}$$

where f_n is the eigenfunction and a_n is the eigenvalue. An eigenvalue equation generally has a set of solutions, so we have attached a subscript n to the eigenfunction and eigenvalue in Eq. (15.2-31) to specify a particular one of the solutions. Solving an eigenvalue equation means finding not only the set of eigenfunctions that satisfy the equation, but also the eigenvalue that belongs to each eigenfunction. Two common cases occur. The first case is that the eigenvalue can take on any value within some range of values (a *continuous spectrum* of eigenvalues). The second case is that there is a discrete set of eigenvalues with the values between the members of the set not permitted (a *discrete spectrum* of eigenvalues). The occurrence of a discrete spectrum of eigenvalues corresponds to quantization.

The time-independent Schrödinger equation is the eigenvalue equation for the Hamiltonian operator. The coordinate wave function is the eigenfunction of the Hamiltonian operator, and is often called the *energy eigenfunction*. The eigenvalue of the Hamiltonian operator, E, is the value of the energy, and is called the *energy eigenvalue*. There are other eigenvalue equations that are important in quantum mechanics, and we will discuss some of them later.

In addition to satisfying the Schrödinger equation a wave function must satisfy other conditions. Since it represents a wave, we assume that it has the following properties, which are generally shared by waves: (1) *the wave function is single-valued*, (2) *the wave function is continuous*, and (3) *the wave function is finite.* These properties will lead to boundary conditions that have important consequences, which we will illustrate in the next section for the simplest case, the particle in a box.

PROBLEMS

Section 15.2: The Schrödinger Equation

15.5 The Schrödinger equation does not determine the magnitude of the wave function.

- **a.** Show that if ψ is replaced by $C\psi$ where C is any constant, the time-independent Schrödinger equation is still satisfied.
- **b.** Show that if Ψ is replaced by $C\Psi$ where C is any constant, the time-dependent Schrödinger equation is still satisfied.

15.6 In classical mechanics, the addition of a constant to a potential energy has no physical effect. The same is true of quantum mechanics.

- **a.** Show that if the potential energy $\mathcal{V}$ is replaced by $\mathcal{V} + \mathcal{V}_0$, where $\mathcal{V}_0$ is a constant, the same wave function satisfies the time-independent Schrödinger equation but the energy eigenvalue is now $E + \mathcal{V}_0$, where E is the original energy eigenvalue.
- **b.** What is the effect on the solution of the time-dependent Schrödinger equation of adding a constant to the potential energy?

15.7 If the potential energy $\mathcal{V}$ in the n-particle Hamiltonian of Eq. (15.2-27) is equal to zero, show that the product wave function

$$\psi_{\text{system}} = \psi_1(x_1, y_1, z_1)\psi_2(x_2, y_2, z_2)\psi_3(x_3, y_3, z_3)\cdots \psi_n(x_n, y_n, z_n)$$

satisfies the time-independent Schrödinger equation of the system.

15.3 The Particle in a Box and the Free Particle

In this section we solve the time-independent Schrödinger equation for the two simplest model systems: the particle in a box and the free particle. This analysis will show how the wave function and the values of the energy are determined by the Schrödinger equation and the three conditions obeyed by the wave function.

The Particle in a One-Dimensional Box

The particle in a one-dimensional box is a model system that consists of a single particle that can move parallel to the x axis. The particle moves without friction, but is confined to a finite segment of the x axis, from $x = 0$ to $x = a$. This interval is called a one-dimensional box, but could also be called a *potential well*. This model system could represent a particle sliding in a frictionless tube with closed ends or a bead sliding on a frictionless wire between barriers. One chemical system that is approximately represented by this model is a pi electron moving in a conjugated system of single and double bonds. We will discuss this application in a later chapter.

We construct the Schrödinger equation for a particular system by inserting the appropriate potential energy function for the system into the equation. Since our particle experiences no force inside the box, its potential energy is constant inside the box, and we choose the value zero for this constant. In order to represent complete confinement within the box we specify that the potential energy outside the box approaches a positive infinite value.

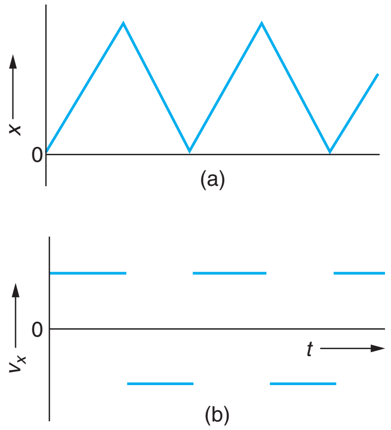

Figure 15.3 Mechanical Variables of a Particle in a One-Dimensional Box. (a) The position according to classical mechanics. (b) The velocity according to classical mechanics.

According to classical mechanics, the particle would move back and forth at constant speed inside the box, reversing direction as it elastically collides with the ends of the box. Figure 15.3a shows the position of the particle as a function of time according to classical mechanics, and Figure 15.3b shows the velocity of the particle as a function of time. Quantum mechanics predicts a very different behavior.

The time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}d^2\psi/dx^2 + \mathscr{V}(x)\psi(x) = E\psi(x) \tag{15.3-1}$$

where $\mathscr{V}(x)$ is the potential energy function. We divide the x axis into three regions and solve separately in each region:

Region I: $x < 0$
Region II: $0 \le x \le a$
Region III: $a < x$

We require that ψ is finite and that it is continuous everywhere, including the boundaries between the regions.

In regions I and III the potential energy approaches an infinite value, so the Schrödinger equation is

$$\frac{d^2\psi}{dx^2} - \lim_{\mathscr{V}\to\infty}\frac{2m\mathscr{V}}{\hbar^2}\psi = -\frac{2mE}{\hbar^2}\psi \tag{15.3-2}$$

We require that ψ is finite, and we assume that E is finite, so the right-hand side of this equation is finite. Since $\mathscr{V}$ approaches an infinite value, the left-hand side would be infinite unless ψ vanishes, so the solution in regions I and III must be

$$\psi^{(\mathrm{I})}(x) = \psi^{(\mathrm{III})}(x) = 0 \tag{15.3-3}$$

For region II (inside the box) the Schrödinger equation is

$$\frac{d^2\psi^{(\mathrm{II})}}{dx^2} = -\kappa^2\psi^{(\mathrm{II})} \tag{15.3-4}$$

where

$$\kappa^2 = \frac{2mE}{\hbar^2} \tag{15.3-5}$$

Equation (15.3-4) is of the same form as Eq. (14.3-10). Its general solution is

$$\psi^{(\mathrm{II})}(x) = B\cos(\kappa x) + C\sin(\kappa x) \tag{15.3-6}$$

We must now make our solution conform to the continuity condition. In order for ψ to be continuous at $x = 0$ and $x = a$, we must require that

$$\psi^{(\mathrm{II})}(0) = \psi^{(\mathrm{I})}(0) = 0; \quad \psi^{(\mathrm{II})}(a) = \psi^{(\mathrm{III})}(a) = 0 \tag{15.3-7}$$

These conditions are similar to the boundary conditions for the vibrations of a string in Section 14.3. In order for $\psi^{(\mathrm{II})}(0)$ to vanish, the constant B must vanish, because $\cos(0) = 1$. The coordinate wave function (energy eigenfunction) for region II is now

$$\psi^{(\mathrm{II})}(x) = C\sin(\kappa x) \tag{15.3-8}$$

The continuity condition has another consequence. The condition that $\psi^{(\mathrm{II})}(a) = 0$ imposes a condition on κ, as in Eq. (14.3-14). The sine function vanishes when its argument is an integral multiple of π, so that the quantity κ can take on the values given by

$$n\pi = \kappa a \quad \text{or} \quad \kappa = n\pi/a \tag{15.3-9}$$

where n is a quantum number that can take on integral values. The energy eigenfunctions inside the box are now given by:

$$\psi_n(x) = C\sin(n\pi x/a) \tag{15.3-10}$$

where we omit the superscript (II). We do not allow $n = 0$, since this would correspond to $\psi = 0$ and the absence of any wave. If there is no wave there is no particle. We also ignore negative values of n, since the sine function is an odd function and replacing n by $-n$ would simply change the sign of the function, corresponding to replacement of C by $-C$. The value of C is unimportant for our present purposes since the Schrödinger equation is satisfied for any value of C and since the energy eigenvalues do not depend on C.

The energy eigenvalues are quantized, with values determined by the value of n:

$$E = E_n = \frac{\hbar^2\kappa^2}{2m} = \frac{\hbar^2 n^2\pi^2}{2ma^2} = \frac{h^2 n^2}{8ma^2} \tag{15.3-11}$$

The quantization of the energy comes from the Schrödinger equation and from the boundary conditions.

Figure 15.4a represents the energy eigenvalues of a particle in a one-dimensional box by horizontal line segments at heights proportional to their energy values, and Figure 15.4b shows the energy eigenfunctions. Each wave function is plotted on an axis that is placed at a height corresponding to its energy eigenvalue. Note that the wave functions in Figure 15.4b resemble the standing waves in Figure 14.7.

The energy in Eq. (15.3-11) is all kinetic energy, since we set the potential energy inside the box equal to zero. Since we do not allow $n = 0$, the minimum possible kinetic energy is equal to $h^2/8ma^2$, corresponding to $n = 1$. This minimum energy is positive and is called the *zero-point energy*. It is not possible for the particle in a box to have zero kinetic energy. This result is very different from that of classical mechanics, which always allows a particle to be at rest.

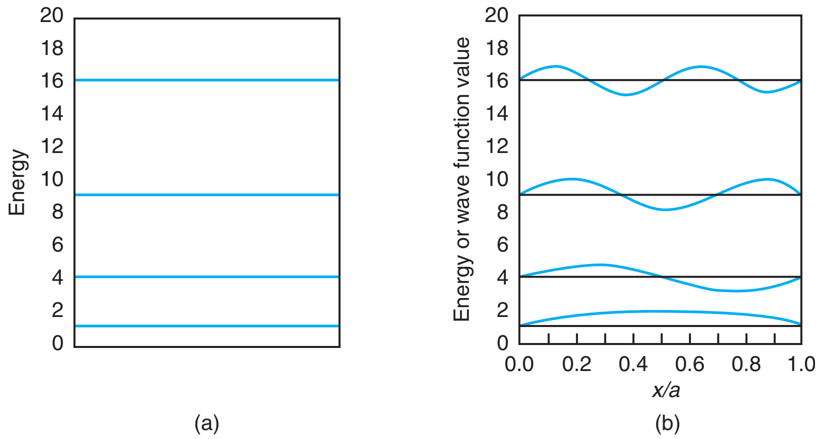

Figure 15.4 The Solutions to the Schrödinger Equation for a Particle in a One-Dimensional Box. (a) The energy eigenvalues. (b) The energy eigenfunctions.

EXAMPLE 15.2

Find the zero-point energy of an electron in a box of length 1.000 nm, roughly equal to the length of a 1,3-butadiene molecule.

Solution

$$E = \frac{(6.6261 \times 10^{-34}\ \mathrm{J\ s})^2(1)^2}{(8)(14.109 \times 10^{-31}\ \mathrm{kg})(1.000 \times 10^{-9}\ \mathrm{m})^2} = 6.025 \times 10^{-20}\ \mathrm{J}$$

Exercise 15.3

How does the energy for a given value of n change if the length of the box is doubled? How does it change if the mass of the particle is doubled?

The Schrödinger Equation and De Broglie Waves

The particle in a box model provides an illustration of the fact that the energy eigenfunction represents de Broglie waves. In the case of zero potential energy

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} \tag{15.3-12}$$

where we use the definition of the momentum, $\mathbf{p} = m\mathbf{v}$. From the de Broglie wavelength formula in Eq. (15.1-3) and Eq. (15.3-12)

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}} \tag{15.3-13}$$

which is the same as

$$E = h^2/2m\lambda^2 \tag{15.3-14}$$

The energy of a de Broglie wave is inversely proportional to the square of its wavelength. The wavelength of the wave function is the value of x such that the argument of the sine function in Eq. (15.3-10) equals 2π.

$$n\pi\lambda/a = 2\pi$$

or

$$\lambda = 2a/n \tag{15.3-15}$$

which is analogous to Eq. (14.2-20). When the relationship between the wavelength and the length of the box is used, the relation in Eq. (15.3-14) becomes the same as the energy expression in Eq. (15.3-11).

Exercise 15.4

a. Show that the value of the wavelength corresponding to ψ_n is equal to $2a/n$.

b. Show that the same formula for the energy as in Eq. (15.3-11) is obtained by substituting the result of part a into Eq. (15.3-14).

As the value of n increases, the energy increases, the wavelength decreases and the number of nodes increases. *It is an important general fact that a wave function with more nodes corresponds to a higher energy.*

If the potential energy inside the box is assigned a nonzero constant value $\mathcal{V}_0$ instead of zero, the energy eigenfunction is unchanged and the energy eigenvalue is increased by $\mathcal{V}_0$.

Exercise 15.5

Carry out the solution of the time-independent Schrödinger equation for the particle in a one-dimensional box with constant potential $\mathcal{V}_0$ in the box. Show that the energy eigenvalue is

$$E_n = \frac{h^2n^2}{8ma^2} + \mathcal{V}_0 \tag{15.3-16}$$

but that the wave function is unchanged.

The result of the previous exercise is generally true. Adding a constant to the potential energy adds the same constant to the energy eigenvalues but leaves the wave function unchanged.

If a particle in a box is electrically charged, it can absorb or emit photons. Because of the conservation of energy, the energy of a photon that is emitted or absorbed is equal to the difference in energy of the initial and final states of the particle.

Exercise 15.6

a. Calculate the wavelength and frequency of the photon emitted if an electron in a one-dimensional box of length 1.00 nm (1.00×10^{-9} m) makes a transition from $n = 3$ to $n = 2$ and the energy difference is entirely converted into the energy of the photon.

b. Obtain formulas for the wavelength and the frequency of the photon emitted if an electron in a one-dimensional box of length 1.000×10^{-9} m makes a transition from $n + 1$ to n and the energy difference is entirely converted into the energy of the photon.

The Time-Dependent Wave Function for a Particle in a Box

Equation (15.2) can be used to obtain the time-dependent wave function for a particle in a one-dimensional box:

$$\begin{aligned}\Psi_n(x,t) &= C\sin\left(\frac{n\pi x}{a}\right)e^{-iE_nt/\hbar}\\ &= C\sin\left(\frac{n\pi x}{a}\right)\big(\cos(E_nt/\hbar) - i\sin(E_nt/\hbar)\big)\end{aligned} \tag{15.3-17}$$

where we use the fact that the cosine is an even function ($\cos(-\alpha) = \cos(\alpha)$) and that the sine is an odd function ($\sin(-\alpha) = -\sin(\alpha)$).

The period τ of an oscillation is the time required for the argument of the sine or cosine function in the time factor to change by 2π.

$$E_nt/\hbar = 2\pi$$

$$\tau = 2\pi\hbar/E_n = h/E_n = 8ma^2/hn^2 \tag{15.3-18}$$

The frequency is

$$v = 1/\tau = E_n/h = hn^2/8ma^2 \tag{15.3-19}$$

Although the coordinate wave functions for the classical vibrating string and the particle in a box are identical, the time-dependent wave functions are not. The frequency of a vibrating string was proportional to n. The frequency of the de Broglie wave given in Eq. (15.3-19) is proportional to n^2. However, the frequency of a de Broglie wave is not physically meaningful. It can have a constant added to it by adding a constant to the potential energy, as seen in the following exercise.

Exercise 15.7

a. Calculate the frequency of the de Broglie wave for the $n = 2$ and $n = 3$ states of an electron in a box of length 1.000 nm. What happens to these frequencies if a constant $\mathcal{V}_0$ is added to the potential energy in the box?

b. Calculate the difference between these frequencies. What happens to the difference between these frequencies if a constant $\mathcal{V}_0$ is added to the potential energy in the box?

c. Compare these frequencies and their difference with the photon frequency in Exercise 15.6a. Do you think there is any simple relationship between these frequencies?

Specification of the State of a Particle in a Box

Instead of specifying the position and velocity of the particle, the state of the quantum-mechanical particle is specified by saying what the wave function of the particle is. We frequently say that a wave function is occupied by a system. There is a wave function for each state and a state for each wave function. We say that there is a *one-to-one correspondence* between a state and a wave function, and we will sometimes use the terms “state,” “state function,” and “wave function” interchangeably.

There are two general classes of wave functions:

1. The wave function of the system is known to be an energy eigenfunction times the appropriate time-dependent factor as in Eq. (15.3-17). The wave function in this case corresponds to a standing wave. Chemists are usually interested in this case.

For example, when a photon is absorbed or emitted by a molecule, the initial and final molecule states correspond to energy eigenfunctions.

2. The wave function is some function other than a product of an energy eigenfunction and a time-dependent factor. The wave function is not proportional to a factor that obeys the time-independent Schrödinger equation, but it must still obey the time-dependent Schrödinger equation.

EXAMPLE 15.3

Show that the following linear combination obeys the time-dependent Schrödinger equation:

$$\Psi(x,t) = \sum_{n=1}^{\infty} A_n \psi_n(x) e^{-iE_n t/\hbar} \qquad (15.3\text{-}20)$$

where $A_1, A_2, \ldots$ are a set of constants and where $\psi_1, \psi_2, \ldots$ represent energy eigenfunctions of the system.

Solution

$$\widehat{H}\Psi = \widehat{H}\sum_{n=1}^{\infty} A_n \psi_n e^{-iE_n t/\hbar} = \sum_{n=1}^{\infty} A_n E_n \psi_n e^{-iE_n t/\hbar}$$

$$i\hbar\left(\frac{\partial\Psi}{\partial t}\right) = i\hbar\left(\frac{\partial}{\partial t}\right)\sum_{n=1}^{\infty} A_n \psi_n e^{-iE_n t/\hbar} = \sum_{n=1}^{\infty} A_n E_n \psi_n e^{-iE_n t/\hbar}$$

It is apparent that Ψ does not obey the time-independent Schrödinger equation, since $\widehat{H}\Psi$ does not equal a single constant times Ψ.

Equation (15.3-20) expresses the *principle of superposition*, which means that an arbitrary wave function can be represented by a linear combination of energy eigenfunctions.

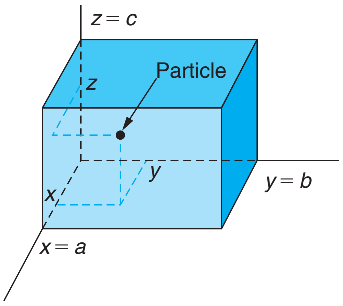

Figure 15.5 A Particle in a Three-Dimensional Box.

The Particle in a Three-Dimensional Box

The principal application of this model system is to represent the translational motion of a gas molecule, and we will discuss this application in Chapters 22 and 26. We assume our three-dimensional box is rectangular and we place the box with its lower left rear corner at the origin of coordinates and its walls perpendicular to the coordinate axes, as depicted in Figure 15.5. We denote the length of the box in the x direction by a, the length in the y direction by b, and the length in the z direction by c.

If the particle is completely confined in the box the potential energy is equal to a constant inside the box and is infinite outside the box. We set the constant equal to zero. The resulting time-independent Schrödinger equation can be solved by separation of variables, as described in Appendix F. The energy eigenfunction (coordinate wave function) is a product of three factors, each one of which is the same as a wave function for a particle in a one-dimensional box of length a, b, or c:

$$\psi_{n_x n_y n_z}(x,y,z) = C\sin\left(\frac{n_x \pi x}{a}\right)\sin\left(\frac{n_y \pi y}{b}\right)\sin\left(\frac{n_z \pi z}{c}\right) \qquad (15.3\text{-}21)$$

where C is a constant and where the quantum numbers n_x, n_y, and n_z are positive integers, not necessarily equal to each other. The energy eigenvalue is the sum of three terms, each of which is an energy eigenvalue for a particle in a one-dimensional box.

$$\boxed{E_{n_z n_y n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)} \tag{15.3-22}$$

A particular energy state is specified by giving the values of the three quantum numbers, which we write in *xyz* order inside parentheses, as for example (1,2,3).

If $a = b = c$ (a cubical box) the energy eigenvalue is

$$E_{n_z n_y n_z} = \frac{h^2}{8ma^2}\left(n_x^2 + n_y^2 + n_z^2\right) \tag{15.3-23}$$

For a cubical box there can be several states that correspond to the same energy eigenvalue. A set of states with the same energy eigenvalue is called an *energy level*, and the number of states making up the energy level is called the *degeneracy* of the level. The lowest-energy state ("the ground state") of this system is *nondegenerate*, because only one state corresponds to its energy eigenvalue.

EXAMPLE 15.4

For an electron in a cubical box of side 1.00×10^{-9} m, find the energy eigenvalue and the degeneracy of the level in which the state corresponding to (1,2,3) occurs.

Solution

The energy eigenvalue is

$$E_{123} = \frac{14h^2}{8ma^2} = \frac{(14)(6.6261 \times 10^{-34}\ \mathrm{J\ s})^2}{(8)(9.109 \times 10^{-31}\ \mathrm{kg})(1.00 \times 10^{-9}\ \mathrm{m})^2}$$
$$= 8.43 \times 10^{-19}\ \mathrm{J}$$

There are six permutations (different orders) of the three distinct numbers: (1,2,3), (2,3,1), (3,1,2), (3,2,1), (1,3,2), and (2,1,3), each of which corresponds to a different state. The degeneracy is 6.

Exercise 15.8

a. For an electron in the cubical box of Example 15.4 find the energy eigenvalues and degeneracies of all energy levels of lower energy than that in Example 15.4. Express the energies as E divided by $h^2/8ma^2$.

b. A certain box is a by a by $4a$. Find the energy levels and degeneracies (if any) for states up to the energy corresponding to (3,3,3). Express the energies as E divided by $h^2/8ma^2$.

The Free Particle in One Dimension

A free particle has no forces acting on it and can move in all of space. The potential energy of the particle is equal to a constant, which we set equal to zero. If a free particle of mass m can move only parallel to the x axis, the time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \tag{15.3-24}$$

or

$$d^2\psi/dx^2 = -\kappa^2\psi \tag{15.3-25}$$

Equation (15.3-24) is the same as Eq. (15.3-4) for the motion of a particle in a box. The general solution to Eq. (15.3-25) is the same as that in Eq. (15.3-6), but it can also be written in a way analogous to Eq. (14.2-22):

$$\psi(x) = De^{i\kappa x} + Fe^{-i\kappa x} \tag{15.3-26}$$

Although the general solution to the Schrödinger equation is the same as for the particle in a box, the boundary conditions are different. The wave function must be continuous and finite, but there are now no walls at which the wave function must vanish. The finiteness condition requires that κ be real. To show this we let

$$\kappa = a + ib \tag{15.3-27}$$

where a and b are real. The solution is now

$$\psi(x) = De^{iax}e^{-bx} + Fe^{-iax}e^{bx} \tag{15.3-28}$$

If b is positive the second term grows without bound for large positive values of x. If b is negative the first term grows without bound if x becomes large and negative. To keep the wave function finite for all values of x, b must vanish and κ must be real.

The energy eigenvalues are given by Eq. (15.3-5):

$$E = \hbar^2\kappa^2/2m \tag{15.3-29}$$

There is no restriction on the values of the parameter κ except that it must be real. The energy eigenvalue E, which is equal to the kinetic energy, can take on any real non-negative value. The energy is not quantized and there is no zero-point energy.

If F vanishes, the time-dependent wave function is

$$\Psi(x,t) = De^{i\kappa x - iEt/\hbar} = De^{i(\kappa x - Et/\hbar)} \tag{15.3-30}$$

where E is given by Eq. (15.3-29). Separating the real and imaginary parts of Ψ by use of the identity

$$e^{i\alpha} = \cos(\alpha) + i\sin(\alpha) \tag{15.3-31}$$

we obtain

$$\psi(x,t) = D\left[\cos\left(\kappa x - \frac{Et}{\hbar}\right) + i\sin\left(\kappa x - \frac{Et}{\hbar}\right)\right] \tag{15.3-32}$$

Comparison of this with Eq. (14.3-26) shows both the real and imaginary parts to be traveling waves moving to the right with a speed given by

$$c = E/\kappa\hbar = \hbar\kappa/2m \tag{15.3-33}$$

and a frequency given by

$$\nu = \frac{2\pi E}{\hbar} = \frac{E}{h} = \frac{\hbar\kappa^2}{4\pi^2 m} = \frac{h\kappa^2}{2\pi m} \tag{15.3-34}$$

A nonzero value of the constant F corresponds to a traveling wave moving to the left.

If D and F are equal, the two traveling waves interfere to produce a standing wave:

$$\psi(x) = D(e^{i\kappa x} + e^{-i\kappa x}) = 2D\cos(\kappa x) \tag{15.3-35}$$

which follows from the identity

$$\cos(\alpha) = \frac{1}{2}\left(e^{i\alpha} + e^{-i\alpha}\right) \tag{15.3-36}$$

The time-dependent wave function corresponding to Eq. (15.3-35) is

$$\Psi(x,t) = 2D\cos(\kappa x)e^{-iEt/\hbar} \tag{15.3-37}$$

If $D = -F$, a different standing wave results.

If the constants D and F are not equal to each other the complete wave function is

$$\Psi(x,t) = De^{i(\kappa x - Et/\hbar)} + Fe^{-i(\kappa x + Et/\hbar)} \tag{15.3-38}$$

which represents a combination of traveling waves, one moving to the right and one moving to the left. A single wave function corresponds to motion in two different directions. This behavior is rather different from that found in classical mechanics, in which one state always corresponds to only one kind of behavior. The idea that a single particle can have a single state corresponding to motion in two different directions at the same time seems unreasonable, but it is permitted in quantum mechanics. A possible interpretation is that since some predictions of quantum mechanics are statistical in nature, a wave function should be thought of as representing the behavior of a large collection (an ensemble) of objects, all in the same state but capable of different outcomes of a particular measurement. We will return to this question in the next chapter.

The Free Particle in Three Dimensions

The time-independent Schrödinger equation for a free particle moving in three dimensions is

$$\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) = -\frac{2mE}{\hbar^2}\psi \tag{15.3-39}$$

This is the same as for a particle inside a three-dimensional box, and it can be solved in the same way by separation of variables. Each factor in the solution can be written either in the form of Eq. (15.3-6) or in the form of Eq. (15.3-26), with κ replaced by κ_x, κ_y, or κ_z. For the special case of a traveling wave with definite values of κ_x, κ_y, and κ_z, we can write a one-term energy eigenfunction as

$$\psi(x,y,z) = De^{i\kappa_x x}e^{i\kappa_y y}e^{i\kappa_z z} \tag{15.3-40}$$

The vector $\boldsymbol{\kappa}$ with components κ_x, κ_y, and κ_z points in the direction in which the traveling wave moves and is called the *wave vector*.

The energy eigenvalue is given by the sum of three terms:

$$E = E_x + E_y + E_z = \frac{\hbar^2}{2m}(\kappa_x^2 + \kappa_y^2 + \kappa_z^2) = \frac{\hbar^2\kappa^2}{2m} \tag{15.3-41}$$

where κ^2 is the square of the magnitude of the wave vector. As in the one-dimensional case the energy is not quantized and there is no zero-point energy.

Just as Eq. (15.3-38) represents a linear combination of waves moving in opposite directions, a wave eigenfunction for a three-dimensional free particle can consist of a superposition (linear combination) of waves moving in various directions with various energies:

$$\psi(x, y, z) = \sum_{\kappa_x} \sum_{\kappa_y} \sum_{\kappa_z} D_{\kappa_x,\kappa_y,\kappa_z} e^{i\kappa_x x} e^{i\kappa_y y} e^{i\kappa_z z} \qquad (15.3\text{-}42)$$

where $\mathrm{D}_{\kappa_x,\kappa_y,\kappa_z}$ represents a constant coefficient. If the particle has a definite energy but not a definite direction, the sums over different values of κ_x, κ_y, and κ_z are constrained so that all wave vectors in the sum have the same magnitude.

The solutions to the Schrödinger equation for the particle in a box and the free particle exhibit some of the most important features of quantum mechanics. We have seen one case of quantized energy (the particle in a box) and one case of energy that is not quantized (the free particle). We have seen that the Schrödinger equation and its boundary conditions together dictate the nature of the wave functions and energy eigenvalues that can occur. We have also seen that the principle of superposition applies: A valid wave function can be a linear combination of simpler wave functions.

PROBLEMS

Section 15.3: The Particle in a Box and the Free Particle

15.8 Derive a formula for the kinetic energy of a particle with de Broglie wavelength equal to $2a/n$ and show that this is the same as the energy of a particle in a one-dimensional box of length a with quantum number n.

15.9 The particle in a one-dimensional box is sometimes used as a model for the electrons in a conjugated π-bond system (alternating double and single bonds).

a. Find the first three energy levels for a π electron in 1,3-butadiene. Assume a carbon–carbon bond length of 1.39×10^{-10} m and assume that the box consists of the three carbon–carbon bonds plus an additional length of 1.39×10^{-10} m at each end.

b. The molecule has four π electrons. Assume that two are in the state corresponding to $n = 1$, and that two are in the state corresponding to $n = 2$. Find the frequency and wavelength of the light absorbed if an electron makes a transition from $n = 2$ to $n = 3$.

15.10 The particle in a one-dimensional box is sometimes used as a model for the electrons in a conjugated π-bond system (alternating double and single bonds).

a. Find the first three energy levels for a π electron in 1,3,5-hexatriene. Assume a carbon–carbon bond length of 1.39×10^{-10} m and assume that the box consists of the five carbon–carbon bonds plus an additional length of 1.39×10^{-10} m at each end.

b. The molecule has six π electrons. Assume that two are in the state corresponding to $n = 1$, two are in the state corresponding to $n = 2$, and that two are in the state corresponding to $n = 3$. Find the frequency and wavelength of the light absorbed if an electron makes a transition from $n = 3$ to $n = 4$.

15.11 **a.** Sketch a graph of the product of ψ_1 and ψ_2, the first two energy eigenfunctions of a particle in a one-dimensional box. Argue from the graph that the two functions are *orthogonal*, which means for real functions that

$$\int_{-\infty}^{\infty} \psi_1(x)\psi_2(x)dx = 0$$

b. Work out the integral and show that ψ_1 and ψ_2 are orthogonal. Remember that $\psi = 0$ outside of the box, so that the integral extends only from $x = 0$ to $x = a$.

15.12 **a.** Sketch a graph of the product of ψ_2 and ψ_3, two energy eigenfunctions of a particle in a one-dimensional box. Argue from the graph that the two functions are orthogonal, which means for real functions that

$$\int_{-\infty}^{\infty} \psi_2(x)\psi_3(x)dx = 0$$

b. Work out the integral and show that ψ_2 and ψ_3 are orthogonal. Remember that $\psi = 0$ outside of the box.

15.13 Think of a baseball on its way from the pitcher's mound to home plate as being a particle in a box of length 60 feet. Assume that the baseball has a mass of 5.1 ounces. If the baseball has a speed of 95 miles per hour, find its kinetic energy and the value of the quantum number n corresponding to this value of E. Find the number of nodes in the wave function and find the wavelength corresponding to this many nodes in a length of 60 feet. Compare this wavelength with the de Broglie wavelength in Example 15.1.

15.14 Assume that a sample of helium has been trapped in a matrix of solid argon at 84 K, and that each helium atom is confined in a cavity such that the center of mass of the helium atom can move ("translate") in a cubical region 5.00×10^{-10} m on a side.

a. Find the energies and degeneracies of the two lowest-energy translational levels.

b. Find the frequency and wavelength of a photon absorbed in a transition between the two levels of part a. Do you think that such a transition would actually be observed spectroscopically?

15.15 An electron is confined in a cubical box 10.0 Å(1.00×10^{-9} m) in length, width, and height.

a. Find the energy eigenvalues of the first two energy levels.

b. Find the degeneracies of the first two energy levels.

c. Find the frequency and wavelength of the light absorbed if the electron makes a transition from the lowest energy level to the next lowest energy level.

d. How do this frequency and this wavelength compare with the corresponding quantities if the particle were in a one-dimensional box of length 10.0?

15.16 Assume that an argon atom can be represented as a particle in a three-dimensional box with height, width, and length all equal to 0.100 m. Assume that the argon atom has an energy equal to $3k_BT/2$ where k_B is Boltzmann's constant and where T is the absolute temperature, assumed to be equal to 298.15 K. Find the value of n_x, n_y, and n_z, assumed equal each other.

15.17 Consider a crude model representing a benzene molecule as a three-dimensional rectangular box with dimensions 3.5 Å by 3.5 Å by 1.25 Å (350 pm by 350 pm by 125 pm). Include only the six π electrons, which are assumed to move in the entire box, and let them occupy the three lowest energy states with paired spins. Find the wavelength of the photon absorbed when an electron makes a transition from the highest occupied state to the lowest unoccupied state. Compare it with the wavelength of the actual transition, 180 nm.

15.18 Consider a model representing the pi electrons of a benzene molecule as electrons moving around a ring of circumference L equal to 8.35 Å (8.35×10^{-10} m) with a constant potential energy set equal to zero. The Schrödinger equation is like that of a particle in a box, except the wave function ψ is a function of x, the distance around the ring from an initial point. The boundary condition is that $\psi(0) = \psi(L)$.

a. Show that an acceptable wave function is $A\sin(2n\pi x/L) + B\cos(2n\pi x/L)$ where n is an integer.

b. Show that another acceptable wave function is $C\exp(2n\pi ix/L)$.

c. Show that the energy eigenvalue is $E_n = (h^2/2mL^2)n^2$.

d. The molecule has six pi electrons. Assume that two occupy the $n = 0$ state, two occupy the $n = 1$ state, and that two occupy the $n = -1$ state. Find the wavelength of the photon absorbed when an electron makes a transition from $n = 2$ to $n = 3$. Compare it with the wavelength of the actual transition, 180 nm.

15.4 The Quantum Harmonic Oscillator

In Chapter 14, we solved the classical equation of motion for a harmonic oscillator. We now solve the time-independent Schrödinger equation for this model system. The Hamiltonian operator must contain the potential energy expression from

Eq. (14.2-32). If we set the constant $\mathcal{V}_0$ equal to zero, the time-independent Schrödinger equation is

$$\widehat{H}\psi = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \frac{1}{2}kx^2\psi = E\psi \qquad (15.4\text{-}1)$$

We define the constants

$$b = \frac{2mE}{\hbar^2}, \qquad a = \frac{\sqrt{km}}{\hbar} \qquad (15.4\text{-}2)$$

so that the Schrödinger equation can be written

$$d^2\psi/dx^2 + (b - a^2x^2)\psi = 0 \qquad (15.4\text{-}3)$$

The Hermite equation is named for Charles Hermite, 1822–1901, a great French mathematician who made many contributions to mathematics, including the proof that e (2.71828...) is a transcendental irrational number.

This differential equation is the same as a famous equation known as the *Hermite equation* (see Appendix F). Hermite solved this equation by assuming that the solution was of the form

$$\psi(x) = e^{-ax^2/2}S(x) \qquad (15.4\text{-}4)$$

where $S(x)$ is a power series

$$S(x) = c_0 + c_1x + c_2x^2 + c_3x^3 + \ldots = \sum_{n=0}^{\infty} c_nx^n \qquad (15.4\text{-}5)$$

with constant coefficients $c_1, c_2, c_3, \ldots$ When Eqs. (15.4-4) and (15.4-5) are substituted into the Hermite equation and the exponential factor is canceled, an equation with power series on both sides results. If two power series are equal to each other for all values of the independent variable, the coefficients of the same power in the two series must be equal to each other. From this fact Hermite obtained the relation

$$c_{n+2} = \frac{2an + a - b}{(n+2)(n+1)}c_n \quad (n = 0, 1, 2, \ldots) \qquad (15.4\text{-}6)$$

Exercise 15.9

Assume that the following equation is valid for any value of x:

$$a_0 + a_1x + a_2x^2 + \ldots = b_0 + b_1x + b_2x^2 + \ldots$$

Show that $a_0 = b_0$ by letting $x = 0$. Differentiate both sides of the equation with respect to x, and show that $a_1 = b_1$ by letting $x = 0$ in the formula for the derivative. Continue to show that $a_n = b_n$ for any value of n.

Equation (15.4-6) is called a *recursion relation.* Given a value of c_n, it provides a value for c_{n+2}. If we pick any value for c_0 and any other value for c_1 and let the recursion relation pick the other values, then Eq. (15.4-4) gives a solution to the Schrödinger equation.

We must now apply the appropriate boundary conditions to our solution. The solution must be finite all values of x, including very large values of $|x|$. If the series is permitted to have infinitely many terms, it is found that the series becomes large very rapidly for large values of $|x|$ and the wave function fails to remain finite.[5] Therefore, the series cannot have infinitely many terms. It must be a polynomial.

We cannot simply require all coefficients past a certain point in the series to vanish if this violates the recursion relation. The function would then fail to satisfy the Hermite equation. Let us assume that c_{v+2} is a vanishing coefficient and that c_v does not vanish. The numerator in the right-hand side of Eq. (15.4-6) must then vanish for $n = v$:

$$2av + a - b = 2av + a - 2mE/\hbar^2 = 2a(v + 1/2) - 2mE/\hbar^2 = 0 \qquad (15.4\text{-}7)$$

We can solve this equation for the energy eigenvalues:

$$E = E_v = \frac{\hbar^2}{2m}2a\left(v + \frac{1}{2}\right) = \frac{h}{2\pi}\sqrt{\frac{k}{m}}\left(v + \frac{1}{2}\right) = h\nu_{\text{class}}\left(v + \frac{1}{2}\right) \qquad (15.4\text{-}8)$$

where ν_{class} is the frequency of the oscillator as predicted by classical mechanics, given in Eq. (14.2-29), and where the quantum number ν equals 0, 1, 2, 3, and so on. The energy is quantized and there is a zero-point energy:

$$E_0 = \frac{1}{2}h\nu_{\text{class}} \quad \text{(zero-point energy)} \qquad (15.4\text{-}9)$$

The recursion relation relates the coefficients of even powers to each other, and the coefficients of the odd powers to each other. Since there is only one recursion relation, each polynomial can contain only even powers or only odd powers. If the power series contained both even and odd powers, the recursion relation would cause only the even powers to terminate or the odd powers to terminate, and the other powers would not terminate, violating the finiteness condition. The series in our solution now represents a polynomial that contains only even powers of x or only odd powers of x. These polynomials are called *Hermite polynomials*.

In the case of the particle in a box, the quantization was produced by the condition that the wave function must be continuous at the ends of the box. In the case of the harmonic oscillator, the energy quantization is produced by the condition that the wave function must be finite for all values of x, which causes the series to terminate.

EXAMPLE 15.5

If a harmonic oscillator has an electric charge, it can absorb or emit electromagnetic radiation.

a. Find a formula for the frequency of a photon with energy equal to the difference in energy between the $v = 0$ state and the $v = 1$ state.

b. How does the frequency of the photon compare with the classical frequency of the oscillator? How do you interpret this comparison?

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[5] This assertion is not obvious. See I. N. Levine, *Quantum Chemistry*, 5th ed., Prentice-Hall, Englewood Cliffs, NJ, 2000, pp. 67–68.

Solution

a.

$$\Delta E = E_2 - E_1 = \frac{3}{2}h\nu - \frac{1}{2}h\nu = h\nu = \frac{h}{2\pi}\sqrt{\frac{k}{m}}$$

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

b. The frequency of the photon is identical with the classical frequency of the oscillator. In the classical picture, if an oscillator is charged, it will emit or absorb electromagnetic radiation with the same frequency as its frequency of oscillation, so that this result seems to correspond with the classical picture.

The first few energy eigenfunctions of the harmonic oscillator are

$$\psi_0 = S_0 e^{-ax^2/2} = c_0 e^{-ax^2/2} = \left(\frac{a}{\pi}\right)^{1/4} e^{-ax^2/2} \tag{15.4-10}$$

$$\psi_1 = \left(\frac{4a^3}{\pi}\right)^{1/4} x\, e^{-ax^2/2} \tag{15.4-11}$$

$$\psi_2 = \left(\frac{a}{4\pi}\right)^{1/4} (2ax^2 - 1)e^{-ax^2/2} \tag{15.4-12}$$

$$\psi_3 = \left(\frac{9a^3}{\pi}\right)^{1/4} \left(\frac{2ax^3}{3} - x\right)e^{-ax^2/2} \tag{15.4-13}$$

The value of the constant factor in each formula corresponds to normalization, which will be discussed in the next chapter. Other energy eigenfunctions can be generated from formulas for the Hermite polynomials in Appendix F, which also contains some useful identities involving Hermite polynomials.

Exercise 15.10

Using information in Appendix F, verify the formula for ψ_3 for the harmonic oscillator. Omit evaluation of the constant factor.

Figure 15.6 shows graphs of the energy eigenfunctions for $v = 0, v = 1, v = 2$, and $v = 3$. Each wave function is plotted on a separate axis that is placed at a height representing the energy eigenvalue. The potential energy as a function of x is also plotted with the same energy scale. The classical turning point for any given energy is the point at which the total energy is equal to the potential energy (the point at which a given axis and the potential energy curve cross). Classical mechanics asserts that the particle cannot oscillate past the turning point. However, each wave function is nonzero in the regions past its turning points. This correspond to penetration of the oscillating particle into the classically forbidden regions, which is called "*tunneling*." We will discuss this phenomenon in the next chapter.

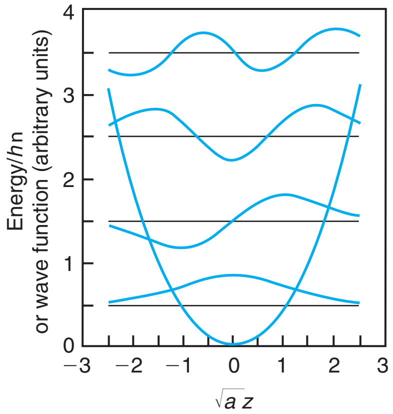

Figure 15.6 Harmonic Oscillator Wave Functions.

A comparison of these graphs with those for the particle in a one-dimensional box in Figure 15.4b shows that in both cases a wave function with a larger number of nodes corresponds to a higher energy. In addition to the nodes at infinite $|x|$ for the harmonic oscillator and at the ends of the box for the particle in a box, the lowest-energy wave function has no nodes, the next-lowest-energy wave function has one node, and so on.

The frequency of oscillation of the wave function has some surprising properties.

EXAMPLE 15.6

Calculate the frequency of oscillation of the wave function corresponding to the $v = 0$, $v = 1$, and $v = 2$ states of a harmonic oscillator. Find the difference between the frequencies for two adjacent values of v.

Solution

The time-dependent factor of the wave function is:

$$\eta(t) = e^{-iEt/\hbar} = e^{-2\pi iEt/h} = \cos(2\pi Et/h) - i\sin(2\pi Et/h)$$

So that the frequency is $\nu = E/h$. For $v = 0$, $E = h\nu_{\text{class}}/2$ and $\nu = \nu_{\text{class}}/2$. For $v = 1$, $E = 3h\nu_{\text{class}}/2$ and $\nu = 3\nu_{\text{class}}/2$. For $v = 2$, $E = 5h\nu_{\text{class}}/2$ and $\nu = 5\nu_{\text{class}}/2$. The difference between any two frequencies is equal to ν_{class}. A potential energy can have an arbitrary constant added to its value, which adds the same constant to all energy eigenvalues of the system. The frequency of the wave function thus can have a constant added to it, indicating that the actual frequency of oscillation of a de Broglie wave is not meaningful. Only differences in frequency are meaningful.

In Section 14.2 we described how two masses connected by a spring oscillate harmonically, and this version of a harmonic oscillator is a good model for the vibration of a diatomic molecule. The only change required in our formulas is the replacement of the mass of the oscillator with the reduced mass of the two nuclei.

EXAMPLE 15.7

Find the classical amplitude of vibration of a hydrogen molecule with an energy equal to that of the $v = 0$ quantum state. Express it as a percentage of the bond length, 0.74×10^{-10} m. The force constant k is equal to $576\ \mathrm{N\ m^{-1}}$ and the reduced mass is equal to 8.363×10^{-28} kg (half the mass of a hydrogen nucleus).

Solution

From Table A.22 of Appendix A, the frequency of vibration is

$$\nu = (4401.2\ \mathrm{cm^{-1}})(2.9979 \times 10^{10}\ \mathrm{cm\ s^{-1}}) = 1.319 \times 10^{14}\ \mathrm{s^{-1}}$$

For the $v = 0$ state,

$$E_1 = \frac{1}{2}h\nu = \frac{1}{2}(6.6261 \times 10^{-34}\mathrm{J\ s})(1.319 \times 10^{14}\mathrm{s^{-1}}) = 4.371 \times 10^{-20}\ \mathrm{J}$$

The amplitude of oscillation corresponds to

$$\mathscr{V}_{\max} = \frac{1}{2}kx_t^2 = E$$

where x_t is the value of x at the turning point.

$$x_t = \frac{\sqrt{2E}}{k} = \left(\frac{2(4.371 \times 10^{-20}\ \mathrm{J})}{576\ \mathrm{N\ m^{-1}}}\right)^{1/2} = 1.23 \times 10^{-11}\ \mathrm{m}$$

This value is 16.6% of the bond length.

PROBLEMS

Section 15.4: The Quantum Harmonic Oscillator

15.19 **a.** Construct an accurate graph of the $v = 2$ wave function of a harmonic oscillator as a function of $\sqrt{a}x$.

b. Express the value of the wave function at the turning point in terms of the parameter a.

c. If m is equal to $m_p/2$, the reduced mass of the H_2 molecule, and if $k = 574.75\ \mathrm{N\ m^{-1}}$, the value for the H_2 molecule, find the value of ψ_2^2 at the turning point. Express your value for ψ_2^2 in $\mathrm{m^{-1}}$ and in $\mathrm{Å^{-1}}$($1\ \mathrm{Å} = 10^{-10}$ m).

15.20 **a.** Construct an accurate graph of the $v = 3$ wave function of a harmonic oscillator as a function of $\sqrt{a}x$.

b. Find the value of the wave function at the turning point.

15.21 Using the recursion relation, Eq. (15.4-6), obtain the unnormalized energy eigenfunctions ψ_4 and ψ_5 for the harmonic oscillator.

15.22 **a.** Sketch a graph of the product of ψ_0 and ψ_1, the first two energy eigenfunctions of a harmonic oscillator and argue from the graph that the two functions are orthogonal, which means for these real functions that

$$\int_{-\infty}^{\infty} \psi_1(x)\psi_2(x)dx = 0$$

b. Work out the integral and show that ψ_0 and ψ_1 are orthogonal.

15.23 **a.** Construct an accurate graph of ψ_2^2, the square of the third energy eigenfunction of the harmonic oscillator.

b. Find the locations of the relative maxima and minima in ψ_2^2 in terms of the parameter a.

c. Express the locations of the relative maxima as fractions of the classical turning point for the energy corresponding to this energy eigenfunction.

d. Express the value of ψ_2^2 in terms of the parameter a at each relative maximum.

15.24 From the recursion relation of Eq. (15.4-6),

a. Show that if c_2 is nonzero and c_4 vanishes, the energy eigenvalue for $v = 2$ results.

b. Show that if $b = 2mE_2/\hbar$ and if $c_0 = -1$, then $c_2 = 2a$, verifying the formula given for ψ_2 in Eq. (15.4-12).

c. Show that the formula in Eq. (F-41) produces coefficients in the same ratio for $H_2(\sqrt{a}\,x)$ as given in Eq. (15.4-12).

d. Generate the Hermite polynomial $H_4(\sqrt{a}\,x)$ from Eq. (F-41) and write the formula for ψ_4 for the harmonic oscillator. Do not include the constant in front, which will be discussed later.

15.25 A two-dimensional harmonic oscillator has the potential energy function

$$\mathscr{V} = \mathscr{V}(x, y) = \frac{k}{2}(x^2 + y^2)$$

a. Write the time-independent Schrödinger equation and find its solutions by separation of variables, using the one-dimensional harmonic oscillator solutions.

b. Find the energy eigenvalues and degeneracies for the first 10 energy levels.

15.26 A three-dimensional harmonic oscillator has the potential energy function

$$\mathscr{V} = \mathscr{V}(x, y) = \frac{k}{2}(x^2 + y^2 + z^2)$$

a. Write the time-independent Schrödinger equation and find its solutions by separation of variables, using the one-dimensional harmonic oscillator solutions.

b. Find the energy eigenvalues and degeneracies for the first 5 energy levels.

15.27 A diatomic molecule vibrates like a harmonic oscillator with mass equal to the reduced mass of the nuclei of the molecule.

a. Calculate the reduced mass of the nuclei of an HBr molecule. Calculate its ratio to the mass of a hydrogen atom.

b. The vibrational frequency of the HBr molecule is $\nu = 7.944 \times 10^{13}\ \mathrm{s}^{-1}$. Find the force constant k.

15.28 A harmonic oscillator potential energy function is modified so that

$$\mathscr{V} = \begin{cases} kx^2/2 & \text{if } |x| < x' \\ \infty & \text{if } |x| > x' \end{cases}$$

where x' is some positive constant that is greater than the classical turning point for the energies that we will consider.

a. Tell qualitatively how this will affect the classical solution.

b. Tell qualitatively how this will affect the quantum-mechanical solution.

c. Will tunneling occur? In what region?

d. Draw a rough sketch of the first two wave functions.

Summary of the Chapter

De Broglie sought a physical justification for Bohr's assumption of quantization, and hypothesized that all particles move with a wave-like character with a wavelength given by

$$\lambda = \frac{h}{mv} = \frac{h}{p}$$

where h is Planck's constant, m is the mass of the particle, and v is its speed. According to the concept of wave–particle duality, electrons and other objects have some of the properties of classical waves and some of the properties of classical particles.

Schrödinger discovered a wave equation for de Broglie waves. The time-independent Schrödinger equation is an eigenvalue equation

$$\widehat{H}\psi = E\psi$$

where E is the energy of the system, ψ is a wave function, and $\widehat{H}$ is the Hamiltonian operator. The time-dependent Schrödinger equation is:

$$\widehat{H}\psi = i\hbar \frac{\partial \Psi}{\partial t}$$

By assuming that the wave function Ψ is a product of a coordinate factor ψ and a time factor η, the coordinate factor is found to obey the time-independent Schrödinger equation.

The solutions to the time-independent Schrödinger equation for three example systems were presented: the particle in a box (in one dimension and in three dimensions), the free particle, and the harmonic oscillator. Sets of energy eigenfunctions and energy eigenvalues were obtained, and in the cases of the particle in a box and the harmonic oscillator, we found a discrete spectrum of energies, corresponding to energy quantization. Two new phenomena occurred. First, the particle in a box and harmonic oscillator exhibited a zero-point energy. Second, the harmonic oscillator has a nonzero wave function in regions where classical mechanics predicts that the particle cannot enter.

ADDITIONAL PROBLEMS

15.29 Describe and discuss the conditions that a one-dimensional wave function must obey at a point where

a. $\mathscr{V}$ is a continuous function.

b. $\mathscr{V}$ is a discontinuous function with a finite step discontinuity.

c. $\mathscr{V}$ is a discontinuous function with an infinite step discontinuity.

15.30 Consider an automobile with a coil spring at each wheel. If a mass of 100 kg is suspended from one such spring, the spring lengthens by 0.020 m. The “unsprung weight” (the effective mass of the wheel and suspension components) of one wheel is equal to 25 kg. The mass of the part of the automobile supported by the springs is 1400 kg.

a. Find the force constant for each spring.

b. Assuming that all four springs are identical and that one-fourth of the supported mass is supported at each wheel, find the distance that each spring is compressed from its equilibrium length when the automobile is resting on its wheels.

c. Find the potential energy of each spring when the automobile is resting on its wheels.

d. Find the period and the frequency of oscillation of a wheel when it is hanging freely.

e. If the automobile is suddenly lifted off its wheels, find the speed of the wheel when the spring passes through its equilibrium length if no shock absorber is present to slow it down.

f. Find the energy of a quantum of energy of an oscillating wheel according to quantum mechanics.

g. Find the value of the quantum number when the energy of the oscillating wheel is equal to the energy of part c.

h. Find the wavelength of the electromagnetic radiation whose photons have energy equal to $h\nu$, where ν is the frequency of oscillation of part d.

15.31 Calculate the de Broglie wavelength of an electron moving with the kinetic energy corresponding to the $n = 5$ state of a hydrogen atom according to the Bohr theory. Show that this wavelength is equal to $1/5$ of the circumference of the fifth Bohr orbit.

15.32 Assume that the motion of the earth around the sun is described by the Bohr hydrogen atom theory. The electrostatic attraction is replaced by the gravitational attraction, given by the formula

$$F = -Gm_1m_2/r^2$$

where G is the gravitational constant, equal to $6.673 \times 10^{-11}\ \mathrm{m^3\,s^{-2}\,kg^{-1}}$ and m_1 and m_2 are the masses of the two objects. The mass of the earth is 5.983×10^{24} kg, and the mass of the sun is larger by a factor of 332958. The earth's orbit is slightly elliptical, but pretend that it is circular, with a radius of 1.4967×10^{11} m.

a. Find the value of the Bohr radius assuming that the sum is stationary (as it would be if it were infinitely massive).

b. Find the ratio of the reduced mass of the earth–sun system to the mass of the earth.

c. Find the value of the Bohr radius using the reduced mass of the earth and the sun.

d. Find the value of the quantum number corresponding to the size of the earth's actual orbit.

e. Find the kinetic energy, the potential energy, and the total energy of the earth's orbital motion.

15.33 Identify each statement as either true or false. If a statement is true only under special circumstances, label it as false.

a. A de Broglie wave can be identified as a transverse wave.

b. A de Broglie wave can be identified as a longitudinal wave.

c. The oscillating quantity in a de Broglie wave cannot be physically identified.

d. The Schrödinger equation has been rigorously derived from first principles.

e. An eigenvalue equation can have solutions for arbitrary values of the eigenvalue.

f. Several different eigenvalues can correspond to the same eigenfunction.

g. Several different energy eigenfunctions can correspond to the same energy eigenvalue.

h. Light can be identified as a wave in a pervasive medium.

i. Light exhibits both wave-like and particle-like properties.

j. Electrons exhibit both wave-like and particle-like properties.

k. If the length of its box is made to approach infinity, a particle in a box behaves like a free particle.

l. A free particle cannot be described by a standing-wave type of wave function, but must be described by a traveling-wave type of wave function.

16

The Principles of Quantum Mechanics. II. The Postulates of Quantum Mechanics

PRINCIPAL FACTS AND IDEAS

1. Quantum mechanics is based on a set of postulates (fundamental hypotheses).
2. The first two postulates establish the role of the wave function in quantum mechanics.
3. The third postulate establishes a connection between each mechanical variable and a mathematical operator.
4. The fourth postulate provides the means to obtain information about the values of mechanical variables.
5. The fifth postulate concerns the determination of the state of a system by experimental measurements.

16.1 The First Two Postulates of Quantum Mechanics

Werner Karl Heisenberg, 1901–1976, was a German physicist who invented matrix mechanics, a form of quantum mechanics equivalent to the Schrödinger formulation. He discovered the uncertainty principle, for which he received the 1932 Nobel Prize in physics.

The Schrödinger equation does not provide a complete theory of quantum mechanics. Schrödinger, Heisenberg, and others devised several **postulates** (unproved fundamental assumptions) that form a consistent logical foundation for nonrelativistic quantum mechanics. In any theory based on postulates, the validity of the postulates is tested by comparing the consequences of the postulates with experimental fact. The postulates of quantum mechanics do pass this test. These postulates can be stated in slightly different ways. We will state five postulates in a form similar to that of Mandl[1] and Levine.[2] The first two postulates were introduced in Chapter 15 without calling them postulates. We now state them explicitly:

Postulate 1. *All information that can be obtained about the state of a mechanical system is contained in a wave function* Ψ*, which is a continuous, finite, and single-valued function of time and of the coordinates of the particles of the system.*

This postulate implies that there is a one-to-one relationship between the state of the system and a wave function. That is, each possible state corresponds to one wave function, and each possible wave function corresponds to one state. The terms "*state function*" and "*wave function*"are often used interchangeably. Information about values of mechanical variables such as energy and momentum must be obtained from the wave function, instead of from values of coordinates and velocities as in classical mechanics. The fourth postulate will provide the method for obtaining this information.

Postulate 2. *The wave function* Ψ *obeys the time-dependent Schrödinger equation*

$$\widehat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t} \tag{16.1-1}$$

where $\widehat{H}$ *is the Hamiltonian operator of the system.*

The time-independent Schrödinger equation can be derived from the time-dependent equation, as was shown in Chapter 15, by assuming that the wave function is a product of a coordinate factor and a time factor:

$$\Psi(q,t) = \psi(q)\eta(t) \tag{16.1-2}$$

where q stands for all of the coordinates of the particles in the system and where the coordinate wave function ψ satisfies the time-independent Schrödinger equation. Not all wave functions consist of the two factors in Eq. (16.1-2), but all wave functions must obey the time-dependent Schrödinger equation.

16.2 The Third Postulate. Mathematical Operators and Mechanical Variables

The time-independent Schrödinger equation determines the energy eigenvalues for a given system. These eigenvalues are the possible values that the energy of the system

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[1] F. Mandl, *Quantum Mechanics*, Butterworths Scientific Publications, London, 1957, p. 60ff.

[2] I. N. Levine, *Quantum Chemistry*, 5th ed., Prentice-Hall, Englewood Cliffs, NJ, 2000.

can take on. The third and fourth postulates must be used to obtain the possible values of other mechanical variables such as the momentum and the angular momentum. The third postulate is:

> **Postulate 3.** *There is a linear hermitian mathematical operator in one-to-one correspondence with every mechanical variable.*

This postulate states that for each operator there is one and only one variable, and for each variable there is one and only one mathematical operator. A *mathematical operator* is a symbol that stands for performing one or more mathematical operations. When the symbol for an operator is written to the left of the symbol for a function, the operation is to be applied to that function. For example, d/dx is a derivative operator, standing for differentiation of the function with respect to x; c is a multiplication operator, standing for multiplication of the function by the constant c; $h(x)$ is also a multiplication operator, standing for multiplication by the function $h(x)$. We usually denote an operator by a letter with a caret ($\widehat{\ }$) over it.

The result of operating on a function with an operator is another function. If $\widehat{A}$ is an operator and f is a function,

$$\widehat{A}\,f(q) = g(q) \tag{16.2-1}$$

where g is another function. The symbol q is an abbreviation for whatever independent variables f and g depend on. Figure 16.1 shows an example of a function, $f(x) = \ln(x)$, and the function $g(x) = 1/x$ that results when the operator d/dx is applied to $\ln(x)$.

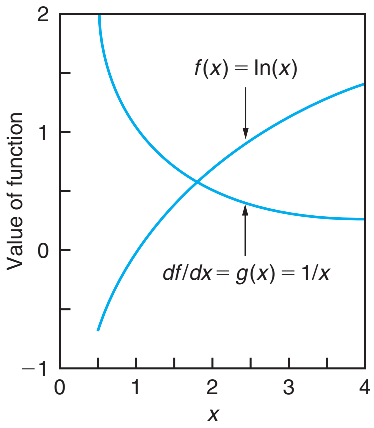

Figure 16.1 A Function and Its Derivative.

Operator Algebra

There is an **operator algebra** according to which we can symbolically manipulate operator symbols without specifying the functions on which the operators act. An operator can be set equal to another operator in an *operator equation*. For example, if

$$\widehat{A}\,f(q) = \widehat{B}\,f(q) \tag{16.2-2}$$

is valid for any well-behaved function $f(q)$, we can write the operator equation

$$\widehat{A} = \widehat{B} \tag{16.2-3}$$

An operator equation means that the operators on the two sides of the equation always produce the same result when applied to any well-behaved function.

The operator that always produces the same function as the one on which it operates is called the *identity operator* and is denoted by $\widehat{E}$. The symbol $\widehat{E}$ comes from the German word “Einheit,” meaning “unity.” It is equivalent to multiplying by unity:

$$\widehat{E}\,f(q) = f(q) \tag{16.2-4}$$

Equation (16.2-4) can be written as the operator equation:

$$\widehat{E} = 1 \tag{16.2-5}$$

where 1 is the operator for multiplication by unity.

The *sum of two operators* is defined by

$$(\widehat{A} + \widehat{B})\,f(q) = \widehat{A}\,f(q) + \widehat{B}\,f(q) \tag{16.2-6}$$

The *product of two operators* is defined as successive application of the operators, and is denoted by writing the two operator symbols adjacent to each other. If we write the operator equation

$$\widehat{C} = \widehat{A}\,\widehat{B} \tag{16.2-7}$$

then this is equivalent to

$$\widehat{C}\,f(q) = \widehat{A}\,\widehat{B}\,f(q) = \widehat{A}\,(\widehat{B}\,f(q)) = \widehat{A}\,g(q) \tag{16.2-8}$$

where $g(q)$ is the function produced when $\widehat{B}$ operates on $f(q)$. The operator written next to the symbol for the function (the operator on the right) always operates first, so operators operate from right to left. The square of an operator means operating twice with that operator.

Operator multiplication is *associative*, which means that

$$\widehat{A}\,(\widehat{B}\,\widehat{C}) = (\widehat{A}\,\widehat{B})\widehat{C} \tag{16.2-9}$$

This means that if the operator product $\widehat{B}\,\widehat{C}$ equals the operator $\widehat{F}$ and the operator product $(\widehat{A}\,\widehat{B})$ equals the operator $\widehat{G}$, then $\widehat{A}\,\widehat{F} = \widehat{G}\,\widehat{C}$.

Operator multiplication and addition are *distributive*, which means that

$$\widehat{A}(\widehat{B} + \widehat{C}) = \widehat{A}\,\widehat{B} + \widehat{A}\,\widehat{C} \tag{16.2-10}$$

Operator multiplication is not necessarily *commutative*. It can happen that

$$\widehat{A}\,\widehat{B} \neq \widehat{B}\,\widehat{A} \quad \text{(in some cases)} \tag{16.2-11}$$

If $\widehat{A}\,\widehat{B} = \widehat{B}\,\widehat{A}$, the operators $\widehat{A}$ and $\widehat{B}$ are said to *commute*.

The *commutator* of two operators $\widehat{A}$ and $\widehat{B}$ is denoted by $[\widehat{A}, \widehat{B}]$ and is defined by

$$[\widehat{A}, \widehat{B}] = \widehat{A}\,\widehat{B} - \widehat{B}\,\widehat{A} \quad \text{(definition of the commutator)} \tag{16.2-12}$$

If two operators commute, their commutator vanishes.

EXAMPLE 16.1

Find the commutator $\left[x, \dfrac{d}{dx}\right]$.

Solution

We let the commutator act on an arbitrary differentiable function, $f(x)$:

$$\left[x, \frac{d}{dx}\right] f(x) = x\frac{df}{dx} - \frac{d(xf)}{dx} = x\frac{df}{dx} - x\frac{df}{dx} - f(x) = -f(x)$$

As an operator equation,

$$\left[x, \frac{d}{dx}\right] = -\widehat{E} = -1$$

Exercise 16.1

Find the commutator $\left[x^2, \dfrac{d}{dx}\right]$.

The following facts about commutation are useful:

1. Every operator commutes with itself.
2. Multiplication operators commute with each other.
3. A constant multiplication operator commutes with all other operators of the types that we will consider.
4. Operators that act on different independent variables commute with each other.
5. A derivative operator almost never commutes with a multiplication operator containing the same independent variable.

EXAMPLE 16.2

Find the operator $\widehat{C} = (\widehat{\mathscr{K}} + \widehat{\mathscr{V}})^2$ if $\widehat{\mathscr{K}}$ and $\widehat{\mathscr{V}}$ are two operators that do not commute.

Solution

$$\widehat{C} = (\widehat{\mathscr{K}} + \widehat{\mathscr{V}})^2 = (\widehat{\mathscr{K}} + \widehat{\mathscr{V}})(\widehat{\mathscr{K}} + \widehat{\mathscr{V}}) = \widehat{\mathscr{K}}^2 + \widehat{\mathscr{K}}\widehat{\mathscr{V}} + \widehat{\mathscr{V}}\widehat{\mathscr{K}} + \widehat{\mathscr{V}}^2$$

The terms $\widehat{\mathscr{K}}\widehat{\mathscr{V}}$ and $\widehat{\mathscr{V}}\widehat{\mathscr{K}}$ are different from each other if the two operators do not commute.

Exercise 16.2

a. Find the operator $(\widehat{\mathscr{K}} + \widehat{\mathscr{V}})^3$ if $\widehat{\mathscr{K}}$ and $\widehat{\mathscr{V}}$ do not commute.
b. Find the operator $(\widehat{A} + \widehat{B})^3$ if $\widehat{A}$ and $\widehat{B}$ commute.

PROBLEMS

Section 16.2: The Third Postulate. Mathematical Operators and Mechanical Variables

16.1 Find an expression for the commutator $\left[x, \dfrac{d^2}{dx^2}\right]$.

16.2 Find an expression for the commutator $\left[x\dfrac{d}{dx}, x\right]$.

16.3 Find a simplified expression for the operator $\left[\dfrac{1}{x} + \dfrac{d}{dx}\right]^2$.

16.4 A *function of an operator* is defined through the Taylor series that represents the function. For example, the function $f(x) = e^x$ is represented by the Taylor series

$$e^x = 1 + x + \frac{1}{2!}x^2 + \frac{1}{3!}x^3 + \cdots \frac{1}{n!}x^n + \cdots$$

where $n!$ stands for n factorial, the product of all of the integers beginning with n and ranging down to 1.

The exponential of an operator is defined as the series

$$e^{\widehat{A}} = 1 + \widehat{A} + \frac{1}{2!}\widehat{A}^2 + \frac{1}{3!}\widehat{A}^3 + \cdots + \frac{1}{n!}\widehat{A}^n + \cdots$$

where the operator products are defined in the usual way, as successive operations of the operator.

a. Write the formula for the result when $e^{\widehat{A}}$ operates on an eigenfunction of $\widehat{A}$.

b. Write the expression for the first three terms of $e^{(\widehat{A}+\widehat{B})}$, where $\widehat{A}$ and $\widehat{B}$ are two operators that do not necessarily commute.

16.5 **a.** Find the expression for $\sin(\widehat{A})$.

b. Find the expression for $\cos(\widehat{A})$.

c. Find the expression for $\ln(\widehat{A})$.

d. Write the expression for the first two terms of $\sin(\widehat{A} + \widehat{B})$, where $\widehat{A}$ and $\widehat{B}$ are two operators that do not necessarily commute.

16.3 The Operator Corresponding to a Given Variable

We need to find the operator that corresponds to a particular mechanical variable. We begin by assuming that the Hamiltonian operator is the mathematical operator that is in one-to-one correspondence with the energy of a system. This is plausible since the time-independent Schrödinger equation

$$\widehat{H}\psi = E\psi \tag{16.3-1}$$

places $\widehat{H}$ and E in a unique relationship to each other.

Any mechanical variable can be written either as a function of coordinates and velocities or as a function of coordinates and momenta. It turns out that the variables need to be expressed in terms of Cartesian coordinates and momentum components. In Cartesian coordinates the momentum of a particle is its mass times its velocity:

$$\mathbf{p} = m\mathbf{v} \tag{16.3-2a}$$

or

$$p_x = mv_x, \quad p_y = mv_y, \quad \text{and} \quad p_z = mv_z \tag{16.3-2b}$$

If a particle moves only in the x direction, the kinetic energy is

$$\mathscr{K} = \frac{1}{2}mv_x^2 = \frac{p_x^2}{2m} \tag{16.3-3}$$

The Hamiltonian is named for Sir William Rowan Hamilton, 1805–1865, a great Irish mathematician, physicist, and astronomer.

The expression for the energy as a function of momenta and coordinates is called *Hamilton's principal function* or the *classical Hamiltonian*, and is denoted by $\mathscr{H}$.

We assert that the classical Hamiltonian $\mathscr{H}$ is in one-to-one correspondence with the Hamiltonian operator:

$$\mathscr{H}(x, p_x) = \mathscr{K} + \mathscr{V} = \frac{p_x^2}{2m} + \mathscr{V}(x) \rightleftharpoons \widehat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \mathscr{V}(x) \tag{16.3-4}$$

where $\mathscr{K}$ is the kinetic energy and $\mathscr{V}$ is the potential energy. In this context the symbol $\rightleftharpoons$ means "is in one-to-one correspondence with." The potential energy function $\mathscr{V}(x)$ occurs on both sides of this correspondence in the same way. We assert that the operator for the potential energy is the multiplication operator $\mathscr{V}(x)$:

$$\widehat{\mathscr{V}} \rightleftharpoons \mathscr{V}(x) \tag{16.3-5}$$

We extend this assertion and postulate that *any function of coordinates corresponds to the operator for multiplication by that function.*

The operator that corresponds to the kinetic energy $\mathscr{K}$ is now

$$\mathscr{K} = \frac{p_x^2}{2m} \rightleftharpoons \widehat{\mathscr{K}} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \tag{16.3-6}$$

The operator for the square of the x component of the momentum must be

$$\widehat{p}_x^2 = -\hbar^2\frac{d^2}{dx^2} \tag{16.3-7}$$

The operator for p_x^2 must equal the square of the operator for p_x. Since the operator for p_x^2 is negative, the operator for p_x must be purely imaginary.

$$p_x \rightleftharpoons \widehat{p}_x = \pm i\hbar \frac{d}{dx} \tag{16.3-8}$$

where i stands for the imaginary unit, $i = \sqrt{-1}$. Since any quantity has two square roots, we have a choice of signs. We take the negative sign and the operator for p_x is

$$\widehat{p}_x = -i\hbar \frac{d}{dx} = \frac{\hbar}{i}\frac{d}{dx} \tag{16.3-9}$$

The sign that we choose in Eq. (16.3-9) gives the momentum the correct sign when a particle is moving in a known direction (see Problem 16.20).

We complete the third postulate by the additional assertion that the pattern of Eq. (16.3-9) holds for all Cartesian momentum components and make the following assertion: *The quantum mechanical operator for any mechanical variable is obtained by (1) expressing the quantity classically in terms of Cartesian coordinates and Cartesian momentum components and (2) replacing the momentum components by* ħ/i *times the derivative with respect to the corresponding Cartesian coordinate.* The validity of the operator must be verified by comparison of the consequences of its action with experimental fact, and this recipe has passed this test in every case.

For a particle moving in three dimensions

$$\mathscr{K} = \frac{1}{2m}\left(p_x^2 + p_y^2 + p_z^2\right) \tag{16.3-10}$$

so that

$$\widehat{\mathscr{K}} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) = -\frac{\hbar^2}{2m}\nabla^2 \tag{16.3-11}$$

where we write partial derivatives since we have more than one coordinate and where ∇^2 is called the *Laplacian operator*.

EXAMPLE 16.3

Construct the operator for the z component of the angular momentum of one particle.

Solution

The angular momentum is defined in Appendix E as the *vector product* (*cross product*)

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \tag{16.3-12}$$

From Eq. (B-42) in Appendix B, the z component is

$$L_z = xp_y - yp_x \tag{16.3-13}$$

The operator for this component is

$$\widehat{L}_z = \frac{\hbar}{i}\left[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right] \tag{16.3-14}$$

The expressions for $\widehat{L}_x$ and $\widehat{L}_y$ can be obtained similarly.

The operator for $|\mathbf{L}|$, the magnitude of the angular momentum, is not usable since

$$|L| = (L^2)^{1/2} = (L_x^2 + L_y^2 + L_z^2)^{1/2} \tag{16.3-15}$$

and we have no procedure for unscrambling the square root when the operator is formed. To obtain information about the magnitude of the angular momentum we will use the L^2 operator.

Exercise 16.3

a. Construct the operator for $\widehat{L}_x$.
b. Construct the operator for $\widehat{L}_y$.
c. Construct the operator for L_z^2 (the square of the operator for L_z).

It is sometimes useful to have operator expressions for commutators.

EXAMPLE 16.4

Find the operator equal to the commutator $[\widehat{x}, \widehat{p}_x]$.

Solution

Operate on an arbitrary differentiable function $f(x)$:

$$[\widehat{x}, \widehat{p}_x] f = \frac{\hbar}{i}\left[x\frac{\partial f}{\partial x} - \frac{\partial(xf)}{\partial x}\right] = -\frac{\hbar}{i} f$$

The operator equation is

$$[\widehat{x}, \widehat{p}_x] = -\frac{\hbar}{i} = i\hbar \tag{16.3-16}$$

Equation (16.3-16) is an important result. Some authors find the form of the operator $\widehat{p}_x$ by postulating that this commutation relation must hold.

Exercise 16.4

a. Find the commutator $[\widehat{p}_x, \widehat{p}_y]$.
b. Show that

$$\left[\widehat{L}_x, \widehat{p}_y\right] = i\hbar\widehat{p}_z \tag{16.3-17}$$

If an operator is needed in another coordinate system, the operator is first constructed in Cartesian coordinates and then transformed to the other coordinate system. For example, if a particle moves in the xy plane, its position can be represented using the polar coordinates ρ and ϕ:

$$\rho = \sqrt{x^2 + y^2} \tag{16.3-18}$$

$$\phi = \arctan(y/x) \tag{16.3-19}$$

EXAMPLE 16.5

For motion in the x–y plane, transform the expression for $\widehat{L}_z$ to plane polar coordinates.

Solution

If f is a differentiable function of x and y and is also expressible as a function of ρ and ϕ, then

$$x\frac{\partial f}{\partial y} = x\frac{\partial f}{\partial \phi}\frac{\partial \phi}{\partial y} + x\frac{\partial f}{\partial \rho}\frac{\partial \rho}{\partial y} = x\frac{\partial f}{\partial \phi}\frac{x}{x^2+y^2} + x\frac{\partial f}{\partial \rho}\frac{y}{(x^2+y^2)^{1/2}}$$

$$y\frac{\partial f}{\partial x} = y\frac{\partial f}{\partial \phi}\frac{\partial \phi}{\partial x} + y\frac{\partial f}{\partial \rho}\frac{\partial \rho}{\partial x} = y\frac{\partial f}{\partial \phi}\frac{-y}{x^2+y^2} - y\frac{\partial f}{\partial \rho}\frac{x}{(x^2+y^2)^{1/2}}$$

Since the second terms cancel when these expressions are added,

$$\widehat{L}_z f = \frac{\hbar}{i}\left(\frac{\partial f}{\partial \phi}\frac{x^2}{x^2+y^2} - \frac{\partial f}{\partial \phi}\frac{-y^2}{x^2+y^2}\right) = \frac{\hbar}{i}\frac{\partial f}{\partial \phi}\left(\frac{x^2+y^2}{x^2+y^2}\right) = \frac{\hbar}{i}\frac{\partial f}{\partial \phi}$$

so that

$$\widehat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial \phi} \tag{16.3-20}$$

When we discuss the hydrogen atom in a later chapter, we will use spherical polar coordinates:

$$r = \sqrt{x^2+y^2+z^2} \tag{16.3-21}$$

$$\theta = \arccos(z/r) \tag{16.3-22}$$

$$\phi = \arctan(y/x) \tag{16.3-23}$$

The expression for the operator $\widehat{L}_z$ in Eq. (16.3-20) also holds for spherical polar coordinates. The operators $\widehat{L}_x$ and $\widehat{L}_y$ are more complicated in spherical polar coordinates than is $\widehat{L}_z$, and we will try to avoid using them. We present the expression for $\widehat{L}^2$ in spherical polar coordinates without derivation:

$$\widehat{L}^2 = -\hbar^2\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial \theta}\sin(\theta)\frac{\partial}{\partial \theta} + \frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial \phi^2}\right] \tag{16.3-24}$$

Equation (16.3-24) can also be written in the form

$$\widehat{L}^2 = -\hbar^2\left[\frac{\partial^2}{\partial \theta^2} + \cot(\theta)\frac{\partial}{\partial \theta} + \frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial \phi^2}\right] \tag{16.3-25}$$

Exercise 16.5

Show that Eq. (16.3-24) and Eq. (16.3-25) are equivalent.

Linear Operators

Quantum mechanical operators are *linear operators*. A linear operator $\widehat{A}$ obeys the two properties

$$\widehat{A}[f(q)+g(q)]=\widehat{A}f(q)+\widehat{A}g(q) \quad \begin{pmatrix}\text{property 1 of}\\ \text{linear operators}\end{pmatrix} \tag{16.3-26}$$

and

$$\widehat{A}[cf(q)]=c\widehat{A}f(q) \quad \begin{pmatrix}\text{property 2 of}\\ \text{linear operators}\end{pmatrix} \tag{16.3-27}$$

where c is an arbitrary constant and where f and g are well-behaved functions (for example, if $\widehat{A}$ is a derivative operator they must be differentiable).

Hermitian Operators

Quantum mechanical operators are *hermitian operators*. A hermitian operator $\widehat{A}$ obeys the relation

$$\int f^*\widehat{A}g\,dq=\int(\widehat{A}f)^*g\,dq=\int(\widehat{A}^*f^*)g\,dq \quad \begin{pmatrix}\text{property of}\\ \text{hermitian operator}\end{pmatrix} \tag{16.3-28}$$

where q is an abbreviation for all of the independent variables on which the functions f and g depend and where the integrations are over all values of the independent variables. For example, if q represents the Cartesian coordinates of a particle that can move in three dimensions, the integral is a three-fold integral and dq stands for $(dxdydz)$. The symbol f^* denotes the *complex conjugate* of the function f, and $\widehat{A}^*$ denotes the complex conjugate of the operator $\widehat{A}$.

Complex quantities are surveyed briefly in Appendix B. If z is a complex quantity it can be written

$$z=x+iy \tag{16.3-29}$$

where the real quantity x is called the *real part* of z and the real quantity y is called the *imaginary part* of z. The complex conjugate of any complex number, function, or operator is obtained by changing the sign of its imaginary part:

$$z^*=x-iy \tag{16.3-30}$$

A real quantity or a real operator is equal to its complex conjugate, and an imaginary quantity or an imaginary operator is equal to the negative of its complex conjugate.

If the particle can move in all of space, the integration limits in Eq. (16.3-28) are $-\infty$ to ∞ for each Cartesian coordinate. The functions f and g must obey boundary conditions such that the integral converges. The functions f and g must approach zero for large magnitudes of the Cartesian coordinates.

Hermitian operators have several important properties:

1. Hermitian operators are linear.
2. Two hermitian operators are not required to commute with each other.

3. A hermitian operator has a set of eigenfunctions and eigenvalues.
4. The eigenvalues of a hermitian operator are real.
5. Two eigenfunctions of a hermitian operator with different eigenvalues are orthogonal to each other.
6. Two commuting hermitian operators can have a set of common eigenfunctions.
7. The set of eigenfunctions of a hermitian operator form a complete set for expansion of functions obeying the same boundary conditions.

EXAMPLE 16.6

a. Show that the operator d/dx is linear.
b. Show that it is not hermitian.

Solution

a.

$$\frac{d}{dx}(f+g) = \frac{df}{dx} + \frac{dg}{dx}$$

$$\frac{d(cf)}{dx} = c\frac{df}{dx}$$

b. We integrate by parts:

$$\int_{-\infty}^{\infty} f(x)^* \frac{dg}{dx}dx = f(x)^* g(x)\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} g(x)\frac{df^*}{dx}dx$$

The functions f and g must vanish at the limits of integration, so we have

$$\int_{-\infty}^{\infty} f(x)^* \frac{dg}{dx}dx = -\int_{-\infty}^{\infty} \frac{df^*}{dx}g(x)dx$$

which is the negative of what we would require for a hermitian operator.

The proofs for Properties 4 and 5 are in Appendix B. Property 5 involves *orthogonality*. Two functions f and g are *orthogonal* to each other if

$$\int f^* g\,dq = \int g^* f\,dq = 0 \quad \begin{pmatrix}\text{definition of}\\ \text{orthogonality}\end{pmatrix} \qquad (16.3\text{-}31)$$

where the integrals are taken over all values of the coordinates. The two integrals in Eq. (16.3-31) are the complex conjugates of each other so that if one vanishes, so does the other.

EXAMPLE 16.7

Show that the first two energy eigenfunctions of the particle in a one-dimensional box of length a are orthogonal to each other.

Solution

The energy eigenfunctions are found in Eq. (15.3-10). The formula contains a constant C, which we assume to be real. Quantum mechanical integrals are taken over all values of the coordinates, but the wave function vanishes outside of the box, and we can omit that part of the integration:

$$\int_{-\infty}^{\infty} \psi_1(x)\,\psi_2(x)\,dx = C^2 \int_0^a \sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{2\pi x}{a}\right)dx = C^2\frac{a}{\pi}\int_0^{\pi} \sin(y)\sin(2y)dy = 0$$

where we have looked the integral up in Appendix C. One can also make a rough graph of the integrand and argue that the positive and negative contributions to the integral cancel each other.

Property 6, that two commuting hermitian operators can have a set of common eigenfunctions, means the following: If $\widehat{A}$ and $\widehat{B}$ are two hermitian operators that commute with each other, then a set of functions $f_{jk}(q)$ can be found such that

$$\widehat{A}\, f_{jk}(q) = a_j\, f_{jk}(q) \tag{16.3-32}$$

$$\widehat{B}\, f_{jk}(q) = b_k\, f_{jk}(q) \tag{16.3-33}$$

where a_j and b_k are constant eigenvalues. Two indices are needed on the functions in the set, because two functions can have the same eigenvalue for $\widehat{A}$ but have different eigenvalues for $\widehat{B}$. An example of simultaneous eigenfunctions is found in the electronic wave functions of the hydrogen atom, which are simultaneous eigenfunctions of the Hamiltonian operator and two angular momentum operators. We discuss these in Chapter 17.

The completeness property specified in Property 7 means that an arbitrary function ψ that obeys the same boundary conditions as the set of eigenfunctions of a hermitian operator $\widehat{A}$ can be exactly represented as a *linear combination* (sum of functions multiplied by constant coefficients) of all of the eigenfunctions of $\widehat{A}$.

$$\psi = \sum_{j=1}^{\infty} c_j\, f_j \tag{16.3-34}$$

where f_1, f_2, f_3, ... are the set of eigenfunctions. This set of functions is called the *basis set* or the set of *basis functions*. The function ψ is said to be *expanded* in terms of the basis functions. The coefficients c_1, c_2, c_3, ... are called *expansion coefficients*. There are generally infinitely many eigenfunctions of a given operator, and all of them must be included in the sum of Eq. (16.3-34) for the representation to be exact. There is apparently no general proof that the eigenfunctions of a hermitian operator form a complete set. However, there are no known counterexamples, and this assertion is generally accepted.

We can represent a time-dependent wave function in terms of time-independent basis functions if the expansion coefficients have the correct time dependence. For example, in Eq. (15.3-20) we chose the energy eigenfunctions as the basis functions and wrote

$$\Psi(x,t) = \sum_{n=1}^{\infty} A_n e^{-iE_n t/\hbar}\psi_n(x) \tag{16.3-35}$$

where the coefficients A_1, A_2, ... are constants. It was shown in Example 15.3 that this function satisfies the time-dependent Schrödinger equation.

The Eigenfunction of a Coordinate Operator

Since the operator for a coordinate x or any other coordinate must have a set of eigenfunctions, the situation is a little bit strange. We must require

$$x\delta(x-a) = a\delta(x-a) \tag{16.3-36}$$

where $\delta(x-a)$ is the eigenfunction and a is the eigenvalue. This looks problematic because we have a variable times a function set equal to a constant times the same function. To make the equation valid, we must define the eigenfunction so that it is nonzero only when $x = a$. However, the integral of the eigenfunction must be nonzero, so we specify that

$$\int_b^c \delta(x-a)\,dx = 1 \tag{16.3-37}$$

if $b < a < c$. This eigenfunction is called the *Dirac delta function*, defined such that $\delta(x-a) \to \infty$ if $x = a$ and $\delta(x-a) = 0$ if $x \neq a$, in such a way that Eq. (16.3-37) is obeyed. A graph of this function has unit area under a single point. It is highly discontinuous, and some mathematicians refuse to call it a function.

EXAMPLE 16.8

Show that the following integral:

$$\int_{-\infty}^{\infty} \delta(x-a)\, f(x)dx$$

is equal to $f(a)$.

Solution

Since the delta function is nonzero only at $x = a$, we can factor $f(a)$ out of the integral without changing its value:

$$\int_{-\infty}^{\infty} \delta(x-a) f(x)dx = f(a)\int_{-\infty}^{\infty} \delta(x-a)dx = f(a) \tag{16.3-38}$$

PROBLEMS

Section 16.3: The Operator Corresponding to a Given Variable

16.6 Determine whether each of the following operators is linear and whether it is hermitian.

a. $\dfrac{d^2}{dx^2}$

b. $\dfrac{d^3}{dx^3}$

c. sin(. . .)

16.7 Determine whether each of the following operators is linear and whether it is hermitian.

a. ln(. . .)

b. $\dfrac{c}{x} + i\dfrac{d}{dx}$, where c is a constant and $i = \sqrt{-1}$.

c. $ix\dfrac{d}{dx}$, where $i = \sqrt{-1}$.

16.8 Find the complex conjugate of each of the following where $z = x + iy$, and x and y are real. Do it once by replacing i by $-i$, and once by separating the real and imaginary parts.

a. $\sinh(z)$

b. $\cos(z)$

c. z^2

16.9 Find the complex conjugate of each of the following where $z = x + iy$, and x and y are real. Do it once by replacing i by $-i$, and once by separating the real and imaginary parts.

a. $\sin(z)$

b. $\cosh(z)$

c. z^3

16.10 **a.** Show that the multiplication operator x is linear and hermitian.

b. Show that the operator $i(d/dx)$ is linear and hermitian.

c. Show that any hermitian operator is linear.

16.11 Show that the first two energy eigenfunctions of the harmonic oscillator are orthogonal to each other.

16.12 Show that the operator for multiplication by a function, $h(x)$, is linear and hermitian.

16.13 Using integration by parts, find the result of performing the integral

$$\int_{-\infty}^{\infty}\left(\frac{d}{dx}\delta(x-a)\right)f(x)dx$$

where $\delta(x)$ is the Dirac delta function.

16.14 Find the commutator $[\,p_x^2, x^2]$.

16.15 **a.** Find the eigenfunctions and eigenvalues of $\widehat{p}_x = -i\hbar(\partial/\partial x)$.

b. Are the energy eigenfunctions for a particle in a one-dimensional box eigenfunctions of this operator? If so, find the eigenvalues.

c. Are the energy eigenfunctions for a free particle eigenfunctions of this operator? If so, find the eigenvalues.

16.16 **a.** Show that $[\widehat{L}_x, \widehat{L}_y] = i\hbar\widehat{L}_z$.

b. Argue from the result of part a that $[\widehat{L}_z, \widehat{L}_x,] = i\hbar\widehat{L}_y$ and that $[\widehat{L}_y, \widehat{L}_z] = i\hbar\widehat{L}_x$.

16.17 Find the commutator $[\widehat{L}_x, \widehat{p}_x]$.

16.18 **a.** Find the quantum mechanical operator for the variable

$$O = \mathbf{r}\cdot\mathbf{p} = xp_x + yp_y + zp_z$$

b. Find the commutators $[\widehat{O}, x]$ and $[\widehat{O}, \widehat{p}_x]$ where $\widehat{O}$ is the operator in part a.

16.19 Find an eigenfunction of the following operator and find its corresponding eigenvalue:

$$\frac{d^2}{dx^2} + 2\frac{d}{dx} + 1$$

16.4 Postulate 4 and Expectation Values

The first postulate of quantum mechanics asserts that the wave function of a system contains all available information about the values of mechanical variables for the state corresponding to the wave function. The third postulate provides a mathematical operator for each mechanical variable. The fourth postulate provides the mathematical procedure for obtaining the available information:

Postulate 4.
(a) *If a mechanical variable* A *is measured without experimental error, the only possible outcomes of the measurement are the eigenvalues of the operator* $\widehat{\mathrm{A}}$ *that corresponds to* A.
(b) *The* expectation value *for the error-free measurement of a mechanical variable* A *if given by the formula*

$$\langle A\rangle = \frac{\displaystyle\int \Psi^*\widehat{A}\Psi dq}{\displaystyle\int \Psi^*\Psi dq} \tag{16.4-1}$$

where $\widehat{\mathrm{A}}$ *is the operator corresponding to the variable* A, *and where* $\psi = \psi(\mathrm{q}, \mathrm{t})$ *is the wave function corresponding to the state of the system at the time of the measurement.*

The expectation value is the predicted mean of a set of many measurements of the variable, given that the system is in the state corresponding to the wave function Ψ at the time of each measurement. As is the case with all quantum mechanical integrations, the integrals in Eq. (16.4-1) extend over all values of the coordinates, which are abbreviated by q. We will see that Eq. (16.4-1) leads to the famous fact that quantum mechanics often provides only statistical information.

Consider first the case of a wave function Ψ that is a product of a coordinate wave function and a time-dependent factor. The complex conjugate of the time-dependent factor can be obtained by changing the sign in front of the i symbol in the exponent (see Appendix B):

$$\left(e^{-iEt/\hbar}\right)^* = e^{iEt/\hbar} \tag{16.4-2}$$

The expectation value of A is given by

$$\langle A \rangle = \frac{\int \psi^* e^{iEt/\hbar} \widehat{A} \psi e^{-iEt/\hbar} dq}{\int \psi^* e^{iEt/\hbar} \psi e^{-iEt/\hbar}\, dq} \tag{16.4-3}$$

Since the operator $\widehat{A}$ contains no time dependence, the time-dependent factors cancel:

$$\boxed{\langle A \rangle = \frac{\int \psi^* \widehat{A} \psi dq}{\int \psi^* \psi dq}} \tag{16.4-4}$$

The expectation value can be obtained from the coordinate wave function and is time-independent if the wave function is the product of a coordinate factor and a time factor. A state corresponding to such a wave function is called *a stationary state*, and corresponds to a standing wave.

Normalization

There is a conventional way to simplify the formula for an expectation value. We use the following fact, established in Problem 15.5: *If any wave function that satisfies the Schrödinger equation is multiplied by an arbitrary constant it will still satisfy the Schrödinger equation and will give the same value for any expectation value.*

EXAMPLE 16.9

Show that the formula in Eq. (16.4-1) for the expectation value is unchanged if Ψ is replaced by $C\Psi$, where C is any constant.

Solution

$$\langle A \rangle = \frac{\int C^* \Psi^* \widehat{A} C \Psi dq}{\int C^* \Psi^* C \Psi dq} = \frac{C^* C \int \Psi^* \widehat{A} \Psi dq}{C^* C \int \Psi^* \Psi dq} = \frac{\int \Psi^* \widehat{A} \Psi dq}{\int \Psi^* \Psi dq}$$

If we choose a value of a constant multiplying a wave function such that

$$\int \Psi^* \Psi \, dq = 1 \quad \text{(definition of normalization)} \tag{16.4-5}$$

the wave function Ψ is then said to be *normalized*. If a normalized wave function is used in Eq. (16.4-1), the denominator in the equation equals unity and

$$\langle A \rangle = \int \Psi^* \widehat{A} \Psi \, dq \quad \text{(if } \Psi \text{ is normalized)} \tag{16.4-6}$$

Some of the coordinate wave functions that we have written are multiplied by *normalization constants* such that the wave functions are normalized.

EXAMPLE 16.10

Show that if

$$\Psi(q, t) = \psi(q) e^{-iEt/\hbar}$$

and if Ψ is normalized then ψ is also normalized.

Solution

$$\int \Psi^* \Psi dq = 1 = \int \psi^*(q) e^{iEt/\hbar} \psi(q) e^{-iEt/\hbar} dq$$
$$= e^{-iEt/\hbar} e^{iEt/\hbar} \int \psi^*(q)\psi(q) dq = \int \psi^*(q)\psi(q) dq$$

EXAMPLE 16.11

Show that the particle-in-a-box energy eigenfunction given in Eq. (16.4-10) is normalized.

Solution

Outside of the range $0 < x < a$, the wave function vanishes. Therefore, we integrate only over the range $0 < x < a$:

$$\int_{-\infty}^{\infty} \psi_n^* \psi_n \, dx = \int_0^a \psi_n^* \psi_n dx = \left(\frac{2}{a}\right) \int_0^a \sin^2(n\pi x/a) dx = \left(\frac{2}{a}\right)\left(\frac{a}{n\pi}\right) \int_0^{n\pi} \sin^2(y) dy$$
$$= \left(\frac{2}{n\pi}\right) \int_0^{n\pi} \sin^2(y) dy = \frac{2}{n\pi}\left[\frac{y}{2} - \frac{\sin(2y)}{4}\right]_0^{n\pi}$$
$$= \frac{2}{n\pi}\left[\frac{n\pi}{2} - \frac{\sin(2n\pi)}{4} - 0 + 0\right] = \frac{2}{n\pi}\frac{n\pi}{2} = 1$$

where we have looked up the integral in Appendix C.

The Predictable Case and the Statistical Case

Part a of the fourth postulate states that if a mechanical variable is measured without experimental error, the outcome must be an eigenvalue of the operator corresponding to that variable. It does not tell which eigenvalue will occur in a single measurement even if the system is in a known state. Information about this comes from part b of the postulate, and we now explore this. There are two cases. For some systems, states, and variables, it is possible to make a precise prediction of the outcome of a measurement from knowledge of the wave function at the time of the measurement. We call this case the *predictable case*. For some states and some variables, the outcomes of individual measurements will be distributed over various eigenvalues, even though the state is the same before each measurement. We call this case the *statistical case*. The existence of the statistical case is one of the most striking differences between classical and quantum mechanics. We first examine the statistical case, which is more interesting and more complicated than the predictable case.

Position Measurements

A position measurement provides an important example of the statistical case. Consider a particle that moves parallel to the x axis. Assume that we make a set of position measurements with the state of the system corresponding to the same wave function, $\Psi(x, t)$, at the time of each measurement. The outcome of any measurement must be an eigenvalue of the position operator. The eigenfunction of the operator x is the *Dirac delta function* in Eq. (16.3-36). Any value of x can be an eigenvalue, denoted by a in Eq. (16.3-36). Any values of x can be an outcome of the position measurement.

The expectation value of x is

$$\langle x \rangle = \int \Psi(x,t)^* x \, \Psi(x,t) dx \tag{16.4-7}$$

where we assume that the wave function Ψ is normalized. Since the multiplication operator x commutes with multiplication by Ψ^* we can write

$$\langle x \rangle = \int x\Psi(x,t)^* \Psi(x,t) dx = \int x|\Psi(x,t)|^2 dx \tag{16.4-8}$$

where we use the fact that any quantity times its complex conjugate is equal to the square of the magnitude of the quantity (see Appendix B). If the wave function is a product of an energy eigenfunction and a time factor, the time factor cancels against its complex conjugate, as in Eq. (16.4-4):

$$\langle x \rangle = \int x|\Psi(x,t)|^2 dx = \int x|\psi(x)|^2 dx \tag{16.4-9}$$

EXAMPLE 16.12

Find the expectation value for the position of a particle in a one-dimensional box of length a for $n = 1$.

Solution

$$\langle x \rangle = \frac{2}{a}\int_0^a \sin\left(\frac{\pi x}{a}\right) x \sin\left(\frac{\pi x}{a}\right) dx = \frac{2}{a}\int_0^a x \sin^2\left(\frac{\pi x}{a}\right) dx = \frac{2}{a}\left(\frac{a}{\pi}\right)^2 \int_0^\pi y \sin^2(y) dy$$

where $y = \pi x/a$. We could look up the integral, but we will go through a little calculus for practice. Using a trigonometric identity

$$\int_0^{\pi} y\sin^2(y)dy = \frac{1}{2}\int_0^{\pi} y\,[1 - \cos(2y)]\,dy = \frac{1}{2}\int_0^{\pi} ydy - \frac{1}{8}\int_0^{2\pi} z\cos(z)dz$$

$$= \frac{\pi^2}{4} - \frac{1}{8}\int_0^{2\pi} z\cos(z)dz$$

where $z = 2y$. Integrating by parts,

$$\int_0^{2\pi} z\cos(z)dz = z\sin(z)|_0^{2\pi} - \int_0^{2\pi} \sin(z)dz = 0 + \cos(z)|_0^{2\pi} = 0$$

$$\int_0^{\pi} y\sin^2(y)\,dy = \frac{\pi^2}{4}$$

$$\langle x\rangle = \frac{2}{a}\left(\frac{a}{\pi}\right)^2\frac{\pi^2}{4} = \frac{a}{2} \tag{16.4-10}$$

Exercise 16.6

Find $\langle x\rangle$ for a particle in a one-dimensional box of length a for the $n = 2$ state. Look up the integral if you want to do so. Comment on the comparison between the value of $\langle x\rangle$ for $n = 1$ and the value for $n = 2$.

Probabilities and Probability Densities

Once we have an expectation value such as $\langle x\rangle$ in Example 16.12, we need to examine whether this prediction of a mean corresponds to a set of equal results or whether there can be a distribution of values. We need to discuss the probabilities of different outcomes. Probabilities can be visualized by thinking of a set of N discrete values of some variable: $w_1, w_2, w_3, \ldots, w_N$. The mean value of w is equal to

$$\langle w\rangle = \frac{1}{N}(w_1 + w_2 + \cdots + w_N) = \frac{1}{N}\sum_{i=1}^{N} w_i \tag{16.4-11}$$

where we introduce the notation for a sum. If some of the values are equal to other values in the set, we place all of the distinct values at the beginning of the set and number them from 1 to M. Let the number of the values in the entire set equal to w_1 be N_1, the number equal to w_2 be N_2, and so on up to N_M. If all members of the set are equally likely to be chosen the probability that a randomly chosen member of the set is equal to w_i is

$$\text{Probability of } w_i = \frac{N_i}{N} = p_i \tag{16.4-12}$$

where $p_i = N_i/N$. The mean value can be simplified by grouping the terms together that are equal to each other:

$$\langle w\rangle = \frac{1}{N}\sum_{i=1}^{M} N_i w_i = \sum_{w=1}^{M} p_i w_i \tag{16.4-13}$$

If u is a variable that can take on any real value in a certain range, we require a formula that is analogous to Eq. (16.4-13). We define the probability that u lies between u' and $u' + du$ by

$$\text{(Probability that } u \text{ lies between } u' \text{ and } u' + du) = f(u')du \tag{16.4-14}$$

The function $f(u)$ is called a *probability density* or a *probability distribution*. It is analogous to the probability p_i for the discrete case, and is a probability per unit length on the u axis. The mean value of u is given by an integral that is analogous to the sum in Eq. (16.4-13):

$$\langle u \rangle = \int u\, f(u)du \tag{16.4-15}$$

where the integral is over all values of the variable u. Comparison of Eq. (16.4-8) with Eq. (16.4-15) shows that the probability of finding the particle between x' and $x' + dx$ is equal to

$$\text{(Probability that } x' < x < x' + dx) = |\Psi(x', t)|^2 dx \tag{16.4-16}$$

where x' is some value of x. This corresponds to

$$\boxed{\text{(Probability density)} = |\Psi(x, t)|^2} \tag{16.4-17}$$

The probability density in this case is a probability per unit length on the x axis. This is an important result, which we generalize to three dimensions and to more than one particle. *The square of the magnitude of the wave function is the probability density for finding the particle or particles*. For the motion of a particle in three dimensions, the probability that the particle lies between x' and $x' + dx$ in the x direction, between y' and $y' + dy$ in the y direction, and between z' and $z' + dz$ in the z direction is analogous to that in Eq. (16.4-16)

$$\text{(Probability)} = |\Psi(x', y', z', t)|^2 dxdydz \tag{16.4-18}$$

so that

$$\boxed{\text{(Probability density)} = |\Psi(x, y, z, t)|^2} \tag{16.4-19}$$

This probability density is a probability per unit volume in three dimensions. For a system of more than one particle moving in three dimensions, the probability density is a probability per unit volume in a 6-dimensional space, a 9-dimensional space, and so forth.

For a stationary state the probability density is time-independent and is equal to the square of the magnitude of the coordinate wave function. For motion in one dimension,

$$|\Psi(x, t)|^2 = \psi(x)^* e^{iEt/\hbar} \psi(x) e^{-iEt/\hbar} = \psi^*(x)\psi(x) = |\psi(x)|^2 \tag{16.4-20}$$

A version of Eq. (16.4-20) can be written for a wave function that depends on more than one coordinate.

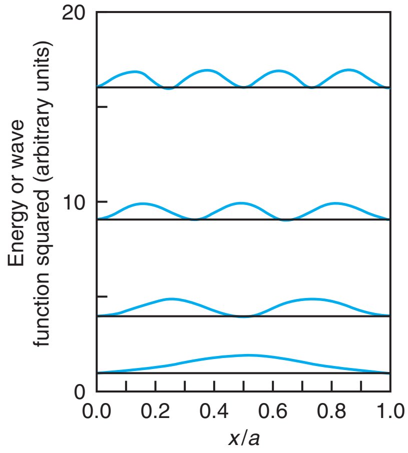

Figure 16.2 The Probability Density for Positions of a Particle in a One-Dimensional Box.

Figure 16.2 shows the probability density for the first four energy eigenfunctions of a particle in a box. Each graph is placed at a height proportional to the energy eigenvalue corresponding to that wave function. These probability densities are very different from the predictions of classical mechanics. If the state of a classical particle in a box is known, the probability at a given time would be nonzero at only one point, as in Figure 16.3a. Since the classical particle moves back and forth with constant

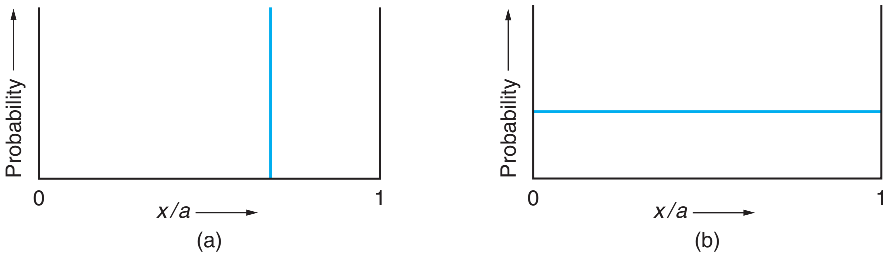

Figure 16.3 The Probability Density for Positions of a Particle in a One-Dimensional Box according to Classical Mechanics. (a) The instantaneous probability. (b) The probability averaged over a long time.

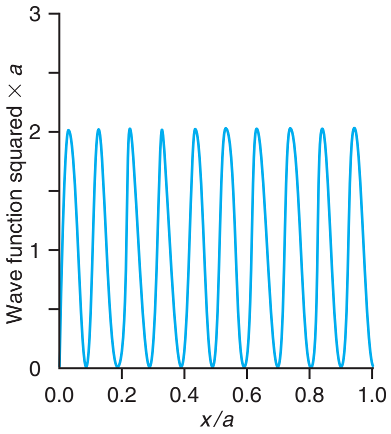

Figure 16.4 The Probability Density for Positions of a Particle in a One-Dimensional Box for $n = 10$.

speed, the classical probability density of a moving particle averaged over a long time is spread over the entire box and is uniform, as shown in Figure 16.3b.

The quantum mechanical probability density for finding a particle in a box is distributed over the entire box but is not uniform. There are points at which the probability density vanishes. However, if we consider a very large value of n, these points become closer and closer together, as schematically shown in Figure 16.4, which is drawn for $n = 10$. As n is larger and larger the width of the oscillations in the curve becomes smaller and smaller until it is smaller than any experimental inaccuracy, and the probability density resembles more nearly that of the long-time average classical probability distribution. This behavior conforms to the *correspondence principle*, which states that for sufficiently large energies and masses, the behavior predicted by quantum mechanics approaches the behavior predicted by classical mechanics. In this case, the classical behavior that is approached is a time-average behavior.

To obtain the probability that a particle is to be found in a finite region, we integrate $|\Psi|^2$ over that region. For motion parallel to the x axis the probability that x lies between b and c is

$$\text{(Probability that } b < x < c) = \int_b^c |\Psi(x,t)|^2 dx \qquad (16.4\text{-}21)$$

The total probability of all positions is equal to the integral of the square of the magnitude of the wave function over all values of the coordinates. This probability equals unity if the wave function is normalized.

EXAMPLE 16.13

For a particle in a one-dimensional box in the stationary state with $n = 2$, find the probability that the particle will be found in each of the regions making up thirds of the box.

Solution

For $0 < x < a/3$,

$$\begin{aligned}\text{(Probability)} &= \int_0^{a/3} \psi(x)^2 dx = \frac{2}{a}\int_0^{a/3} \sin^2\left(\frac{2\pi x}{a}\right) dx \\ &= \frac{2}{a}\frac{a}{2\pi}\int_0^{2\pi/3} \sin^2(y)dy = \frac{1}{\pi}\left[\frac{y}{2} - \frac{1}{4}\sin(2y)\right]\Bigg|_0^{2\pi/3} \\ &= \frac{1}{\pi}\left[\frac{\pi}{3} - \frac{1}{4}\sin(4\pi/3)\right] = 0.402249\end{aligned}$$

The right one-third of the box will have the same probability as the left one-third because of the symmetry of the probability density. The probability of finding the particle in the center region will be

$$(\text{Probability}) = 1 - 2(0.402249) = 0.195501$$

The node in the wave function at $x = a/2$ results in a smaller probability for the middle third of the box than for the left third or right third of the box.

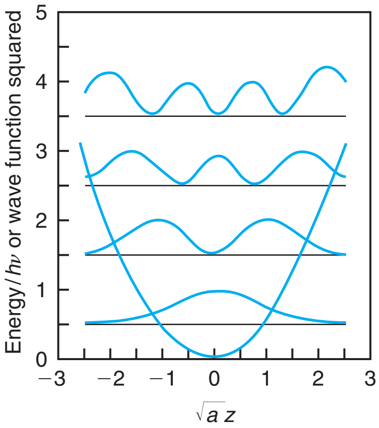

Figure 16.5 The Probability Density for the First Few Energy Eigenstates of the Harmonic Oscillator.

Figure 16.5 shows the probability densities for the first few energy eigenfunctions of a harmonic oscillator. The horizontal axis for each graph is placed at a height in the figure equal to its energy eigenvalue, and the potential energy is also plotted in the figure. The classical turning point for each state is located where the axis for that state crosses the potential energy curve, since that is the point where the classical energy equals the potential energy and the kinetic energy vanishes. Classical mechanics predicts that the oscillator cannot go beyond the turning point. For the quantum-mechanical harmonic oscillator the probability density is nonzero in the classically forbidden region. This penetration into a classically forbidden region is called *tunneling*. The name was chosen because a tunnel into a hillside allows access to a location under an inaccessible location of high gravitational potential energy.

EXAMPLE 16.14

Calculate the probability that the harmonic oscillator will be found in the classically forbidden region for the $v = 0$ state.

Solution

For a classical energy equal to the quantum mechanical energy for $v = 0$, the turning point is given by

$$x_t^2 = \frac{h\nu}{k} = \frac{h}{k}\frac{1}{2\pi}\sqrt{\frac{k}{m}} = \frac{\hbar}{\sqrt{km}} = \frac{1}{a}$$

$$|x_t| = \sqrt{\frac{1}{a}}$$

The probability that the harmonic oscillator is in the classically permitted region is:

$$(\text{Probability}) = \left(\frac{a}{\pi}\right)^{1/2}\int_{-\sqrt{1/a}}^{\sqrt{1/a}} e^{-ax^2}\,dx = 2\left(\frac{a}{\pi}\right)^{1/2}\int_0^{\sqrt{1/a}} e^{-ax^2}\,dx$$

where we have used the fact that since the integrand is an even function, the integral from 0 to $\sqrt{1/a}$ is equal to half of the integral from $-\sqrt{1/a}$ to $\sqrt{1/a}$. This integral is related to the *error function*, which is discussed in Appendix C. The error function is defined by the equation:[3]

$$\text{erf}(z) = \frac{2}{\sqrt{\pi}}\int_0^z e^{-y^2}dy \quad (\text{definition}) \qquad (16.4\text{-}22)$$

---

[3] M. Abramowitz and I. A. Stegun, eds., *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, U.S. Government Printing Office, Washington, DC, 1964. See Appendix C.

This integral cannot be carried out explicitly. A table of its numerical value is found in Appendix C. We make the substitution $y = \sqrt{a}x$. From the table of values of the error function in Appendix C,

$$\text{(Probability)} = \frac{2}{\sqrt{\pi}} \int_0^1 e^{-y^2}\, dy = \operatorname{erf}(1) = 0.8427 \tag{16.4-23}$$

The probability that the oscillating particle is farther away from its equilibrium position than the classical turning point is $1.0000 - 0.8427 = 0.1573$, or 15.73% (7.86% probability of being past either end of the classically permitted region). This probability is represented by the two shaded areas in Figure 16.6, which shows the probability density for the $v = 0$ state superimposed on a graph of the potential energy function.

Exercise 16.7

Calculate the value of the following ratio for $v = 0$ state of the harmonic oscillator

$$\text{Ratio} = \frac{|\psi_0(x_t)|^2}{|\psi_0(0)|^2}$$

Explain in words what this ratio represents.

If a region is small enough, the probability is approximately equal to $|\Psi|^2$ multiplied by the length or volume of the region. For motion of one particle in one dimension and for a sufficiently small value of Δx,

$$\text{(Probability that } x' < x < x' + \Delta x) \approx |\Psi(x', t')|^2 \Delta x \quad \text{(for a small value of } \Delta x) \tag{16.4-24}$$

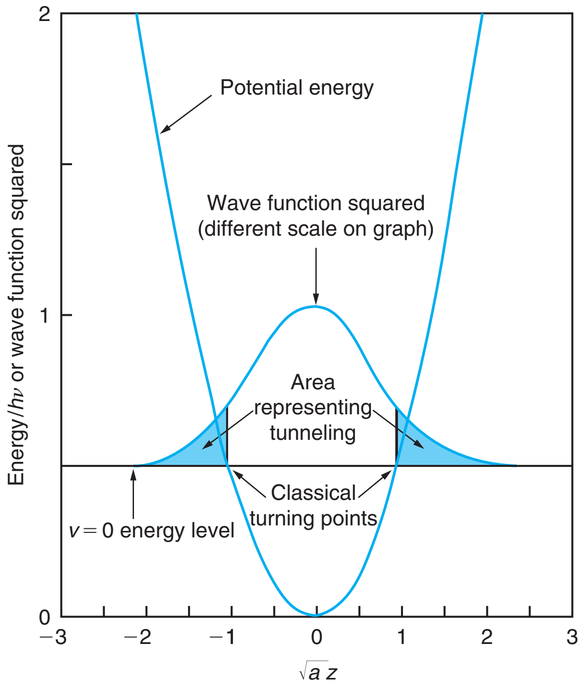

Figure 16.6 The Probability Density of a Harmonic Oscillator in Its Ground State, Showing Tunneling.

For motion of one particle in three dimensions and for sufficiently small $\Delta x \Delta y \Delta z$

$$\begin{pmatrix}\text{Probability that the particle} \\ \text{is in } \Delta x \Delta y \Delta z \text{ at time } t'\end{pmatrix} \approx |\Psi(x', y', z', t')|^2 \Delta x \Delta y \Delta z \tag{16.4-25}$$

For a region of appreciable size, the integration in Eq. (16.4-21) must be carried out.

For a stationary state, the time-dependent wave function Ψ in Eq. (16.4-24) or Eq. (16.4-25) can be replaced by the coordinate wave function ψ.

EXAMPLE 16.15

For the $n_x = 1$, $n_y = 1$, $n_z = 1$ state of a particle in a three-dimensional box, find the probability that the particle is in a small rectangular region at the center of the box such that the length of the region in each direction is equal to 1.000% of the length of the box in that direction. Compare your probability with the fraction of the volume of the box represented by your region.

Solution

The dimensions of the box are a by b by c.

$$\begin{aligned}\text{Probability} \approx \psi^* \psi \Delta x \Delta y \Delta z &= \left(\frac{8}{abc}\right) \sin^2(\pi x/a) \sin^2(\pi y/b) \sin^2(\pi z/c) \Delta x \Delta y \Delta z \\ &\approx \left(\frac{8}{abc}\right) \sin^6(\pi/2) \Delta x \Delta y \Delta z \\ &\approx \left(\frac{8}{abc}\right)(1.000)(0.01000a)(0.01000b)(0.01000c) \\ &\approx 8(0.01000)^3 = 8.000 \times 10^{-6}\end{aligned}$$

This value is 8 times as large as it would be if the probability were uniform within the box.

Exercise 16.8

Repeat the calculation of the previous example for the $n_x = 2$, $n_y = 2$, $n_z = 2$ state. Explain your result.

Distinguishing the Predictable Case from the Statistical Case

A common measure of the "spread" or "width" of a probability distribution is the *standard deviation*, which is defined for the measurement of a variable A by

$$\sigma_A = \left(\langle A^2 \rangle - \langle A \rangle^2\right)^{1/2} \quad \begin{pmatrix}\text{definition of the} \\ \text{standard deviation}\end{pmatrix} \tag{16.4-26}$$

The square of the standard deviation is called the *variance*. Equation (16.4-26) can also be written

$$\sigma_A = \langle (A - \langle A \rangle)^2 \rangle^{1/2} \tag{16.4-27}$$

Exercise 16.9

Show that Eq. (16.4-26) and Eq. (16.4-27) are equivalent.

In the predictable case all outcomes of repeated measurements will be equal to each other and to the mean value. The standard deviation will equal zero. In the statistical case the outcomes will vary and the standard deviation will be nonzero.

EXAMPLE 16.16

Find σ_x, the standard deviation of the position of a particle in a one-dimensional box of length a for the $n = 1$ state.

Solution

$$\langle x^2\rangle = \frac{2}{a}\int_0^a \sin\left(\frac{\pi x}{a}\right) x^2 \sin\left(\frac{\pi x}{a}\right) dx$$
$$= \frac{2}{a}\left(\frac{a}{\pi}\right)^3 \int_0^\pi y^2 \sin(y)dy = a^2\left[\frac{1}{3} - \frac{1}{2\pi^2}\right] = 0.282673a^2$$

From Example 16.12 we have $\langle x\rangle = a/2$, so that

$$\sigma_x = \left[0.282673a^2 - (a/2)^2\right]^{1/2} = 0.180756a$$

The fact that the standard deviation is nonzero shows that the statistical case applies. Inspection of the probability distribution also reveals this fact, since it is nonzero at more than one point.

EXAMPLE 16.17

Calculate the probability that a particle in a one-dimensional box of length a will be found within one standard deviation of its mean position if the wave function is the $n = 1$ energy eigenfunction.

Solution

The probability is given by integrating the probability density from $\langle x\rangle - \sigma_x$ to $\langle x\rangle + \sigma_x$:

$$(\text{Probability}) = \frac{2}{a}\int_{0.319244a}^{0.6807566a} \sin^2\left(\frac{\pi x}{a}\right) dx = \frac{2}{\pi}\int_{1.00293}^{2.13866} \sin^2(y)dy$$
$$= \frac{2}{\pi}\left[\frac{y}{2} - \frac{\sin(2y)}{4}\right]\Bigg|_{1.00293}^{2.13866} = 0.65017$$

For most probability distributions, approximately two-thirds of the probability lies within one standard deviation of the mean.

The probability distribution for the harmonic oscillator in the $v = 0$ state is an example of a *Gaussian distribution*, which is defined by

The Gaussian distribution is name for Carl Friedrich Gauss, 1777–1855, a great German mathematician who made many contributions to mathematics.

$$f(u) = \frac{1}{\sqrt{2\pi}\sigma} e^{-(u-\mu)^2/2\sigma^2} \quad \text{(Gaussian distribution)} \qquad (16.4\text{-}28)$$

where μ is the mean value and where σ is the standard deviation. The Gaussian distribution is also called the *normal distribution* and if its standard deviation equals unity, it is called the *standard normal distribution*.

The predictable case is always identifiable by calculating the standard deviation of the measurement. Here is an important fact: *If a system is in a state corresponding to an eigenfunction of the variable to be measured, the measurement belongs to the predictable case*.

EXAMPLE 16.18

For a particle in a one-dimensional box, find $\langle E \rangle$ and σ_E for the $n = 1$ stationary state.

Solution

$$\sigma_E = \left[\langle E^2 \rangle - \langle E \rangle^2\right]^{1/2}$$

$$\langle E \rangle = \int \psi_1^* \widehat{H} \psi dx = \int \psi_1^* E_1 \psi_1 dx = E \int \psi_1^* \psi_1 dx = E_1 = \frac{h^2}{8ma^2}$$

$$\langle E^2 \rangle = \int \psi_1^* \widehat{H}^2 \psi_1 dx = \int \psi_1^* {E_1}^2 \psi_1 dx = E_1^2 \int \psi_1^* \psi_1 dx = E_1^2$$

where we have used the fact that $\widehat{H}^2 = \widehat{H}\widehat{H}$. The standard deviation vanishes:

$$\sigma_E = (E_1^2 - E_1^2)^{1/2} = 0$$

The outcome of the energy measurement is completely predictable if the particle is in this stationary state, which corresponds to an energy eigenfunction.

Exercise 16.10

a. For a general system whose wave function ψ_j is an eigenfunction of the operator $\widehat{A}$ with eigenvalue a_j, show that $\langle A \rangle = a_j$ and that $\sigma_A = 0$.

b. For a one-dimensional harmonic oscillator, find $\langle E \rangle$ and σ_E for the state corresponding to the $v = 1$ energy eigenfunction.

Wave Functions That Are Not Energy Eigenfunctions

The wave function of a system at a given instant can be any function that obeys the proper boundary conditions. There is no requirement that it must obey the time-independent Schrödinger equation. However, since the energy eigenfunctions are a complete set, any wave function at a fixed time can be written as a linear combination of energy eigenfunctions, as in Eqs. (15.3-20) and (16.3-35) with t set equal to zero.

EXAMPLE 16.19

For a one-dimensional harmonic oscillator, find $\langle E \rangle$ and σ_E if the state just prior to the measurement corresponds to the normalized wave function

$$\psi = \sqrt{\frac{1}{2}}(\psi_0 + \psi_1)$$

where ψ_0 and ψ_1 are the first two energy eigenfunctions, given in Eqs. (15.4-10) and (15.4-11).

Solution

We use the fact that ψ_0 and ψ_1 are normalized and orthogonal to each other.

$$\langle E\rangle = \frac{1}{2}\int_{-\infty}^{\infty}(\psi_0^* + \psi_1^*)\widehat{H}(\psi_0 + \psi_1)dx = \frac{1}{2}\int_{-\infty}^{\infty}(\psi_0^* + \psi_1^*)(E_0\psi_0 + E_1\psi_1)dx$$

$$= \frac{1}{2}\left[E_0\int_{-\infty}^{\infty}\psi_0^*\psi_0 dx + E_1\int_{-\infty}^{\infty}\psi_0^*\psi_1 dx + E_0\int_{-\infty}^{\infty}\psi_1^*\psi_0\, dx + E_1\int_{-\infty}^{\infty}\psi_1^*\psi_1 dx\right]$$

$$= \frac{1}{2}(E_0 + 0 + 0 + E_1) = \frac{1}{2}(E_0 + E_1) = \frac{1}{2}\left(\frac{1}{2}h\nu + \frac{3}{2}h\nu\right) = h\nu$$

$$\langle E^2\rangle = \frac{1}{2}\int_{-\infty}^{\infty}(\psi_0^* + \psi_1^*)\widehat{H}^2(\psi_0 + \psi_1)\, dx$$

$$= \frac{1}{2}\int_{-\infty}^{\infty}(\psi_0^* + \psi_1^*)(E_0^2\psi_0 + E_1^2\psi_1)$$

When we multiply out the integrand, there are four terms. The terms that contain both ψ_0 and ψ_1 vanish after integration because they are orthogonal. The integral of ψ_0^2 or ψ_1^2 equals unity by normalization. We now have

$$\langle E^2\rangle = \frac{1}{2}(E_0^2 + E_1^2) = \frac{5}{4}(h\nu)^2$$

$$\sigma_E = \left(\langle E^2\rangle - \langle E\rangle^2\right)^{1/2} = \left[\frac{5}{4}(h\nu)^2 - (h\nu)^2\right]^{1/2} = \frac{h\nu}{2}$$

This example shows that the statistical case applies if the wave function just prior to the measurement is not an eigenfunction of the operator corresponding to the variable being measured.

If the wave function at a certain time is given by a linear combination such as that in Example 16.19, the time-dependent wave function is determined by this function and the time-dependent Schrödinger equation.

EXAMPLE 16.20

If the wave function at $t = 0$ is that of the preceding example, we know from Eq. (15.3-20) that the wave function at time t is

$$\Psi(q,t) = \sqrt{\frac{1}{2}}\left(\psi_0(q)\, e^{-iE_0t/\hbar} + \psi_1(q)\, e^{-iE_1t/\hbar}\right)$$

a. Show that $\langle E\rangle$ is time-independent.

b. Show that σ_E is time-independent.

Solution

a.

$$\langle E\rangle = \frac{1}{2}\int(\psi_0^*(q)e^{iE_0t/\hbar} + \psi_1^*(q)e^{iE_1t/\hbar})\widehat{H}(\psi_0(q)e^{-iE_0t/\hbar} + \psi_1(q)e^{-iE_1t/\hbar})dq$$

$$= \frac{1}{2}\int(\psi_0^*(q)e^{iE_0t/\hbar} + \psi_1^*(q)e^{iE_1t/\hbar})(E_0\psi_0(q)e^{-iE_0t/\hbar} + E_1\psi_1(q)e^{-iE_1t/\hbar})dq$$

When we multiply out the integrand, there are four terms. Since ψ_0 and ψ_1 are orthogonal to each other, the terms containing both ψ_0 and ψ_1 vanish after integration.

$$\begin{aligned}\langle E\rangle &= \frac{1}{2}\int \psi_0^*(q)e^{iE_0t/\hbar}E_0\psi_0(q)e^{-iE_0t/\hbar}dq \\ &+ \frac{1}{2}\int \psi_1^*(q)e^{iE_1t/\hbar}E_1\psi_1(q)e^{-iE_1t/\hbar})dq\end{aligned}$$

We can factor the E values out of the integrals. The complex time factors cancel, and since ψ_0 and ψ_1 are normalized

$$\langle E\rangle = \frac{1}{2}(E_0 + E_1)$$

b. To show that $\langle E^2\rangle$ is time-independent, we carry out exactly the same steps as in part a except that we operate twice with $\widehat{H}$, obtaining equations exactly as in part a except that we have E^2 values instead of E values. The result is that

$$\langle E^2\rangle = \frac{1}{2}(E_0^2 + E_1^2)$$

so that σ_E is time-independent and has the same value as in the previous example.

Since the eigenfunctions of any hermitian operator form a complete set, we can express a wave function at a fixed time as the following linear combination

$$\psi = \sum_{k=1}^{\infty} c_k f_k^* \tag{16.4-29}$$

where f_1, f_2, and so on are eigenfunctions of a quantum-mechanical operator $\widehat{A}$. We substitute the expansion of Eq. (16.4-29) into the expression for the expectation value $\langle A\rangle$:

$$\langle A\rangle = \int \psi^*\widehat{A}\psi dq = \sum_{j=1}^{\infty}\sum_{k=1}^{\infty} c_j^* c_k a_k \int f_j^* f_k dq \tag{16.4-30}$$

where a_k is the eigenvalue of $\widehat{A}$ corresponding to f_k. We have used the eigenfunction property, have factored the constants out of the integrals, and have exchanged the order of integrating and summing. This exchange is acceptable if the sums and integrals are uniformly convergent, which means that the sum and the integral converge with at least a certain rate for all values of the variables on which they depend after summation or integration.

Since the functions $f_1, f_2, \ldots$ are orthogonal to each other, those integrals in which $j \neq k$ will vanish, and since the functions are normalized the integrals with $j = k$ will equal unity. We write

$$\int f_j{}^* f_k dq = \delta_{jk} = \begin{cases}1 & \text{if } j = k \\ 0 & \text{if } j \neq k\end{cases} \tag{16.4-31}$$

This equation defines the quantity δ_{jk}, which equals unity when its two indices are equal to each other and equals zero otherwise. It is called the *Kronecker delta*. When the sum over k is performed, only the $j = k$ term will be nonzero. The sum over k collapses to a single term with $k = j$:

$$\langle A\rangle = \sum_{j=1}^{\infty}\sum_{k=1}^{\infty} c_j^* c_k a_k \delta_{jk} = \sum_{j=1}^{\infty} c_j^* c_j a_j = \sum_{j=1}^{\infty} |c_j|^2 a_j \tag{16.4-32}$$

Comparison of Eq. (16.4-32) with Eq. (16.4-13) shows that the probability that the eigenvalue a_j will occur is

$$\text{Probability of } a_j = p_j = |c_j|^2 \tag{16.4-33}$$

Exercise 16.11

Find the probability of each of the eigenvalues in Example 16.19 and in Example 16.20.

PROBLEMS

Section 16.4: Postulate 4 and Expectation Values

16.20 Show that the momentum operator $(\hbar/i)\partial/\partial x$ gives the correct sign for $\langle p_x\rangle$ for a traveling wave given by

$$\Psi = e^{i\kappa x}e^{-iEt/\hbar}$$

16.21 **a.** Find the eigenfunctions $\Phi(\phi)$ of the operator for the z component of the angular momentum, $\widehat{L}_z = -i\hbar(\partial/\partial\phi)$.

b. Since $\phi = 0$ and $\phi = 2\pi$ refer to the same location, impose the boundary condition

$$\Phi(0) = \Phi(2\pi)$$

and find the eigenvalues of $\widehat{L}_z$.

16.22 Carry out the integration to show that the harmonic oscillator coordinate wave function in Eq. (15.4-10) is normalized.

16.23 Obtain a formula for the expectation value of the potential energy of a harmonic oscillator in the $v = 1$ state. How does this relate to the total energy of the harmonic oscillator in this state?

16.24 **a.** For a particle in a hard box of length a, find the expectation value of the quantity p_x^4 for the $n = 1$ state.

b. Find the standard deviation of p_x^2. Compare it with the square of the standard deviation of p_x. Explain your result.

16.25 **a.** Draw sketches of the first two energy eigenfunctions of a particle in a one-dimensional box of length a. Without doing the integral explicitly, argue from the graphs that the two functions are orthogonal.

b. Draw sketches of the first two energy eigenfunctions of a harmonic oscillator. Without doing the integral explicitly, argue from the graphs that the two functions are orthogonal.

16.26 **a.** Show for a harmonic oscillator in the $v = 0$ state that $\langle\mathscr{V}\rangle = \langle\mathscr{K}\rangle$ where $\mathscr{V}$ is the potential energy and $\mathscr{K}$ is the kinetic energy. *Hint:* One way to proceed is to calculate $\langle\mathscr{K}\rangle$ and use the fact that $\langle\mathscr{K}\rangle + \langle\mathscr{V}\rangle = E$.

b. Do you think that this will also be true for the other energy eigenfunctions? Check it out for $v = 1$.

16.27 **a.** Calculate $\langle p_x^2\rangle$ for each of the first three energy eigenfunctions for the particle in a one-dimensional box. *Hint:* Use the energy eigenvalues to avoid detailed calculations.

b. Obtain a formula (a function of n) for $\langle p_x^2\rangle$ for a general energy eigenfunction of a particle in a one-dimensional box.

c. Find the limit of the expression of part b as $n \to \infty$.

16.28 From inspection of Figure 16.2, estimate the probability of finding the particle in the left one-third of the box for the $n = 1$ state. After making this estimate, make a calculation of the probability.

16.29 **a.** Find a formula representing the turning point for a classical harmonic oscillator that has the same energy as the $v = 1$ quantum-mechanical energy.

b. Construct an accurate graph of the square of the $v = 1$ wave function for a harmonic oscillator as a function of $\sqrt{a}\,z$.

c. Calculate the probability that a quantum-mechanical oscillator in the $v = 1$ state is farther from its equilibrium position than the turning-point value. You can use the identity

$$\int_0^x t^2 e^{-at^2}\,dt = \frac{\sqrt{\pi}}{4a^{3/2}}\operatorname{erf}(\sqrt{a}\,x) - \frac{x}{2a}e^{-ax^2}$$

16.30 **a.** Calculate the probability that a particle in a one-dimensional box will be found within one standard deviation of its mean position for the $n = 2$ stationary state. Compare your result with the value for the $n = 1$ state from the previous example.

b. Calculate the probability that a particle in a one-dimensional box will be found within one standard deviation of its mean position for the $n = 3$ stationary state.

16.31 **a.** Show that application of the definition of the standard deviation in Eq. (16.4-26) to the Gaussian probability distribution in Eq. (16.4-28) gives the same standard deviation as specified in that equation.

b. By comparison with the Gaussian distribution, find an expression for the standard deviation of the position of the harmonic oscillator in the $v = 0$ state.

c. For a Gaussian distribution, show that the probability that the variables lies between $\mu - \sigma$ and $\mu + \sigma$ is equal to 0.683.

16.32 For a particle in a one-dimensional box, find $\langle E\rangle$ and σ_E for the coordinate wave function

$$\psi = \sqrt{\frac{1}{3}}\psi_1 + \sqrt{\frac{2}{3}}\psi_2$$

where ψ_1 and ψ_2 are the first two energy eigenfunctions.

16.5 The Uncertainty Principle of Heisenberg

If the statistical case applies we want to be able to predict the uncertainty in a proposed measurement. If a single measurement is to be made, there is roughly a two-thirds probability that the result will lie within one standard deviation of the expectation value. We will use the standard deviation as a prediction of the uncertainty. In Example 16.16 we determined that the standard deviation of the position of a particle in a one-dimensional box of length a is equal to $0.180756a$ for the $n = 1$ state. We now find the standard deviation of the momentum for this state.

EXAMPLE 16.21

Find $\langle p_x\rangle$, $\langle p_x^2\rangle$, and σ_{p_x} for the $n = 1$ state of a particle in a one-dimensional box.

Solution

$$\langle p_x\rangle = \frac{2}{\pi}\int_0^a \sin\left(\frac{\pi x}{a}\right)\frac{\hbar}{i}\frac{d}{dx}\sin\left(\frac{\pi x}{a}\right)dx = \frac{2\hbar}{\pi i}\int_0^a \sin\left(\frac{\pi x}{a}\right)\cos\left(\frac{\pi x}{a}\right)dx = 0$$

$$\begin{aligned}\langle p_x^2\rangle &= \frac{2}{a}\int_0^a \sin\left(\frac{\pi x}{a}\right)(-\hbar^2)\frac{d^2}{dx^2}\sin\left(\frac{\pi x}{a}\right)dx \\ &= \frac{2}{a}\hbar^2\left(\frac{\pi}{a}\right)^2\int_0^a \sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{\pi x}{a}\right)dx \\ &= \frac{2}{a}\hbar^2\left(\frac{\pi}{a}\right)^2\frac{a}{2} = \frac{\hbar^2\pi^2}{a^2}\end{aligned}$$

$$\sigma_{p_x} = \left[\langle p_x^2\rangle - \langle p_x\rangle^2\right]^{1/2} = \langle p_x^2\rangle^{1/2} = \frac{\hbar\pi}{a} = \frac{h}{2a}$$

There is roughly a two-thirds probability that the momentum lies between $-h/2a$ and $h/2a$. The statistical case applies, as it did with the position. We can predict the mean and the standard deviation of a set of many measurements of the momentum, but it is not possible to predict the outcome of a single measurement.

The product $\sigma_x \sigma_{px}$ is a measure of the combined uncertainty of x and p_x, and is called an *uncertainty product*. This kind of uncertainty product is involved in the Heisenberg uncertainty principle. From Examples 16.16 and 16.21 the value of the uncertainty product of x and p_x for the $n = 1$ state of the particle in a one-dimensional box is

$$\sigma_x \sigma_{p_x} = (0.180756a)\frac{\hbar\pi}{a} = 0.56786\hbar = 0.09038h \tag{16.5-1}$$

Table 16.1 gives some values of σ_x, σ_{p_x}, and $\sigma_x \sigma_{p_x}$ for several states of a particle in a one-dimensional box.

The coordinate x and the momentum component p_x are examples of *conjugate variables* in the sense of Eq. (E-20) of Appendix E. The operators of this pair of variables do not commute, as shown in Example 16.4. The *Heisenberg uncertainty principle* is a general statement of the combined uncertainties of two conjugate variables: *The product of the uncertainties of two conjugate variables is always equal to or larger than* $\mathrm{h}/4\pi$, *where* h *is Planck's constant.* If we use the symbols Δx and Δp_x for the uncertainties of a coordinate and its conjugate momentum, then the uncertainty principle is

$$\boxed{\Delta x \Delta p_x\, \varepsilon \geq \frac{h}{4\pi} = \frac{\hbar}{2} \quad \text{(uncertainty principle)}} \tag{16.5-2}$$

The minimum value in Eq. (16.5-2) corresponds to the use of standard deviations as measures of uncertainty:

$$\Delta x = \sigma_x \tag{16.5-3}$$

and

$$\Delta p_x = \sigma_{p_x} \tag{16.5-4}$$

Table 16.1 Values of the Uncertainty Product for a Particle in a One-Dimensional Box

n	σx	σ_{p_x}	$\sigma_x \sigma_{p_x}$
1	$0.18076a$	$h/2a$	$0.09038h = 0.56786\hbar$
2	$0.26583a$	h/a	$0.26583h = 1.67029\hbar$
3	$0.27876a$	$3h/2a$	$0.41813h = 2.62720\hbar$
...	...	...	...
∞	$0.28868a$	∞	∞

Numerical Values for a Box of Length 10.0×10^{-10} m (Model for Pi Electrons in 1,3,5-Hexatriene)

n	σ_x/m	$\sigma_{p_x}/\mathrm{kg\,m\,s^{-1}}$	$\sigma_x \sigma_{p_x}/\mathrm{kg\,m^2\,s^{-1}}$
1	1.808×10^{-10}	3.313×10^{-25}	5.909×10^{-35}
2	2.626×10^{-10}	6.626×10^{-25}	1.761×10^{-34}
3	2.788×10^{-10}	9.939×10^{-25}	2.771×10^{-34}
...	...	...	...
∞	2.887×10^{-10}	∞	∞

Other measures of the uncertainty give a different minimum value. For a Gaussian probability distribution, the uncertainty in a prediction at the 95% probability level is equal to 1.96 times the standard deviation. At this level of uncertainty the right-hand side of Eq. (16.5-2) would be replaced by a larger value.

The value of the uncertainty product depends on the system and on the state considered. The uncertainty product for the $n = 1$ state of the particle in a box, $0.09038h$, is slightly larger than $h/(4\pi)$, which equals $0.079577h$. The uncertainty product for the $v = 0$ state of the harmonic oscillator is exactly equal to $h/(4\pi)$ and seems to be the smallest uncertainty product for any system and any state. (See Problem 16.36.) The uncertainty product for higher-energy states is larger.

Coordinates and momenta are not the only variables that have nonzero uncertainty products. There is a general relation

$$\Delta A \Delta B \geq \left| \frac{1}{2} \int \psi^* \left[\widehat{A}, \widehat{B} \right] \psi \, dq \right| \qquad (16.5\text{-}5)$$

where $\left[\widehat{A}, \widehat{B}\right]$ is the commutator of the operators $\widehat{A}$ and $\widehat{B}$.[4] From the commutator of two angular momentum components, we can see that two components of the angular momentum obey an uncertainty relation. (See Problem 16.16.)

Exercise 16.12

Use Eqs. (16.5-5) and (16.3-16) to obtain the same uncertainty relation for x and p_x that was given in Eq. (16.5-2).

The uncertainty principle is a rather subtle concept, and deserves more discussion than we give it in this book. However, the main idea is that it requires that the statistical case applies to at least one of a conjugate pair of variables, and if the predictable case applies to one of the variables, the other variable has an infinite uncertainty.

EXAMPLE 16.22

Find $\langle p_x \rangle$ and σ_{p_x} for a free particle in a state corresponding to the wave function of Eq. (15.3-28) with F set equal to zero.

Solution

We cancel the time-dependent factors to obtain

$$\langle p_x \rangle = \frac{\dfrac{\hbar}{i} D^* D \displaystyle\int e^{-i\kappa x} \frac{d}{dx} e^{i\kappa x} dx}{D^* D \displaystyle\int e^{-i\kappa x} e^{i\kappa x} dx} \hbar\kappa = \hbar\kappa \frac{D^* D \displaystyle\int e^{-i\kappa x} e^{i\kappa x} dx}{D^* D \displaystyle\int e^{-i\kappa x} e^{i\kappa x} dx} = \hbar\kappa \frac{\displaystyle\int dx}{\displaystyle\int dx}$$

We specify that the limits of the integrals are $-L$ and L, with the intention of taking the limit that $L \to \infty$ since all values of x are possible. We cancel the integrals in the last quotient of integrals prior to taking the limit, and obtain

$$\langle p_x \rangle = \hbar\kappa \qquad (16.5\text{-}6)$$

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[4] Levine (*Quantum Chemistry*, 5th ed., Prentice-Hall, Englewood Cliffs, NJ, 2000, pp. 96, 206) assigns the proof as a homework problem. A lot of hints are included, but it is a fairly long proof.

To calculate σ_{px}, we require $\langle p_x^2\rangle$, which is obtained in the same way as $\langle p_x\rangle$ except that the square of the momentum operator is used. The result is

$$\langle p_x^2\rangle = \hbar^2\kappa^2 \tag{16.5-7}$$

The square of the standard deviation is:

$$\sigma_{px}^2 = \langle p_x^2\rangle - \langle p_x\rangle^2 = \hbar^2\kappa^2 - \hbar^2\kappa^2 = 0 \tag{16.5-8}$$

The uncertainty in one of a pair of conjugate variables can vanish only if the uncertainty in the other variable is infinite, so in this case the uncertainty in x is infinite. If the momentum is known exactly, we cannot say where the particle is with any finite uncertainty.

EXAMPLE 16.23

Write the integral that represents σ_x for the free particle of Example 16.22 and argue that its value is infinite.

Solution

We write the integrals prior to taking the limit that $L \to \infty$.

$$\langle x\rangle = \frac{D^*D\displaystyle\int_{-L}^{L} e^{-i\kappa x}xe^{i\kappa x}dx}{D^*D\displaystyle\int_{-L}^{L} e^{-i\kappa x}e^{i\kappa x}dx} = \frac{\displaystyle\int_{-L}^{L} xdx}{\displaystyle\int_{-L}^{L} dx} = \frac{L^2/2 - L^2/2}{2L} = 0$$

$$\langle x^2\rangle = \frac{D^*D\displaystyle\int_{-L}^{L} e^{-i\kappa x}x^2e^{i\kappa x}dx}{D^*D\displaystyle\int_{-L}^{L} e^{-i\kappa x}e^{i\kappa x}dx} = \frac{\displaystyle\int_{-L}^{L} x^2dx}{\displaystyle\int_{-L}^{L} dx} = \frac{L^3/3 + L^3/3}{2L} = \frac{L^2}{3}$$

$$s_x = \left(\frac{L^2}{3} - 0\right)^{1/2} = \left(\frac{L^2}{3}\right)^{1/2}$$

When the limit $L \to \infty$ is taken, this becomes infinite.

From the expectation value of the momentum of a free particle we can now justify the apparently arbitrary choice of sign that we made in Eq. (16.3-8). It appeared at that time that either $i\hbar\, d/dx$ or $-i\hbar\, d/dx$ could have been chosen as the operator for p_x. The free-particle wave function $De^{i\kappa x}$ corresponds to a positive value of $\langle p_x\rangle$, as shown in Example 16.22. If we combine this coordinate wave function with the appropriate time factor, $\exp(-iEt/\hbar)$, we obtain the time-dependent wave function

$$\Psi = D\exp^{i(\kappa x - Et/\hbar)} \tag{16.5-9}$$

which represents a traveling wave moving to the right (with positive value of p_x). If $i\hbar\, d/dx$ had been chosen for the p_x operator, a negative value for $\langle p_x\rangle$ would have resulted, indicating motion in the wrong direction.

Exercise 16.13

Show that taking the opposite sign for the momentum operator leads to a negative value of $\langle p_x\rangle$ for the wave function of Eq. (15.3-28) if $F = 0$ is taken.

The speed of propagation of the de Broglie wave is not necessarily the same as the expectation value of the momentum divided by the mass of the particle. This fact is somewhat surprising, but reminds us of the fact that the de Broglie wave is not a directly measurable quantity.

EXAMPLE 16.24

The energy of a free particle moving in the x direction is

$$E = \frac{\hbar^2\kappa^2}{2m}$$

so the time-dependent wave function can be written as

$$\Psi = D\exp\left[i\left(\kappa x - \frac{\hbar^2\kappa^2 t}{2m\hbar}\right)\right] = D\exp\left[i\kappa\left(x - \frac{\hbar\kappa t}{2m}\right)\right]$$

Find an expression for the speed of propagation of the de Broglie wave and compare it with the expectation value of the speed of the particle (the momentum divided by the mass).

Solution

The speed is obtained by determining the speed at which a node of the de Broglie wave moves. By inspection of the arguments of the complex exponentials, the speed of the de Broglie wave is

$$\text{speed} = \frac{\hbar\kappa}{2m}$$

We also have

$$\langle p_x \rangle = \hbar\kappa$$

so that

$$\langle v_x \rangle = \frac{\hbar\kappa}{m}$$

which differs by a factor of 2 from the speed of the de Broglie wave.

The Time–Energy Uncertainty Relation

Like position and momentum, energy and time obey an uncertainty relation:

$$\Delta E \Delta t \geq \frac{h}{4\pi} \tag{16.5-10}$$

The time–energy uncertainty relation is even more mysterious than that of position and momentum, but it has been verified by many experiments. Time is not a mechanical variable that can be expressed in terms of coordinates and momenta and does not correspond to any quantum mechanical operator, so we cannot calculate a standard deviation of a time. The standard interpretation of the time–energy uncertainty relation is that if Δt is the time during which the system is known to be in a given state (the *lifetime of the state*) then there is a minimum uncertainty ΔE in the energy of the system that is given by

$$\Delta E \geq \frac{h}{4\pi\Delta t} \tag{16.5-11}$$

This relation must hold even if the state corresponds to a definite energy eigenvalue, for which $\sigma_E = 0$. When a system makes a transition into such a state, the energy of the system does not immediately attain the new energy eigenvalue, but has an inherent uncertainty that rapidly decreases as time passes. This uncertainty in the energy is important only if the system is observed very soon after making a transition, but it can be observed experimentally. It imposes a broadening on spectral lines that is larger if the system spends a shorter time in a given state. This phenomenon is known as *uncertainty broadening*.

EXAMPLE 16.25

The lowest energy eigenvalue for a hydrogen atom is −13.6 eV. Calculate the uncertainty in the energy if a hydrogen atom is known to have been in the state corresponding to this energy for 1.0 nanosecond.

Solution

$$\begin{aligned}\Delta E \geq \frac{\hbar}{2}\frac{1}{\Delta t} &= \frac{6.6261\times 10^{-34}\ \mathrm{J\,s}}{4\pi}\frac{1}{1.0\times 10^{-9}\ \mathrm{s}} = 5.3\times 10^{-26}\ \mathrm{J}\\ &= (5.3\times 10^{-26}\ \mathrm{J})\left(\frac{1\ \mathrm{eV}}{1.6022\times 10^{-19}\ \mathrm{J}}\right)\\ &= 3.3\times 10^{-7}\ \mathrm{eV}\end{aligned}$$

This uncertainty is smaller than the energy eigenvalue by a factor of 2.4×10^{-8}, and would be even smaller if the time period were longer.

Exercise 16.14

If the energy of a system is to be measured to an uncertainty of 1.0×10^{-21} J, find the minimum time during which the system must be in the state at the measured energy.

PROBLEMS

Section 16.5: The Uncertainty Principle of Heisenberg

16.33 **a.** A free electron (not confined in any kind of box) is known at some specific time to be passing through a region 10.0 Å in length and is known to be moving toward the positive end of the x axis. Find the minimum uncertainty in p_x and the corresponding uncertainty in v_x, the x component of its velocity.

b. If the expectation value of the kinetic energy corresponding only to the motion of the electron in the x direction is equal to 5.00 eV, estimate the smallest upper bound of v_x and the largest lower bound of v_x.

16.34 A free electron is known to be passing through a three-dimensional cubical region that is 10.0 Å on a side at a certain time.

a. Estimate the uncertainty in each of the three components of its momentum.

b. Estimate the uncertainty in the energy of the electron if its energy is near 1.00 eV.

16.35 **a.** Calculate the uncertainty product $\sigma_x\sigma_{p_x}$ for a particle in a box of length a for the $n = 1$ state.

b. Without doing any calculations, state whether the uncertainty product for the $n = 2$ state would be smaller than, equal to, or larger than the product for the $n = 1$ state.

c. Calculate the uncertainty product $\sigma_x\sigma_{p_x}$ for a particle in a box of length a for the $n = 2$ state. Compare it with the value for the $n = 1$ state, and explain the difference.

d. Calculate the uncertainty product $\sigma_x\sigma_{p_x}$ for a particle in a box of length a for the $n = 3$ state. Compare it with the value for the $n = 2$ state, and explain the difference.

e. Obtain a formula for $\sigma_x\sigma_{p_x}$ for a particle in a box of length a as a function of n. Find the limit as $n \to \infty$.

16.36 **a.** Calculate the uncertainty product $\sigma_x\sigma_{p_x}$ for a harmonic oscillator in the $v = 0$ state.

b. Without doing any calculations, state whether the uncertainty product for the $v = 1$ state would be smaller than, equal to, or larger than the product for the $v = 0$ state.

c. Calculate the uncertainty product $\sigma_x\sigma_{p_x}$ for a harmonic oscillator for the $v = 1$ state. Compare it with the value for the $v = 0$ state, and explain the difference.

d. Calculate the uncertainty product $\sigma_x\sigma_{p_x}$ for a harmonic oscillator for the $v = 2$ state. Compare it with the value for the $v = 1$ state, and explain the difference.

16.37 **a.** Find the commutator $[\widehat{x}, \widehat{L}_z]$.

b. Using Eq. (16.5-5), find an uncertainty relation for $\widehat{x}$ and $\widehat{L}_z$ for a particular state, the lowest-energy state of a particle in a cubical box of size a by a by a.

16.38 Construct a graph representing the time-average probability density for finding a harmonic oscillator at a given position according to classical mechanics. Start your graph at $x = -0.99x_t$ and end it at $0.99x_t$, where x_t represents the magnitude of the coordinate at the turning point. Comment on the relative value at the turning points.

16.39 Consider a particle in a one-dimensional box of length a with a wave function at $t = 0$ given by

$$\Psi(x, 0) = \frac{1}{\sqrt{2}}(\psi_1 + \psi_2)$$

where ψ_1 and ψ_2 are the first two energy eigenfunctions.

a. Construct a graph of the wave function at $t = 0$.

b. Write expressions for the real and imaginary parts of $\Psi(q, t)$ at time $t = 2ma^2/h$.

c. Write an expression for $\Psi(x, t)$ at time $t = 4ma^2/h$. Construct a graph of the magnitude of the wave function at this time.

d. Write an expression for $\Psi(x, t)$ at time $t = 2ma^2/h$. Draw separate graphs of the real and imaginary parts of the wave function at this time.

e. Does this wave function represent a standing wave? Does it satisfy the time-independent Schrödinger equation?

f. Calculate $\langle E\rangle$ and σ_E at time $t = 0$.

g. Calculate $\langle E\rangle$ and σ_E at time $t = 2ma^2/h$.

h. Calculate $\langle E\rangle$ and σ_E at time $t = 4ma^2/h$.

16.6

Postulate 5. Measurements and the Determination of the State of a System

The fifth and final postulate gives information about the state of a system following a measurement.

> **Postulate 5.** *Immediately after an error-free measurement of the mechanical variable* A *in which the outcome was the eigenvalue* $\mathrm{a_j}$, *the state of the system corresponds to a wave function that is an eigenfunction of* $\widehat{\mathrm{A}}$ *with eigenvalue equal to* $\mathrm{a_j}$.

This postulate says very little about the state of the system prior to a single measurement of the variable A, because the act of measurement can change the state of the system. To understand physically how a measurement can change the state of a system consider the determination of the position of a particle by the scattering of electromagnetic radiation. When an airplane reflects a radar wave, the effect on the airplane is negligible because of the large mass of the airplane. When an object of small mass such as an electron scatters ultraviolet light or X-rays, the effect is not negligible.

EXAMPLE 16.26

Assume that we want to find the location of an electron in a box of length 1.0 nm to the nearest 0.1 nm (one-tenth of the length of the box). This requires X-rays with wavelength no longer than 0.1 nm, since the scattering of a wave can reveal the position of the scatterer only to an uncertainty of one wavelength. Compare the energy of a photon of wavelength 0.10 nm with E_1 for electron in a one-dimensional box of length 1.0 nm.

Solution

$$\begin{aligned} E(\text{photon}) &= h\nu = \frac{hc}{\lambda} = \frac{(6.6261 \times 10^{-34}\ \text{J s})(3.00 \times 10^{8}\ \text{m s}^{-1})}{1.00 \times 10^{-10}\ \text{m}} \\ &= 1.99 \times 10^{-15}\ \text{J} \\ E(\text{electron}) &= \frac{h^2}{8ma^2} = \frac{(6.6261 \times 10^{-34}\ \text{J s})^2}{8(9.1094 \times 20^{-31}\text{kg})(1.00 \times 10^{-9}\ \text{m})^2} \\ &= 6.02 \times 10^{-20}\ \text{J} \end{aligned}$$

The photon energy is about 30,000 times as large as the kinetic energy of the electron, so that the energy transferred to the electron in a measurement can be much larger than the original kinetic energy of the electron. We cannot use electromagnetic radiation to determine the position of an electron without drastically changing its state.

Let us try to find out what we can about the state of the system if we make a single measurement of a variable A with outcome a_j, one of the eigenvalues of the operator $\widehat{A}$. Prior to the measurement the wave function could have been represented by a linear combination of all of the eigenfunctions of the operator. From our discussion of Postulate 4, we know that if the outcome of the measurement is the eigenvalue a_j, then we can say that the coefficient of at least one of the eigenfunctions belonging to that eigenvalue was nonzero in this linear combination. However, this is all that we can say about the state prior to the measurement.

Information about the State of a System after a Measurement

After the measurement the wave function is an eigenfunction belonging to the eigenvalue that was the result of the measurement. If the eigenvalue is nondegenerate, the measurement has put the system it into the state corresponding to that eigenvalue. If the outcome of a measurement of a variable A is an eigenvalue that is degenerate, the act of measurement has put it into a state corresponding to a linear combination of all eigenfunctions that correspond to that eigenvalue. Say that the outcome of the measurement of the variable A is a_i and that this eigenvalue has degeneracy g_i.

$$\psi(\text{after}) = \sum_{j=1}^{g_i} c_j f_j \tag{16.6-1}$$

where $f_1, f_2, \ldots, f_{g_i}$ are the eigenfunctions of $\widehat{A}$ corresponding to the observed eigenvalue a_i. Only the functions with the same value for the eigenvalue are included in the sum, but we do not know what the coefficients $c_1, c_2, c_3, \ldots, c_{g_i}$ are. We have gained some information, but we do not yet know exactly what the state is.

Exercise 16.15

Show that the linear combination in Eq. (16.6-1) is an eigenfunction of the operator $\widehat{A}$ for any set of values of $c_1, c_2, c_3, \ldots, c_{g_i}$, so long as all of the functions in the linear combination have the same eigenvalue of $\widehat{A}$.

If there are other variables whose operators commute with $\widehat{A}$, measurement of enough of these variables can put the system into a known state. We say that such a set of variables is a *complete set of commuting observables*. For example, assume that the operators $\widehat{A}$ and $\widehat{B}$ commute and that they have a set of common eigenfunctions f_{11}, $f_{12}, \ldots,\ f_{21},\ f_{22}, \ldots$ such that

$$\widehat{A}\, f_{ij} = a_i\, f_{ij} \tag{16.6-2}$$

$$\widehat{B}\, f_{ij} = b_j\, j_{ij} \tag{16.6-3}$$

Assume that a measurement of A gives the result a_k. The wave function immediately after this measurement is the same as in Eq. (16.6-1):

$$\psi' = \sum_{j=1}^{g_k} c'_j\, f_{kj} \tag{16.6-4}$$

where the sum now includes only those eigenfunctions of $\widehat{B}$ that are eigenfunctions of $\widehat{A}$ corresponding to the eigenvalue a_k. Assume that a measurement of B gives the result b_m. The state after this measurement corresponds to the wave function

$$\psi'' = f_{km} \tag{16.6-5}$$

If the variables A and B constitute a complete set of commuting observables the system is now in the state corresponding to the wave function f_{km}. If there are other commuting observables in the complete set, additional measurements must be made. We will see an important example of this principle in Chapter 17, when we will find that four variables constitute a complete set of commuting observables for the electronic motion of a hydrogen atom.

Information about the State Prior to a Measurement

A single measurement gives us information about the state after the measurement but says very little about the state prior to the measurement. Some information about the original wave function of a quantum mechanical system can be obtained by repeated measurements if we have some way to put the system back into the original state before each measurement or if we have a supply of identical systems, all of which are in the same state.

Consider the nondegenerate case, that each eigenfunction of the operator $\widehat{A}$ has a distinct eigenvalue. Since the set of eigenfunctions is assumed to be a complete set, the wave function immediately prior to a measurement of A can be represented as a linear combination of eigenfunctions of $\widehat{A}$, as in Eq. (16.3-34):

$$\psi(\text{prior}) = \sum_{j=1}^{\infty} c_j(\text{prior})\, f_j \tag{16.6-6}$$

We now make a set of many measurements of A, ensuring somehow that the system is in the same state prior to each measurement. Each outcome will be an eigenvalue of $\widehat{A}$. Let the fraction that results in the value a_j be equal to p_j. By Eq. (16.4-33),

$$|c_j(\text{prior})| = \sqrt{p_j} \tag{16.6-7}$$

If all of the measurements give the same result, say a_i, and if the state corresponding to f_i is nondegenerate, then p_i equals unity and we can assert that the state prior to the measurement must have been the state corresponding to f_i. If the measurements yield more than one value, we can determine the magnitudes of the c_j(prior) coefficients from the probabilities of the different eigenvalues. We cannot know the real and imaginary parts of each expansion coefficient, so we cannot know exactly what the wave function was prior to the measurements. If the eigenvalues are degenerate, we cannot even tell the magnitudes of the individual coefficients prior to the measurements, but can only get a collective value for each energy level.

EXAMPLE 16.27

The energy of a harmonic oscillator is measured repeatedly with the oscillator restored to the same unknown state before each measurement. The results are summarized as follows:

Value of the energy	Probability
$h\nu/2$	0.375
$3h\nu/2$	0.25
$5h\nu/2$	0.25
$7h\nu/2$	0.125

What can you say about the state prior to the measurement?

Solution

The only values obtained correspond to E_0, E_1, E_2, and E_3. The wave function just prior to the measurement must be represented by

$$\psi(\text{prior}) = c_0\psi_0 + c_1\psi_1 + c_2\psi_2 + c_3\psi_3$$

where

$$|c_0| = \sqrt{0.375}$$
$$|c_1| = \sqrt{0.25}$$
$$|c_2| = \sqrt{0.25}$$
$$|c_3| = \sqrt{0.125}$$

We cannot give the real and imaginary parts of the c coefficients.

Exercise 16.16

Show that the wave function represented by the linear combination in the previous example is normalized.

PROBLEMS

Section 16.6: Postulate 5. Measurements and the Determination of the State of a System

16.40 **a.** Find $\langle E\rangle$ for the coordinate wave function

$$\psi(x)=\sqrt{\frac{1}{3}}\psi_0+\sqrt{\frac{1}{3}}\psi_1+\sqrt{\frac{1}{3}}\psi_2$$

where ψ_0, ψ_1, and ψ_2 are the three lowest-energy harmonic oscillator energy eigenfunctions.

b. Show that the function is normalized.

c. Find σ_E for the wave function in part a.

d. Tell what values would occur in a set of many measurements of E, given that the system is in the state corresponding to the wave function of part a immediately before each measurement. Give the probability of each value.

16.41 **a.** A measurement of the energy of a particle in a three-dimensional cubic box gives a value $14h^2/(8ma^2)$. Tell what eigenfunctions are included in the linear combination representation of the wave function after the measurement.

b. How could the particle be put into a known state?

16.42 The energy of a particle in a one-dimensional box of length a is measured repeatedly with the particle restored to a specific but unknown state before each measurement. The results are summarized as follows:

Value	Probability
$h^2/(8ma^2)$	0.25
$4h^2/(8ma^2)$	0.375
$9h^2/(8ma^2)$	0.125
$16h^2/(8ma^2)$	0.25

What can you say about the state prior to the measurement?

Summary of the Chapter

In this chapter we have presented five postulates that are the theoretical basis of quantum mechanics. The first two postulates establish a one-to-one correspondence between the mechanical state of a system and a wave function and establish the time-dependent Schrödinger equation, which governs the wave functions.

The third postulate asserts that there is a hermitian mathematical operator for each mechanical variable. To write the operator for a given variable: (1) write the classical expression for the variable in terms of Cartesian coordinates and momentum components, (2) replace each momentum component by the relation

$$p_x \rightleftharpoons \frac{\hbar}{i}\frac{\partial}{\partial x}$$

and its analogues.

The first part of the fourth postulate asserts that the only possible outcomes of a measurement of a variable are the eigenvalues of the operator corresponding to that variable. The second part of the fourth postulate asserts that the expectation value of the variable A is given by

$$\langle A\rangle=\frac{\displaystyle\int \Psi^*\widehat{A}\Psi dq}{\displaystyle\int \Psi^*\Psi dq}$$

By study of the standard deviation of A, given by

$$\sigma_A=[\langle A^2\rangle-\langle A\rangle^2]^{1/2}$$

it was established that if the state just before a measurement of A corresponds to an eigenfunction of $\widehat{A}$, the only possible outcome of the measurement is the eigenvalue corresponding to that eigenfunction. This is called the predictable case. If the wave function is not an eigenfunction of $\widehat{A}$, the standard deviation gives a measure of the spread of the distribution of results. This is called the statistical case.

The fifth postulate states that in a measurement of A, if the result is a_j, one of the eigenvalues of $\widehat{A}$, then the state of the system immediately after the measurement corresponds to a wave function that is a linear combination only of those eigenfunctions whose eigenvalues equal a_j.

The measurement on the same system of a complete set of commuting observables suffices to put the system into a state that is completely known, even though only partial information is available about the state of the system prior to the measurements.

ADDITIONAL PROBLEMS

16.43 **a.** Show that the operator $\widehat{L}_z$ is hermitian. Use spherical polar coordinates.

b. Repeat the proof using Cartesian coordinates.

16.44 **a.** Obtain a formula for the uncertainty product $\sigma_x \sigma_{p_x}$ for each of the first three energy eigenfunctions of a particle in a one-dimensional box. Comment on any trend that you see in these values.

b. Evaluate the uncertainty product for each of the first three energy eigenfunctions of an electron in a box of length 10.0 Å (1.00×10^{-9} m).

16.45 A free particle that can move only in the x direction has a wave function given by

$$\psi = \sqrt{\frac{2}{3}}e^{iax} + \sqrt{\frac{1}{3}}e^{-iax}$$

where a is a real constant.

a. Find $\langle p_x \rangle$ and σ_{p_x}.

b. Find the possible values that could occur in a single measurement.

c. For each of the possible outcomes in part b, tell what the wave function would be immediately after the measurement.

d. For each of the values in part b, tell what the outcome of a second measurement immediately after the first measurement would be.

16.46 **a.** Obtain a formula for the uncertainty σ_x for a particle in a one-dimensional box of length a for a state corresponding to a general energy eigenfunction ψ_n.

b. Find the limit of the formula of part a as $n \to \infty$.

c. Obtain a formula for the uncertainty σ_{p_x} for a particle in a one-dimensional box of length a for a state corresponding to a general energy eigenfunction ψ_n.

d. Obtain a formula for the uncertainty product $\sigma_x \sigma_{p_x}$ corresponding to a general energy eigenfunction ψ_n for a particle in a one-dimensional box of length a.

e. For the baseball in Problem 15.13, find the value of the uncertainty σ_x.

f. For the baseball in Problem 15.13, find the value of the uncertainty σ_{p_x}.

g. For the baseball in Problem 15.13, find the value of the uncertainty product $\sigma_x \sigma_{p_x}$.

16.47 Label each statement as either true or false. If a statement is true only under certain circumstances, label it as false.

a. Every correct nonrelativistic wave function of an isolated system satisfies the time-independent Schrödinger equation.

b. Every correct wave function satisfies the time-dependent Schrödinger equation.

c. Knowledge of the time-independent wave function provides all available information about mechanical variables of a system.

d. Knowledge of the time-dependent wave function provides all available information about mechanical variables of a system.

e. Measurement of the energy of a particle in a one-dimensional box determines the state of the system.

f. Measurement of the energy of a particle in a three-dimensional box determines the state of the system.

g. The uncertainty in the position of a particle can vanish only if nothing is known about its momentum.

h. The uncertainty in the momentum of a particle can vanish only if nothing is known about its position.

i. If a system is known to be in a state corresponding to an energy eigenfunction, the time during which the system is known to be in that state is infinite.

j. If a free particle moving in one dimension is known to be in a state corresponding to an eigenfunction of the momentum operator, nothing can be said about the position of the particle.

17

The Electronic States of Atoms. I. The Hydrogen Atom

PRINCIPAL FACTS AND IDEAS

1. The hydrogen atom is an example of a central-force system (a two-particle system in which the potential energy depends only on the distance between the two particles).
2. The Schrödinger equation for the hydrogen atom can be separated into one equation for the motion of the center of mass and one equation for the motion of the electron relative to the nucleus.
3. The relative Schrödinger equation can be solved in spherical polar coordinates by separation of variables, assuming that $\psi = R(r)\Theta(\theta)\Phi(\phi)$. These wave functions are called orbitals.
4. The energy eigenvalues for the relative motion are the same as in the Bohr theory.
5. The square of the orbital angular momentum of the electron and one component of this angular momentum can have predictable values if a hydrogen atom is in a state corresponding to an energy eigenfunction. The angular momentum values are different from the Bohr theory.
6. Electrons have intrinsic (spin) angular momentum in addition to the angular momentum of orbital motion.

17.1

The Hydrogen Atom and the Central Force System

The hydrogen atom is one of the few systems for which the Schrödinger equation can be solved. It consists of a single electron with mass m_e and charge $-e$ and a nucleus consisting of a single proton with mass m_n and charge e, as depicted in Figure 17.1. We first assume that the atom is not confined in any container. Its potential energy depends only on the distance between the particles and is given by *Coulomb's law*, for which the potential energy is given in Eq. (14.4-16):

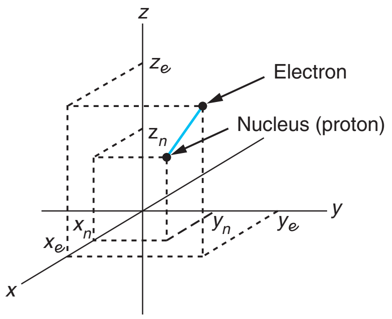

Figure 17.1 The Hydrogen Atom System Consisting of a Nucleus and an Electron.

$$\mathscr{V}(r) = -\frac{e^2}{4\pi\varepsilon_0 r} \tag{17.1-1}$$

where ε_0 is the permittivity of the vacuum, and where r is the distance between the nucleus and the electron. This formula corresponds to the choice that the potential energy is equal to zero when the electron and nucleus are infinitely far apart. The hydrogen atom is an example of a *central-force system*, which is any two-particle system with a potential energy that depends only on the distance between the particles.

We denote the Cartesian coordinates of the nucleus by x_n, y_n, and z_n, and the Cartesian coordinates of the electron by x_e, y_e, and z_e. The distance between the particles is given by a three-dimensional version of the theorem of Pythagoras:

$$r = \left((x_e - x_n)^2 + (y_e - y_n)^2 + (z_e - z_n)^2\right)^{1/2} \tag{17.1-2}$$

This is an inconvenient function of all six coordinates. To simplify the expression for the potential energy, we will make two transformations of coordinates. We first transform to relative coordinates and center-of-mass coordinates. The *relative coordinates* x, y, and z are defined by

$$x = x_e - x_n \tag{17.1-3a}$$

$$y = y_e - y_n \tag{17.1-3b}$$

$$z = z_e - z_n \tag{17.1-3c}$$

The *center-of-mass coordinates* x_c, y_c, and z_c are given by:

$$x_c = \frac{m_e x_e + m_n x_n}{M} \tag{17.1-4a}$$

$$y_c = \frac{m_e y_e + m_n y_n}{M} \tag{17.1-4b}$$

$$z_c = \frac{m_e z_e + m_n z_n}{M} \tag{17.1-4c}$$

where the sum of the masses is denoted by M:

$$M = m_e + m_n \tag{17.1-5}$$

The kinetic energy can be expressed in terms of the velocity of the center of mass and the relative velocity, as shown in Appendix E:

$$\mathscr{K} = \frac{M}{2}(v_{cx}^2 + v_{cy}^2 + v_{cz}^2) + \frac{\mu}{2}(v_x^2 + v_y^2 + v_z^2) \tag{17.1-6}$$

where $\mathbf{v}_c$ and $\mathbf{v}$ are the velocity of the center of mass and the relative velocity:

$$v_{cx} = \frac{dx_c}{dt} \quad \text{and} \quad v_x = \frac{dx}{dt} \tag{17.1-7}$$

with similar equations for v_{cy}, v_{cz}, v_y, and v_z. The *reduced mass* μ is defined by

$$\mu = \frac{m_n m_{e}}{m_n + m_{e}} = \frac{m_n m_{e}}{M} \tag{17.1-8}$$

Since the nucleus is much more massive than the electron, the reduced mass is nearly equal to the electron mass and the center of mass is close to the nucleus.

In order to construct the Hamiltonian operator for the hydrogen atom we must express the kinetic energy in terms of momentum components. The center of mass momentum components are

$$p_{cx} = Mv_{cx}, \quad p_{cy} = Mv_{cy}, \quad p_{cz} = Mv_{cz} \tag{17.1-9}$$

The components of the relative momentum are

$$p_x = \mu v_x, \quad p_y = \mu v_y, \quad p_z = \mu v_z \tag{17.1-10}$$

The classical Hamiltonian is

$$\mathscr{H}_{\text{cl}} = \frac{1}{2M}\left(p_{cx}^2 + p_{cy}^2 + p_{cz}^2\right) + \frac{1}{2\mu}\left(p_x^2 + p_y^2 + p_z^2\right) + \mathscr{V}(r) \tag{17.1-11}$$

where r is now expressed in terms of x, y, and z:

$$r = (x^2 + y^2 + z^2)^{1/2} \tag{17.1-12}$$

The Hamiltonian operator is obtained by the replacements specified in Eq. (16.3-8) and its analogues:

$$\begin{aligned} \widehat{H} &= -\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial x_c^2} + \frac{\partial^2}{\partial y_c^2} + \frac{\partial^2}{\partial z_c^2}\right) - \frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \mathscr{V}(r) \\ &= -\frac{\hbar^2}{2M}\nabla_c^2 - \frac{\hbar^2}{2\mu}\nabla^2 + \mathscr{V}(r) \end{aligned} \tag{17.1-13}$$

The two operators ∇_c^2 and ∇^2 are *Laplacian operators*, as defined in Eq. (15.2-26) and in Eq. (B-45) of Appendix B.

The first term in the Hamiltonian operator is the *center-of-mass Hamiltonian*

$$\widehat{H}_c = -\frac{\hbar^2}{2M}\nabla_c^2 \tag{17.1-14}$$

and the other two terms are the *relative Hamiltonian*

$$\widehat{H}_{\text{rel}} = -\frac{\hbar^2}{2\mu}\nabla^2 + \mathscr{V}(r) \tag{17.1-15}$$

The time-independent Schrödinger equation is

$$\left(\widehat{H}_c + \widehat{H}_{\text{rel}}\right)\Psi = E\Psi \tag{17.1-16}$$

In previous chapters we used a capital Ψ to represent a time-dependent wave function. In the next few chapters we will use Ψ for a time-independent wave function of two or more particles.

Equation (17.1-16) can be solved by the separation of variables. We assume the trial function:

$$\Psi = \psi_c(x_c, y_c, z_c)\psi(x, y, z) \tag{17.1-17}$$

When the product function of Eq. (17.1-17) is substituted into Eq. (17.1-16) and the variables are separated, we obtain the two equations

$$\widehat{H}_c\psi_c = E_c\psi_c \tag{17.1-18}$$

$$\widehat{H}_{\text{rel}}\psi = E_{\text{rel}}\psi \tag{17.1-19}$$

where E_c is the center-of-mass energy and E_{rel} is the relative energy and where

$$E = E_c + E_{\text{rel}} \tag{17.1-20}$$

Exercise 17.1

Carry out the steps to obtain Eqs. (17.1-18) to (17.1-20).

Equation (17.1-18) is the same as the Schrödinger equation for a free particle in three dimensions, which we discussed in Chapter 15. Equation (17.1-19) is mathematically equivalent to the Schrödinger equation for the motion of a particle of mass μ relative to a fixed origin (see Appendix E). Figure 17.2 depicts this equivalence. The vector from the nucleus (labeled n) to the electron (labeled e) in Figure 17.2a is equal to the vector from the fixed origin to the fictitious particle of mass μ in Figure 17.2b. Since the nucleus is much more massive than the electron the motion of the electron is nearly the same as though the nucleus were stationary, and we will often refer to the relative motion as electronic motion.

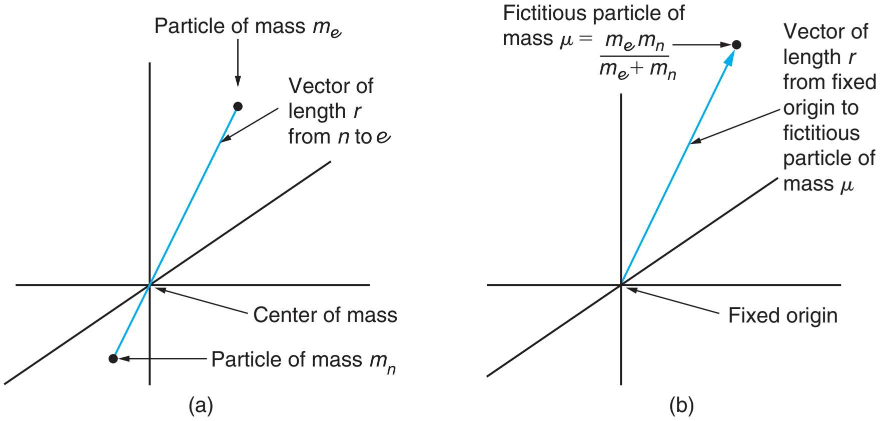

Figure 17.2 Figure to Illustrate the Equivalence between the Motion of a Particle of Mass μ around a Fixed Center and the Relative Motion of Two Particles. (a) The actual two-particle system. (b) The fictitious particle of mass μ.

EXAMPLE 17.1

The electron mass is 9.10939×10^{-31} kg and the proton mass is 1.672623×10^{-27} kg. Calculate the ratio of the reduced mass of the hydrogen atom to the mass of the electron.

Solution

$$\mu = \frac{m_e m_p}{m_e(m_e + m_p)} = \frac{(1.672623 \times 10^{-27}\ \text{kg})(9.10939 \times 10^{-31}\ \text{kg})}{1.672623 \times 10^{-27}\ \text{kg} + 9.10939 \times 10^{-31}\ \text{kg}}$$

$$= 9.10443 \times 10^{-31}\ \text{kg}$$

$$\frac{\mu}{m_e} = \frac{9.10443 \times 10^{-31}\ \text{kg}}{9.10939 \times 10^{-31}\ \text{kg}} = 0.99946$$

PROBLEMS

Section 17.1: The Hydrogen Atom and the Central Force System

17.1 The electron mass is 9.10939×10^{-31} kg and the proton mass is 1.672623×10^{-27} kg. For a hydrogen atom with the electron at a distance 1.000×10^{-10} m from the nucleus, find the distance from the center of mass to the nucleus and to the electron. The calculation is easier if you assume that the particles are temporarily on the x axis with the nucleus at the origin.

17.2 The mass of the earth is 5.98×10^{24} kg and the mass of the sun is 1.99×10^{30} kg. Find the reduced mass of the earth and the sun and express it as a percentage of the mass of the earth.

17.3 The mass of the earth is 5.98×10^{24} kg and the mass of the sun is 1.99×10^{30} kg. Assume that the earth is 1.4957×10^{8} km from the sun and find the distance from the center of the sun to the center of mass of the earth and the sun.

17.4 **a.** The mass of the moon is 7.34×10^{22} kg and the mass of the earth is 5.98×10^{24} kg. Assume that the moon is 3.818×10^{5} km from the earth and find the distance from the center of the earth to the center of mass of the moon and the earth.

b. Find the reduced mass of the moon and the earth and express it as a percentage of the mass of the moon.

17.2 The Relative Schrödinger Equation. Angular Momentum

The relative Schrödinger equation cannot be solved in Cartesian coordinates. We transform to spherical polar coordinates in order to have an expression for the potential energy that contains only one coordinate. Spherical polar coordinates are depicted in Figure 17.3. The expression for the Laplacian operator in spherical polar coordinates is found in Eq. (B-47) of Appendix B. The relative Schrödinger equation is now

$$\widehat{H}_{\text{rel}}\psi = -\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial \psi}{\partial r}\right) + \frac{1}{\sin(\theta)}\frac{\partial}{\partial \theta}\left(\sin(\theta)\frac{\partial \psi}{\partial \theta}\right) + \frac{1}{\sin^2(\theta)}\frac{\partial^2 \psi}{\partial \phi^2}\right] + \mathscr{V}(r)\psi$$

$$= E_{\text{rel}}\psi \qquad (17.2\text{-}1)$$

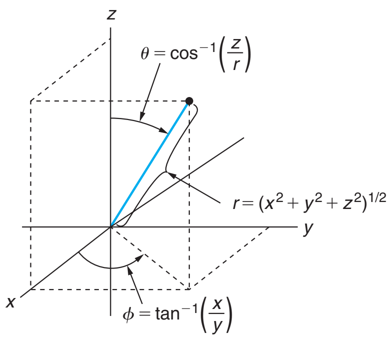

Figure 17.3 Spherical Polar Coordinates.

Equation (17.2-1) is a partial differential equation with three independent variables. Comparison with Eq. (16.3-24) shows that the operator for the square of the angular momentum is contained in the equation, so we can write the equation in the form:

$$-\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right) + \frac{1}{2\mu r^2}\widehat{L}^2\psi + \mathcal{V}(r)\psi = E_{\text{rel}}\psi \tag{17.2-2}$$

The potential energy in Eq. (17.2-2) is expressed in terms of only one of the three coordinates and the operator in the first term contains only the variable r, which suggests that we should try a separation of variables.

The First Separation of Variables

We separate r from θ and ϕ by assuming the trial solution

$$\psi(r,\theta,\phi) = R(r)Y(\theta,\phi) \tag{17.2-3}$$

where we call $R(r)$ the *radial factor* and $Y(\theta,\phi)$ the *angular factor*. The $\widehat{L}^2$ operator contains only θ and ϕ, so the radial factor $R(r)$ is treated as a constant when $\widehat{L}^2$ operates. The angular factor $Y(\theta,\phi)$ is treated as a constant when differentiation with respect to r is carried out. Substitution of the trial solution into Eq. (17.2-2) gives

$$-\frac{\hbar^2}{2\mu r^2}\left[Y\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{R}{\hbar r^2}\widehat{L}^2 Y\right] + (\mathcal{V} - E_{\text{rel}})RY = 0 \tag{17.2-4}$$

We divide this equation by RY and also multiply by $2\mu r^2/\hbar$. This separates r from the other variables, giving the equation

$$-\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu r^2}{\hbar^2}(\mathcal{V} - E_{\text{rel}}) + \frac{1}{\hbar^2}\frac{1}{Y}\widehat{L}^2 Y = 0 \tag{17.2-5}$$

The final term on the left-hand side of Eq. (17.2-5) does not depend on r and the other terms do not depend on θ or ϕ. Since r can be held fixed while θ and ϕ vary, the last term must be a constant function of θ and ϕ, which we set equal to the constant K. Multiplication by $\hbar^2 Y$ gives the equation

$$\widehat{L}^2 Y = \hbar^2 K Y \tag{17.2-6}$$

The angular factor Y is an eigenfunction of $\widehat{L}^2$ with eigenvalue $\hbar^2 K$. We will determine what the eigenvalues are later. Writing out the expression for $\widehat{L}^2$ we obtain

$$-\hbar^2\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial Y}{\partial\theta}\right) + \frac{1}{\sin^2(\theta)}\frac{\partial^2 Y}{\partial\phi^2}\right] = \hbar^2 K Y \tag{17.2-7}$$

The Second Separation of Variables

To separate the variables θ and ϕ we assume the trial solution

$$Y(\theta,\phi) = \Theta(\theta)\Phi(\phi) \tag{17.2-8}$$

Substitution of $\Theta(\theta)\Phi(\phi)$ into Eq. (17.2-7) followed by division by $\Theta(\theta)\Phi(\phi)$ and multiplication by $\sin^2(\theta)$ gives

$$\frac{\sin(\theta)}{\Theta}\frac{d}{d\theta}\left(\sin(\theta)\frac{d\Theta}{d\theta}\right)+\frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2}=-K\sin^2(\theta) \tag{17.2-9}$$

The variables θ and ϕ are now separated.

The Φ Functions

The last term on the left-hand side of Eq. (17.2-9) depends only on ϕ and the other terms depend only on θ. The independent variable θ can be held fixed while ϕ ranges, so the last term must be a constant function of ϕ. We denote the constant by $-m^2$. With this choice, m will turn out to be a real integer. Multiplication by Φ gives the equation

$$\frac{d^2\Phi}{d\phi^2}=-m^2\Phi \tag{17.2-10}$$

Except for the symbols used Eq. (17.2-10) is the same as several equations already encountered. Its general solution can be written in the form of Eq. (15.3-6)

$$\Phi=C\cos(m\phi)+D\sin(m\phi) \tag{17.2-11}$$

or in the form of Eq. (15.3-26)

$$\Phi=Ae^{im\phi}+Be^{-im\phi} \tag{17.2-12}$$

where A, B, C, and D are constants.

We always assume that a wave function must be continuous at all locations. The variable ϕ ranges from 0 to 2π when measured in radians. Since $\phi=0$ and $\phi=2\pi$ refer to the same location for given values of r and θ, we must require that

$$\Phi(0)=\Phi(2\pi) \tag{17.2-13}$$

This condition is satisfied only if m is real and equal to an integer.

Exercise 17.2

Show that m is real and equal to an integer if $\Phi(0)=\Phi(2\pi)$.

There are two versions of the Φ function. The first version of Φ is an eigenfunction of $\widehat{L}_z$, which is given in spherical polar coordinates by Eq. (16.3-20):

$$\widehat{L}_z=\frac{\hbar}{i}\frac{\partial}{\partial\phi} \tag{17.2-14}$$

We operate on the version of Φ in Eq. (17.2-12) with $\widehat{L}_z$:

$$\widehat{L}_z\Phi=\frac{\hbar}{i}\left(imAe^{im\phi}-imBe^{-im\phi}\right) \tag{17.2-15}$$

This function is an eigenfunction of $\widehat{L}_z$ with eigenvalue $\hbar m$ if B is chosen to equal zero, or an eigenfunction of $\widehat{L}_z$ with eigenvalue $-\hbar m$ if A is chosen to equal zero. If we set B equal to zero the Φ function is

$$\Phi = \Phi_m = Ae^{im\phi} = \frac{1}{\sqrt{2\pi}}e^{im\phi} \tag{17.2-16}$$

We will refer to the Φ_m functions as the *complex* Φ *functions*. The constant $1/(\sqrt{2\pi})$ is chosen for normalization. The eigenvalue equation for $\widehat{L}_z$ is

$$\widehat{L}_z\Phi = \hbar m\Phi \tag{17.2-17}$$

The z component of the angular momentum is quantized, with eigenvalues 0, $\pm\hbar$, $\pm 2\hbar$, and so on.

The second set of Φ functions contains two types of functions:

$$\Phi_{mx} = \frac{1}{\sqrt{\pi}}\cos(m\phi) \quad (m \neq 0) \tag{17.2-18}$$

and

$$\Phi_{my} = \frac{1}{\sqrt{\pi}}\sin(m\phi) \quad (m \neq 0) \tag{17.2-19}$$

where the constants are chosen for normalization. We call Φ_{mx} and Φ_{my} the *real* Φ *functions*. The function Φ_0 is real and belongs to both sets of Φ functions. We use the subscript mx because Φ_{mx} has its maximum value at the x axis and the subscript my because Φ_{my} has its maximum value at the y axis for odd values of m. The real Φ functions for $m \neq 0$ are not eigenfunctions of $\widehat{L}_z$.

The real Φ functions and the complex Φ functions are related by the identities

$$\cos(\alpha) = \frac{1}{2}(e^{i\alpha} + e^{-i\alpha}) \tag{17.2-20}$$

and

$$\sin(\alpha) = \frac{1}{2i}(e^{i\alpha} + e^{-i\alpha}) \tag{17.2-21}$$

Either the complex Φ functions or the real Φ functions can be factors in the energy eigenfunctions. The complex Φ_m functions are more useful when we discuss angular momentum, and the real Φ_{mx} and Φ_{my} functions are more useful in discussions of chemical bonding.

Exercise 17.3

a. Show that $\Phi_{mx}(\phi) = \frac{1}{\sqrt{2}}\big(\Phi_m(\phi) + \Phi_{-m}(\phi)\big)$ for $m \neq 0$.

b. Relate $\Phi_{my}(\phi)$ to $\Phi_m(\phi)$ and $\Phi_{-m}(\phi)$.

c. Show that Φ_{mx} and Φ_{my} are not eigenfunctions of $\widehat{L}_z$ for $m \neq 0$.

The Θ Function

After replacement of the last term on the left-hand side of Eq. (17.2-9) by $-m^2$ and multiplication by Θ, we obtain

$$\sin(\theta)\frac{d}{d\theta}\left(\sin(\theta)\frac{d\Theta}{d\theta}\right) - m^2\Theta + K\sin^2(\theta)\Theta = 0 \tag{17.2-22}$$

This equation can be transformed into a famous equation called the *associated Legendre equation* by the change of variables:

$$y = \cos(\theta), \quad P(y) = \Theta(\theta) \tag{17.2-23}$$

The equation is named for Adrien-Marie Legendre, 1752–1833, a famous French mathematician who solved the equation.

We do not discuss the associated Legendre equation, but give its solutions in Appendix F. The solutions are called *associated Legendre functions* and are derivatives of polynomials known as *Legendre polynomials*.

For a solution of the associated Legendre equation to exist that obeys the relevant boundary conditions, it turns out that the constant K must be equal to $l(l+1)$ where l is a positive integer at least as large as the magnitude of m. There is one solution for each set of values of the two quantum numbers l and m:

$$\Theta(\theta) = \Theta_{lm}(\theta) \tag{17.2-24}$$

Since the equation contains m^2, the solutions are the same for a given value of m and its negative:

$$\Theta_{lm}(\theta) = \Theta_{l,-m}(\theta) \tag{17.2-25}$$

where we insert a comma to avoid confusing two subscripts having values l and $-m$ with a single subscript having a value $l-m$.

If we choose the complex Φ functions, the Y functions are called *spherical harmonic functions*.

$$Y = Y_{lm}(\theta, \phi) = \Theta_{lm}(\theta)\Phi_m(\phi) \tag{17.2-26}$$

Table 17.1 gives the normalized spherical harmonic functions for $l = 0$, $l = 1$, and $l = 2$. Additional functions can be derived from formulas in Appendix F.

Angular Momentum Values

The spherical harmonic functions, $Y_{lm}(\theta, \phi)$, are eigenfunctions of $\widehat{L}^2$ with eigenvalue $\hbar^2 K$, as in Eq. (17.2-6).

$$\widehat{L}^2 Y_{lm} = \widehat{L}^2 \Theta_{lm}\Phi_m = \hbar^2 l(l+1)\Theta_{lm}\Phi_m \quad (l = 0, 1, 2, \ldots) \tag{17.2-27}$$

The square of the angular momentum can take on any of the values

$$L^2 = 0,\ 2\hbar^2,\ 6\hbar^2,\ 12\hbar^2,\ 20\hbar^2, \ldots, l(l+1)\hbar^2, \ldots \tag{17.2-28}$$

The magnitude of the angular momentum can take on any of the values

$$L = |\mathbf{L}| = 0,\ \sqrt{2}\hbar,\ \sqrt{6}\hbar,\ \sqrt{12}\hbar, \ldots, R\left(\sqrt{l(l+1)}\right)\hbar, \ldots \tag{17.2-29}$$

Table 17.1 Normalized Spherical Harmonic Functions $Y_{lm}(\theta,\phi) = \Theta_{lm}(\theta)\,\Phi_m(\phi)$

Complex Φ functions, eigenfunctions of $\widehat{L}_z$.

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}}\,e^{im\phi}$$

Real Φ functions, not necessarily eigenfunctions of $\widehat{L}_z$.

$$\Phi_{mx}(\phi) = \frac{1}{\sqrt{\pi}}\cos(m\phi)$$

$$\Phi_{my}(\phi) = \frac{1}{\sqrt{\pi}}\sin(m\phi)$$

Θ functions:

$$\Theta_{00}(\theta) = \frac{\sqrt{2}}{2}$$

$$\Theta_{10}(\theta) = \frac{\sqrt{6}}{2}\cos(\theta); \quad \Theta_{11}(\theta) = \Theta_{1,-1}(\theta) = \frac{\sqrt{3}}{2}\sin(\theta)$$

$$\Theta_{20}(\theta) = \frac{\sqrt{10}}{4}(3\cos^2(\theta) - 1)$$

$$\Theta_{21}(\theta) = \Theta_{2,-1}(\theta) = \frac{\sqrt{15}}{2}\sin(\theta)\cos(\theta)$$

$$\Theta_{22}(\theta) = \Theta_{2,-2}(\theta) = \frac{\sqrt{15}}{4}\sin^2(\theta)$$

$$\Theta_{30}(\theta) = \frac{3\sqrt{14}}{4}\left(\frac{5}{3}\cos^3(\theta) - \cos(\theta)\right)$$

$$\Theta_{31}(\theta) = \Theta_{3,-1}(\theta) = \frac{\sqrt{42}}{8}\sin(\theta)(5\cos^2(\theta) - 1)$$

$$\Theta_{32}(\theta) = \Theta_{3,-2}(\theta) = \frac{\sqrt{105}}{4}\sin^2(\theta)\cos(\theta)$$

$$\Theta_{33}(\theta) = \Theta_{3,-3}(\theta) = \frac{\sqrt{70}}{8}\sin^3(\theta)$$

Additional Θ functions can be obtained from formulas in Appendix F.

The values in Eq. (17.2-29) differ from the assumed values $\hbar, 2\hbar, 3\hbar, \ldots$, in the Bohr theory of the hydrogen atom. The Bohr theory also did not provide for states of zero angular momentum or for different values of L_z corresponding to a given value of $|\mathbf{L}|$.

The function Φ_m is an eigenfunction of $\widehat{L}_z$ with eigenvalue $\hbar m$, so that Y_{lm} is an eigenfunction of $\widehat{L}_z$:

$$\widehat{L}_z Y_{lm} = \Theta_{lm}\widehat{L}_z\Phi_m = \Theta_{lm}\hbar m\Phi_m = \hbar m Y_{lm} \quad (m = 0, \pm 1, \ldots, \pm l) \tag{17.2-30}$$

The possible values of L_z are:

$$L_z = m\hbar = 0, \quad \pm\hbar, \quad \pm 2\hbar, \quad \pm 3\hbar, \ldots \pm l\hbar \tag{17.2-31}$$

For every value of l there are $2l + 1$ values of m (l positive values, l negative values, plus zero). The degeneracy of a value of $|L|$ equal to $\hbar\sqrt{l(l+1)}$ is

$$g_l = 2l + 1 \tag{17.2-32}$$

The Y_{lm} functions and the possible values of L^2 and L_z are the same for any central-force system, no matter what the potential energy function $\mathcal{V}(r)$ is. In a later chapter we will study a model for the rotation of a diatomic molecule that is a central-force system. The angular momentum of this model takes on the same values as that of the hydrogen atom.

EXAMPLE 17.2

Show that $\widehat{H}_{\mathrm{rel}}$, $\widehat{L}^2$, and $\widehat{L}_z$ commute with each other.

Solution

$$\widehat{H}_{\mathrm{rel}} = -\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}\left[r^2\frac{\partial}{\partial r}\right] + \frac{1}{2\mu r^2}\widehat{L}^2 + \mathcal{V}(r)$$

$$\widehat{L}^2 = -\hbar^2\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left[\sin(\theta)\frac{\partial}{\partial\theta}\right] + \frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}\right]$$

$$\widehat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi}$$

$\widehat{H}_{\mathrm{rel}}$ commutes with $\widehat{L}^2$ because $\widehat{L}^2$ commutes with itself and contains no r dependence while the other terms in $\widehat{H}_{\mathrm{rel}}$ contain no θ or ϕ dependence. $\widehat{L}^z$ commutes with $\widehat{L}^2$ because the first term in $\widehat{L}^2$ contains no ϕ dependence, and $\dfrac{\partial}{\partial\phi}$ commutes with $\dfrac{1}{\sin^2(\theta)}\dfrac{\partial^2}{\partial\phi^2}$. $\widehat{H}_{\mathrm{rel}}$ commutes with $\widehat{L}_z$ if $\widehat{L}^2$ commutes with $\widehat{L}_z$, since the first term in $\widehat{H}_r$ contains no ϕ dependence.

Since $\widehat{H}_{\mathrm{rel}}$, $\widehat{L}_z$, and $\widehat{L}^2$ commute with each other, they can possess a common set of eigenfunctions. That is, the energy eigenfunctions can also be eigenfunctions of the $\widehat{L}_z$ and $\widehat{L}^2$ operators. The magnitude of the angular momentum and its z component will simultaneously have predictable values if the wave function is an eigenfunction of both $\widehat{L}^2$ and $\widehat{L}_z$. The operators $\widehat{L}_x$, $\widehat{L}_y$, and $\widehat{L}_z$ do not commute with each other, so these three operators cannot have a full set of common eigenfunctions. Only statistical predictions can be made about L_x and L_y if the wave function is an eigenfunction of $\widehat{L}_z$.

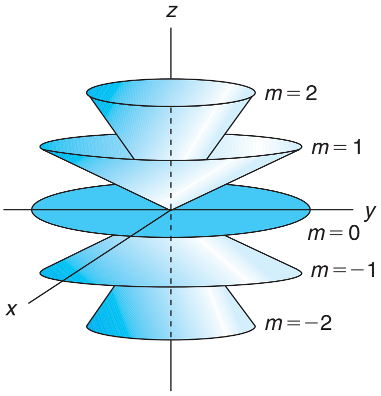

Figure 17.4 Cones of Possible Angular Momentum Directions for $l = 2$. These cones represent possible directions for the angular momentum vector.

Figure 17.4 depicts the possible angular momentum values for the case that $l = 2$, for which m can take on the values $2, 1, 0, -1$, and -2. The magnitude of L is $\sqrt{6}\hbar = 2.4495\hbar$, and the possible values of L_z are $2\hbar, \hbar, 0, -\hbar$, and $-2\hbar$. If the angular momentum vector is measured without experimental error, it can point in any direction on any one of the five cones drawn in the figure. Notice the similarity between each cone on Figure 17.4 and the cone of directions around which a gyroscope axis precesses, as shown in Figure E.3 of Appendix E. For a given value of l, there are $2l + 1$ cones, one for each possible value of m. If the wave function is known to correspond to a particular value of l and a particular value of m, it is known which cone applies, but the direction on that cone is not known.

There is nothing unique about the z direction. One could choose $\widehat{L}_x$ or $\widehat{L}_y$ as a member of a set of commuting observables instead of $\widehat{L}_z$. In that event, the Φ functions would be different, and would correspond to cones in Figure 17.4 that would be oriented around either the x axis or the y axis. We choose to emphasize L_z since its operator is simpler in spherical polar coordinates than those of the other components.

Exercise 17.4

Transform the expression for $\Theta_{11}\Phi_{1x}$ to Cartesian coordinates. Show that this function is an eigenfunction of the operator $\widehat{L}_x$, and find its eigenvalue.

PROBLEMS

Section 17.2: The Relative Schrödinger Equation. Angular Momentum

17.5 Using formulas in Appendix F, write the formulas for the spherical harmonic functions Y_{43} and Y_{42}.

17.6 Sketch graphs of the functions and of their squares:

- **a.** $\Theta_{10}(\theta)$
- **b.** $\Theta_{11}(\theta)$
- **c.** $\Theta_{20}(\theta)$
- **d.** $\Theta_{21}(\theta)$
- **e.** $\Theta_{22}(\theta)$

17.7 Sketch graphs of the real and imaginary parts of

- **a.** $\Phi_2(\phi)$
- **b.** $\Phi_3(\phi)$
- **c.** $\Phi_4(\phi)$
- **d.** $\Phi_5(\phi)$

17.8 **a.** Show that the functions $\Theta_{00}(\theta)$ and $\Theta_{10}(\theta)$ are orthogonal to each other.

b. Show that the functions $\Theta_{11}(\theta)$ and $\Theta_{21}(\theta)$ are orthogonal to each other.

17.9 Calculate the expectation value and the standard deviation of θ for a hydrogen atom in a state corresponding to Y_{00}.

17.10 Calculate the expectation value and the standard deviation of θ for a hydrogen atom in a state corresponding to Y_{11}. Explain what the value means.

17.11 **a.** Calculate the expectation value and the standard deviation of ϕ for a hydrogen atom in the $2p_x$ state.

b. Calculate the expectation value and the standard deviation of ϕ for a hydrogen atom in the $2p_y$ state.

17.12 **a.** Use Eq. (16.5-5) and the expression for the commutator $[\widehat{L}_x, \widehat{L}_y]$ in Problem 16.16 to obtain an uncertainty relation for $\widehat{L}_x$ and $\widehat{L}_y$ for the state corresponding to the spherical harmonic function Y_{21}.

b. Repeat part a using the spherical harmonic function Y_{00}. Comment on your result.

17.3 The Radial Factor in the Hydrogen Atom Wave Function. The Energy Levels of the Hydrogen Atom

In Section 17.2, we wrote the energy eigenfunction for any central-force system as

$$\psi(r,\theta,\phi) = R(r)Y_{lm}(\theta,\phi) = R(r)\Theta_{lm}(\theta)\Phi_m(\phi) \qquad (17.3\text{-}1)$$

The spherical harmonic functions $Y_{lm}(\theta,\phi) = \Theta_{lm}(\theta)\Phi_m(\phi)$ are the same functions for any system with a potential energy depending only on r. We now seek the differential equation for the radial factor for the hydrogen atom. We replace $\widehat{L}^2 Y$ by $\hbar^2 l(l+1)Y$ in Eq. (17.2-5), according to Eq. (17.2-27), and multiply the resulting equation by R to obtain the differential equation for the radial factor:

$$-\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu r^2}{\hbar^2}(\mathcal{V} - E)R + l(l+1)R = 0 \qquad (17.3\text{-}2)$$

where we now omit the subscript "rel" from E_{rel}. The radial factor $R(r)$ is different for each choice of the potential energy function $\mathcal{V}(r)$. In a later chapter we will choose a representation for $\mathcal{V}(r)$ that will allow us to use Eq. (17.3-2) for the rotation and vibration of a diatomic molecule. To apply it to the hydrogen atom, we substitute the expression for the potential energy given in Eq. (17.1-1) into this equation, and expand the derivative term into two terms:

$$-r^2\frac{d^2R}{dr^2} - 2r\frac{dR}{dr} - \frac{2\mu r^2}{\hbar^2}\left(E + \frac{e^2}{4\pi\varepsilon_0 r}\right)R + l(l+1)R = 0 \tag{17.3-3}$$

We make the following substitutions:

$$\alpha^2 = -\frac{2\mu E}{\hbar^2}, \quad \beta = \frac{\mu e^2}{4\pi\varepsilon_0\alpha\hbar^2}, \quad \rho = 2\alpha r \tag{17.3-4}$$

When the resulting equation is divided by ρ^2 we obtain an equation that is known as the *associated Laguerre equation*:

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} - \frac{R}{4} + \frac{\beta R}{\rho} - l(l+1)\frac{R}{\rho^2} = 0 \tag{17.3-5}$$

where $R(\rho)$ is the function of ρ that is equal to $R(r)$.

Exercise 17.5

Carry out the manipulations to obtain Eq. (17.3-5) from Eq. (17.3-3).

This equation is named for Edmund Laguerre, 1834–1866, the famous French mathematician who solved it.

Laguerre assumed that the solution of the associated Laguerre equation can be written as

$$R(\rho) = G(\rho)e^{-\rho/2} \tag{17.3-6}$$

where $G(\rho)$ is a power series

$$G(\rho) = \sum_{j=0}^{\infty} a_j\rho^j \tag{17.3-7}$$

with constant coefficients $a_1, a_2, a_3, \ldots$. We do not discuss the solution that leads to expressions for these coefficients. As with the harmonic oscillator equation, the series must terminate to satisfy the boundary condition that the wave function is finite.[1] This turns the series G into a polynomial.

The termination of the series G turns out to require that the parameter β is equal to an integer that must be at least as large as $l + 1$.[2] We denote this integer by n. Solving the second equality in Eq. (17.3-4) for α, we obtain

$$\alpha = \frac{\mu e^2}{4\pi\varepsilon_0\hbar^2\beta} = \frac{\mu e^2}{4\pi\varepsilon_0\hbar^2 n} \tag{17.3-8}$$

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[1] F. L. Pilar, *Elementary Quantum Chemistry*, McGraw-Hill, New York, 1968, p. 151ff.

[2] I. N. Levine, *Quantum Chemistry*, 6th ed., Prentice-Hall, Upper Saddle River, N.J., 2000, p. 136ff.

From the first relation in Eq. (17.3-4), the energy is quantized and determined by the value of n:

$$E = E_n = -\frac{\hbar^2\alpha^2}{2\mu} = -\frac{\mu \mathscr{e}^4}{2(4\pi\varepsilon_0\hbar n)^2} = -\frac{2\pi^2\mu \mathscr{e}^4}{(4\pi\varepsilon_0 h)^2}\frac{1}{n^2} \tag{17.3-9}$$

This is the same expression for the energy as in the Bohr theory. However, the quantization now arises from the Schrödinger equation and its boundary conditions, and not from an arbitrary assumption as in the Bohr theory. Since the Bohr theory is based on assuming the wrong values for the angular momentum, its success with the energy eigenvalues seems to be fortuitous and at the least is somewhat mysterious.

The zero of the potential energy function is chosen so that it vanishes at $r \to \infty$. The negative values of the energy eigenvalue E in Eq. (17.3-9) correspond to *bound states*, in which there is not enough energy for the electron to escape from the nucleus. There are also nonbound states called *scattering states* in which the energy is positive so that the electron moves toward the nucleus, passes it, and continues on its way, generally in a new direction. We will not discuss these states, which do not have quantized energy values.[3]

Exercise 17.6

Substitute the values of the constants into Eq. (17.3-9) to show that the relative energy of a hydrogen atom can take on the values

$$E = E_n = -\frac{2.1787 \times 10^{-18}\,\mathrm{J}}{n^2} = -\frac{13.60\,\mathrm{eV}}{n^2} \tag{17.3-10}$$

where 1 eV (1 *electron volt*) is the energy required to move one electron through an electric potential difference of 1 volt, equal to 1.602177×10^{-19} J.

The *Bohr radius* given in Eq. (14.4-15) is equal to the radius of the first orbit of a hydrogen atom in the Bohr theory assuming a stationary nucleus. If we correct for the motion of the nucleus by replacing the electron mass by the reduced mass,

$$a = \frac{\hbar^2 4\pi\varepsilon_0}{\mu^2} = 5.2947 \times 10^{-11}\ \mathrm{m} = 52.947\ \mathrm{pm} = 0.52947\ \text{Å} \tag{17.3-11}$$

where Å represents the angstrom unit, 10^{-10} m. When we express the energy in terms of the Bohr radius, we get

$$E = E_n = -\frac{\hbar^2\alpha^2}{2\mu} = -\frac{\mathscr{e}^2}{2(4\pi\varepsilon_0)an^2} \tag{17.3-12}$$

This energy is equal to half of the potential energy of an electron at a distance from the nucleus equal to an^2, the radius of the corresponding Bohr orbit.

Exercise 17.7

Verify Eqs. (17.3-11) and (17.3-12).

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[3] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Systems*, Plenum, New York, 1977, p. 21ff, p. 32ff.

In the (fictitious) limit that the nucleus is infinitely massive compared to the electron, the electron moves about the stationary nucleus, and the reduced mass becomes

$$\lim_{m_n\to\infty}\mu = \lim_{m_n\to\infty}\left(\frac{m_e\,m_n}{m_e+m_n}\right) = \frac{m_e\,m_n}{m_n} = m_e \tag{17.3-13}$$

where m_e is the mass of the electron. The Bohr radius becomes the same as in Eq. (14.4-15);

$$\lim_{m_n\to\infty} a = a_0 = \frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2} = 5.29198\times 10^{-11}\ \mathrm{m} \tag{17.3-14}$$

Exercise 17.8

Calculate the percentage error in the hydrogen atom Bohr radius and in the hydrogen atom energy introduced by replacing the reduced mass by the mass of the electron.

The rules that the hydrogen atom quantum numbers obey can be restated:

$$n = 1, 2, 3, \ldots \tag{17.3-15a}$$

$$l = 0, 1, 2, \ldots, n-1 \tag{17.3-15b}$$

$$m = 0, \pm 1, \pm 2, \ldots, \pm l \tag{17.3-15c}$$

The quantum number n is called the *principal quantum number*. It determines the energy. The quantum number l has been called the *azimuthal quantum number*, but could also be called the *angular momentum quantum number*. It determines the magnitude of the angular momentum. The quantum number m has been called the *magnetic quantum number*, but could also be called the *angular momentum projection quantum number*. It determines the z component of the angular momentum. The energy eigenvalue depends only on the value of the principal quantum number n, so the set of states with a given value of n but with different values of l and m constitute an energy level that is degenerate. Figure 17.5 depicts the energy levels for the first few bound states of a hydrogen atom. Each state is represented by a horizontal line segment at the appropriate height for its energy level.

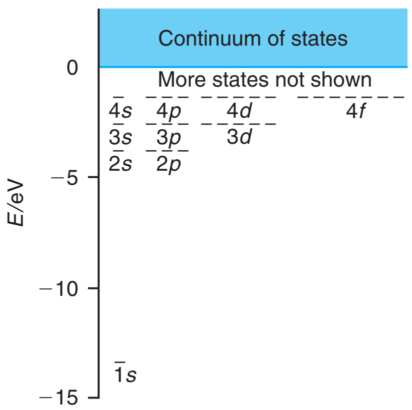


Figure 17.5 Energy Levels of the Hydrogen Atom.

EXAMPLE 17.3

Find an expression for the degeneracy of the hydrogen atom energy levels.

Solution

For a given value of n, the possible values of l range from 0 to $n-1$. For a given value of l, the values of m range from $-l$ to l. The number of possible values of m for a given value of l is $2l+1$, since m can have any of l positive values, any of l negative values, or can be equal to zero. The degeneracy g_n is

$$\begin{aligned} g_n &= \sum_{l=0}^{n-1}(2l+1) = 2\sum_{l=0}^{n-1} l + \sum_{l=0}^{n-1} 1 = 2n\left(\frac{0+n-1}{2}\right) + n \\ &= n^2 - n + n = n^2 \end{aligned} \tag{17.3-16}$$

We have used the fact that the sum of a set of consecutive integers is the mean of the first integer and the last integer times the number of members of the set (a fact reportedly first discovered by Gauss when he was seven years old).

The radial factor R for the hydrogen atom consists of an exponential factor and a polynomial denoted by $G(\rho)$. These polynomials are related to the *associated Laguerre functions*. Appendix F describes these functions and the *Laguerre polynomials* of which they are derivatives and gives formulas for generating the polynomials. To express R in terms of r, we use Eqs. (17.3-4), (17.3-8), and (17.3-11) to write

$$\rho = 2\alpha r = \frac{2r}{na} \tag{17.3-17}$$

where a is the Bohr radius and n is the principal quantum number. There is a different radial factor R for each set of values of the quantum numbers n and l so we attach these two subscripts to the symbol R_{nl}.

Table 17.2 gives the R_{nl} functions for $n = 1, 2$, and 3. The entries in the table are for the *hydrogen-like atom*, which is a hydrogen atom with the nuclear charge equal to a number of protons denoted by Z. The He^+ ion corresponds to $Z = 2$, the Li^{2+} ion corresponds to $Z = 3$, and so on. This modification to the R_{nl} functions will be useful when we discuss multielectron atoms in the next chapter. To obtain the radial factors and the energy levels of a hydrogen-like atom we need to replace the variable ρ by

$$\rho = 2\alpha r = \frac{2Zr}{na} \tag{17.3-18}$$

and the energy eigenvalue by

$$E = E_n = -\frac{\hbar^2\alpha^2}{2\mu} = -\frac{Z^2 e^2}{2(4\pi\varepsilon_0)an^2} = -(13.60\,\mathrm{eV})\,\frac{Z^2}{n^2} \tag{17.3-19}$$

The constants at the first of each formula in the table provide for normalization, which we discuss later.

Table 17.2 Radial Factors for Hydrogen-Like Energy Eigenfunctions

$$R_{10}(r) = R_{1s}(r) = \left(\frac{Z}{a}\right)^{3/2} 2\,e^{-Zr/a}$$

$$R_{20}(r) = R_{2s}(r) = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a}\right)^{3/2}\left(2 - \frac{Zr}{a}\right)e^{-Zr/2a}$$

$$R_{21}(r) = R_{2p}(r) = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)e^{-Zr/2a}$$

$$R_{30}(r) = R_{3s}(r) = \frac{1}{9\sqrt{3}}\left(\frac{Z}{a}\right)^{3/2}\left[6 - \frac{4Zr}{a} + \left(\frac{2Zr}{3a}\right)^2\right]e^{-Zr/3a}$$

$$R_{31}(r) = R_{3p}(r) = \frac{2}{27\sqrt{6}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{4Zr}{a} - \frac{2Z^2r^2}{3a^2}\right)e^{-Zr/3a}$$

$$R_{32}(r) = R_{3d}(r) = \frac{1}{9\sqrt{30}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{2Zr}{3a}\right)^2 e^{-Zr/3a}$$

Additional functions can be obtained from formulas in Appendix F.

PROBLEMS

Section 17.3: The Radial Factor in the Hydrogen Atom Wave Function. The Energy Levels of the Hydrogen Atom

17.13 Calculate $\langle r \rangle$, the expectation value of r for the $2s$ and $2p$ states of a hydrogen-like atom. Comment on your answer.

17.14 **a.** Find the value of the distance b such that there is a 95% chance that an electron in a hydrogen atom in the $1s$ state is no farther from the nucleus than the distance b.

b. Find the ratio of the $1s$ wave function at $r = b$ to the same function at $r = 0$.

c. Repeat parts a and b for 90% probability instead of 95%.

17.15 For a hydrogen atom in a $1s$ state, find the probability that the electron is no farther from the nucleus than (a) a, (b) $2a$, (c) $3a$ where a is the Bohr radius.

17.16 Calculate $\langle z \rangle$ and σ_z for the electron in a hydrogen atom in the $1s$ state. Explain the meaning of the values. What can you say about $\langle x \rangle$ and σ_x? What can you say about $\langle y \rangle$ and σ_y?

17.17 Find the most probable value of the electron's distance from the nucleus for a hydrogen atom in the $1s$, the $2s$, and the $2p$ states.

17.18 Using formulas in Appendix F, verify the formula given in Table 17.2 for R_{32}.

17.19 **a.** Construct the formula that represents R_{40}, using formulas in Appendix F.

b. Construct a graph of the radial distribution function for the $4s$ (400) state.

17.20 **a.** Construct a graph of the radial distribution function for the $3d$ states of a hydrogen atom.

b. Find the values of r at which the radial distribution function vanishes.

c. Find the values of r at which the radial distribution function has relative maxima.

17.21 Find the shortest wavelength of light emitted by hydrogen atoms in transitions between bound states. In what region of the spectrum (visible, infrared, ultraviolet, etc.) does it lie?

17.22 **a.** Calculate the percent difference between the energy of an ordinary hydrogen atom and a deuterium atom in the ground state.

b. Calculate the percent difference between the energy of an ordinary hydrogen atom and a deuterium atom in the $2s$ state.

c. Calculate the percent difference between the energy of a ${}^4\text{He}^+$ ion and a ${}^3\text{He}^+$ ion in the $2s$ state.

17.23 Calculate the expectation values of p_x and of p_x^2 for the electron in a hydrogen atom in the $1s$ state. Why does $\langle p_x^2 \rangle$ not equal $\langle p_x \rangle^2$?

17.24 A positronium atom is a hydrogen-like atom consisting of an electron and a positron (an antielectron with charge $+e$ and mass equal to the electron mass). Find the energy of a positronium atom in the $1s$ state. Describe the classical motion of the two particles about the center of mass. Find the value of the Bohr radius for positronium.

17.25 Calculate the expectation value of the kinetic energy for a hydrogen-like atom in the $1s$ state for $Z = 2$, $Z = 3$, and $Z = 4$.

17.26 Explain verbally why $\langle L^2 \rangle$ and $\langle L_z \rangle$ are independent of Z for all stationary states of the hydrogen-like atom. Since the average distance from the nucleus depends on Z, what does this mean about the average speed of the electron around the nucleus for the 211 state?

17.4 The Orbitals of the Hydrogen-Like Atom

Wave functions of single electrons are called *orbitals*. We can choose between real and complex orbitals. Each complex hydrogen atom orbital contains complex Φ_m functions:

$$\psi_{nlm} = R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\phi) \tag{17.4-1}$$

The complex orbitals are eigenfunctions of $\widehat{H}$, $\widehat{L}^2$, and $\widehat{L}_z$. The real orbitals contain either Φ_{mx} or Φ_{my}. They are eigenfunctions of $\widehat{H}$and $\widehat{L}^2$ but are not eigenfunctions of $\widehat{L}_z$. The complex orbitals are more useful in discussing properties that relate to angular momentum, and the real orbitals are more useful in discussions of chemical bonding.

The set of states with the same value of n correspond to the same value of the energy and are called a *shell*. This term is used because the expectation value of the distance of the electron from the nucleus is roughly the same for all states in a shell. The shells are labeled with the value of n, the principal quantum number. There is also an older notation in which the first ($n = 1$) shell is called the K shell, the second ($n = 2$) shell is called the L shell, and so on. Within a given shell, the states with a given value of l constitute a *subshell*. The $l = 0$ state of a shell is called its ***s*** *subshell*. The three states with $l = 1$ constitute a *p subshell*. A *d subshell* consists of the five $l = 2$ states. An *f subshell* consists of the seven $l = 3$ states. Any further subshells are given the letters g, h, i, and so on (in alphabetical order after f). The letters s, p, d, and f came from the old spectroscopic terms "sharp," "principal," "diffuse," and "fundamental," but these names have no connection with the present usage. There are n subshells in the nth shell. The first shell has only the $1s$ subshell, while the seventh shell has the $7s$, $7p$, $7d$, $7f$, $7g$, $7h$, and $7i$ subshells, and so on.

Exercise 17.9

Give the value of each of the three quantum numbers for each state of the fourth ($n = 4$) shell.

Table 17.3 contains formulas for the real hydrogen-like orbitals for the first three shells. The complex wave functions can be generated by replacing the real Φ functions by the complex Φ functions. As indicated in the table, we can use the letter of the subshell as a subscript instead of the value of the subscript l. The 211 orbital can be called the $2p1$ orbital, the $21x$ orbital can be called the $2p_x$ orbital, and the 210 orbital can be called the $2p0$ orbital or the $2p_z$ orbital. The $3d_{z^2}$ orbital is the same as the 320 orbital. The $3d_{xz}$ and $3d_{yz}$ orbitals are linear combinations of the 321 and 32, -1 orbitals, and the $3d_{xy}$ and the $3d_{x^2-y^2}$ orbitals are linear combinations of the 322 and 32, -2 orbitals.

EXAMPLE 17.4

Write the formula for ψ_{211}.

Solution

$$\Phi_1(\phi) = \frac{1}{\sqrt{2\pi}}e^{i\phi}$$

$$\Theta_{11}(\theta) = \sqrt{\frac{3}{4}}\sin(\theta)$$

$$R_{21}(\rho) = \left(\frac{Z}{a}\right)^{3/2}\frac{1}{2\sqrt{6}}\rho\, e^{-\rho/2}$$

$$\Psi_{211} = \left(\frac{Z}{a}\right)^{3/2}\frac{1}{8\sqrt{\pi}}\rho e^{-\rho/2}\sin(\theta)e^{i\phi} = \left(\frac{Z}{a}\right)^{3/2}\frac{1}{8\sqrt{\pi}}\frac{Zr}{a}e^{-Zr/2a}\sin(\theta)e^{i\phi}$$

Table 17.3 Real Hydrogen-Like Energy Eigenfunctions

$$\psi_{10} = \psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$$

$$\psi_{20} = \psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(2 - \frac{Zr}{a}\right)e^{-Zr/2a}$$

$$\psi_{21x} = \psi_{2p_x} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)e^{-Zr/2a}\sin(\theta)\cos(\phi)$$

$$\psi_{21y} = \psi_{2p_y} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)e^{-Zr/2a}\sin(\theta)\sin(\phi)$$

$$\psi_{210} = \psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)e^{-Zr/2a}\cos(\phi)$$

$$\psi_{300} = \psi_{3s} = \frac{1}{18\sqrt{3\pi}}\left(\frac{Z}{a}\right)^{3/2}\left[6 - \frac{4Zr}{a} + \left(\frac{2Zr}{3a}\right)^{2}\right]e^{-Zr/3a}$$

$$\psi_{310} = \psi_{3p_z} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{6Zr}{a} - \frac{Z^2r^2}{a^2}\right)e^{-Zr/3a}\cos(\theta)$$

$$\psi_{31x} = \psi_{3p_x} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{6Zr}{a} - \frac{Z^2r^2}{a^2}\right)e^{-Zr/3a}\sin(\theta)\cos(\phi)$$

$$\psi_{31y} = \psi_{3p_y} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{6Zr}{a} - \frac{Z^2r^2}{a^2}\right)e^{-Zr/3a}\sin(\theta)\sin(\phi)$$

$$\psi_{320} = \psi_{3d_{z^2}} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)^{2} e^{-Zr/3a}[3\cos^2(\theta) - 1]$$

$$\psi_{3d_{xz}} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)^{2} e^{-Zr/3a}\sin(\theta)\cos(\theta)\cos(\phi)$$

$$\psi_{3d_{yz}} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)^{2} e^{-Zr/3a}\sin(\theta)\cos(\theta)\sin(\phi)$$

$$\psi_{3d_{x^2-y^2}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)^{2} e^{-Zr/3a}\sin^2(\theta)\cos(2\phi)$$

$$\psi_{3d_{xy}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)^{2} e^{-Zr/3a}\sin^2(\theta)\sin(2\phi)$$

The Qualitative Properties of the Hydrogen-Like Orbitals

It is important to have a grasp of the qualitative properties of the hydrogen-like orbitals in three-dimensional space and to realize that they represent three-dimensional de Broglie waves. The real orbitals that we have obtained correspond to standing waves, with stationary nodes. We can visualize these waves by considering where they vanish. A three-dimensional wave can vanish at a surface (a *nodal surface*). Since each orbital is a product of three factors, the orbital vanishes if any one of the factors vanishes.

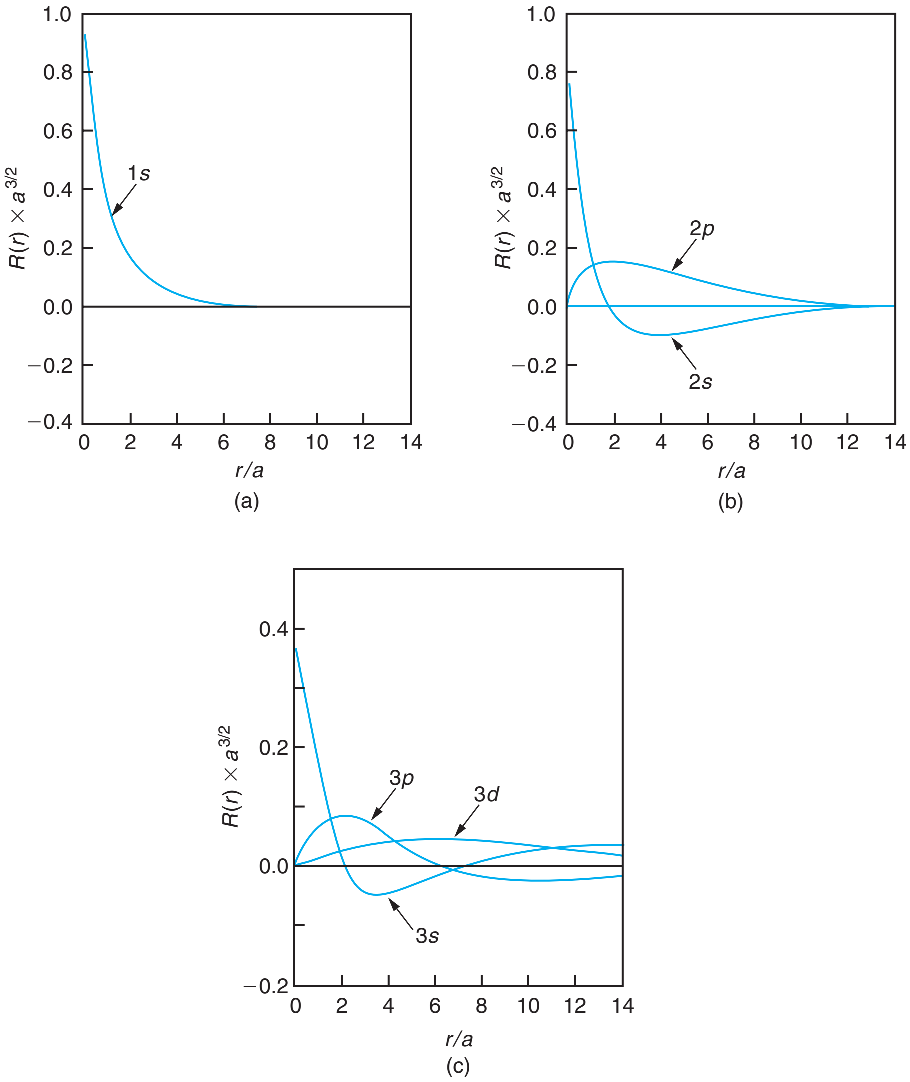


Figure 17.6 Radial Factors for Hydrogen-Like Energy Eigenfunctions. (a) $n = 1$. (b) $n = 2$. (c) $n = 3$. As n is increased with l fixed, the number of spherical nodal surfaces increases. As l is increased with n fixed, the number of spherical nodal surfaces decreases.

If the R factor in a wave function vanishes at some value of r, this corresponds to a spherical nodal surface. Figure 17.6 shows graphs of the R functions for the first three shells. It is possible to construct rough graphs of the R functions without referring to the formulas, using the following pattern: (1) the $s(l = 0)$ radial factors (R_{n0} or R_{ns}) are nonzero at the origin but all of the other R_{nl} functions vanish at the origin; (2) A curve representing a given R_{nl} function crosses the axis $n - l - 1$ times and must approach the axis for large values of r, corresponding to $n - l$ nodal spheres including the one at $r \to \infty$. A node at the origin does not count in this number of nodal spheres. For example, R_{1s} vanishes only at $r \to \infty$. The curve representing the R_{20} (R_{2s}) function crosses the axis once, corresponding to one spherical nodal surface in addition to the nodal surface at $r \to \infty$. The R_{21} (R_{2p}) function vanishes only at the origin and at $r \to \infty$. The $R_{30}(R_{3s})$ function corresponds to two spherical nodal surfaces in addition to the nodal surface at $r \to \infty$. The R_{31} function vanishes at the origin and produces a single spherical nodal surface in addition to the nodal surface at $r \to \infty$. The R_{32} function vanishes at the origin but has no nodal surface in addition to the nodal surface at $r \to \infty$.

Exercise 17.10

Sketch rough graphs of the following R functions:

a. $R_{32} = R_{3d}$
b. $R_{40} = R_{4s}$
c. R_{53}
d. R_{74}

A zero value in the Θ function produces a nodal surface that is a cone, except that a node at $\theta = 0$ and $\theta = \pi$ corresponds to a line at the z axis, and a node at $\theta = \pi/2$ corresponds to a nodal cone that is flattened into the xy plane. You can sketch rough graphs of the Θ functions from the following pattern: (1) The Θ_{lm} function has a number of nodal cones equal to $l - m$; (2) the Θ_{l0} functions are nonzero at $\theta = 0$ and $\theta = \pi$; (3) if l is odd, $\Theta_{l0}(0) = -\Theta_{l0}(\pi)$ and if l is even, $\Theta_{l0}(0) = \Theta_{l0}(\pi)$; (3) the Θ_{lm} functions for $m \geq 1$ vanish at $\theta = 0$ and $\theta = \pi$. Note that the nodal line $\theta = 0$ and $\theta = \pi$ is not included in the number of nodal cones. It is part of nodal planes from the Φ function.

EXAMPLE 17.5

Give the number of nodal cones for the following Θ_{lm} functions:

a. Θ_{00}
b. Θ_{10}
c. Θ_{11}
d. Θ_{20}

Solution

a. The Θ_{00} function has no nodal surface and is equal to a nonzero constant.
b. The Θ_{10} function has one nodal cone. Since the cones are generally arranged symmetrically, the nodal cone is flattened into the xy plane.
c. The Θ_{11} function vanishes at $\theta = 0$ and $\theta = \pi$, but has no nodal cones.
d. The Θ_{20} function has two nodal cones. A graph of it starts at a nonzero constant at $\theta = 0$, crosses the axis twice, and has the same value at $\theta = \pi$ as at $\theta = 0$.

A zero value in a Φ function produces a nodal surface that is a vertical half-plane containing the z axis. There are always two nodal half-planes that combine to produce a vertical plane containing the z axis. These nodal surfaces follow the pattern: (1) The Φ_0 function has no nodal planes; (2) for $m \geq 1$ the real Φ functions have a number of equally spaced nodal planes equal to m ($2m$ half-planes). The Φ_{mx} functions are nonzero at $\phi = 0$ and $\phi = \pi$, so their nodal planes do not contain the x axis. The Φ_{my} functions are equal to zero at $\phi = 0$ and $\phi = \pi$, so that one of their nodal planes contains the x axis. The real part of the complex Φ_m function is proportional to Φ_{mx} and has the same nodal planes as Φ_{mx}. The imaginary part of Φ_m is proportional to Φ_{my} and has the same nodal planes as Φ_{my}. Several graphs of Θ and Φ functions are shown in

Figure 17.7. It is possible to draw rough graphs of other Θ and Φ functions from the patterns of their nodes.

Exercise 17.11

Draw approximate graphs of the following functions:

a. Φ_{3y}
b. Φ_{4x}
c. Θ_{32}
d. Θ_{40}
e. Θ_{53}

The total number of nodal surfaces for any hydrogen-like orbital is

$$\text{Total number of nodal surfaces} = n - l + l - m + m = n \tag{17.4-2}$$

which includes the nodal sphere at $r \to \infty$. The pattern of nodal surfaces is summarized in Table 17.4. It is possible to draw rough sketches of the nodal surfaces for any hydrogen-like orbital from the patterns of the nodes of the three factors.

Table 17.4 Nodal Surface for the Hydrogen-Like Orbitals

R_{nl}	$n - l$ nodal spheres including $r \to \infty$ nonzero at origin only if $l = 0$
Θ_{lm}	$l - m$ nodal cones not including zeros at $\theta = 0$ and $\theta = \pi$ nonzero at $\theta = 0$ and $\theta = \pi$ only if $m = 0$
Φ_{mx}	m vertical nodal planes, none containing the x axis
Φ_{my}	m vertical nodal planes, including one containing the x axis
Φ_m	real part: same as Φ_{mx} imaginary part: same as Φ_{my}

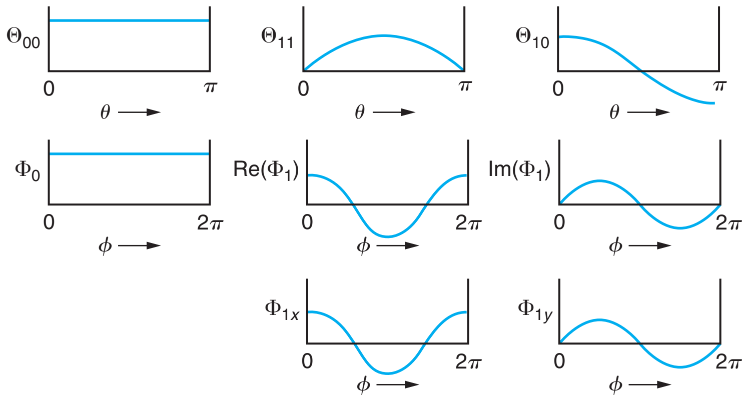


Figure 17.7 Some Θ and Φ Functions.

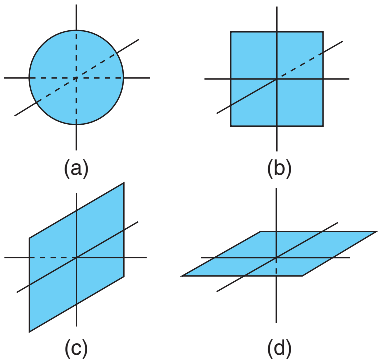


Figure 17.8 The Nodal Surfaces of the Real Energy Eigenfunctions of the Second Shell. (a) The nodal sphere of the $2s$ wave function. (b) The nodal plane of the $2p_x$ wave function. (c) The nodal plane of the $2p_y$ wave function. (d) The nodal plane of the $2p_z$ wave function.

EXAMPLE 17.6

Describe the nodal surfaces for the real orbitals of the second shell.

Solution

Each of the orbitals of the second shell has two nodal surfaces including a nodal sphere at $r \to \infty$. The ψ_{2s} function has only a spherical nodal surface at a finite value of r. The ψ_{2pz} (ψ_{210}) orbital has a nodal plane in the xy plane. The ψ_{2px} orbital has a nodal plane in the yz plane. The ψ_{2py} orbital has a nodal plane in the xz plane. Figure 17.8 depicts the nodal surfaces in the real orbitals of the second shell.

Exercise 17.12

Describe the nodal surfaces for the real orbitals of the $3d$ subshell.

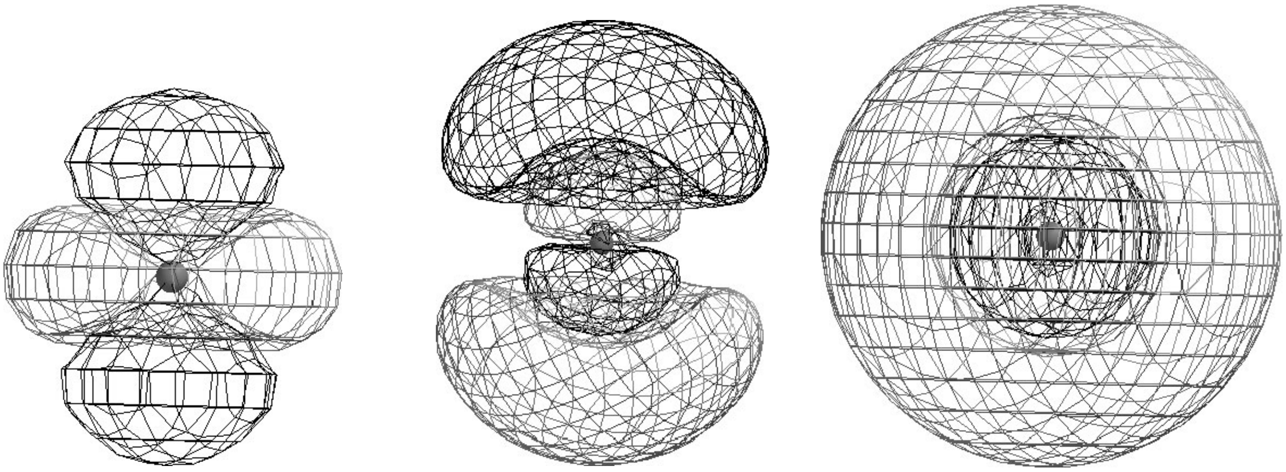
Orbital Regions

The *orbital region* is the region in space inside which the magnitude of an orbital function is larger than some specified small value. The magnitude of the orbital function has the same value on all parts of the boundary of the orbital region and this surface is sometimes called an *isosurface*. Since the square of the magnitude of the orbital function is the probability density, the orbital region is the region inside which the electron is most likely to be found. A common policy chooses a magnitude of the orbital at the boundary of the orbital regions such that 90% of the total probability of finding the electron lies inside the orbital region.

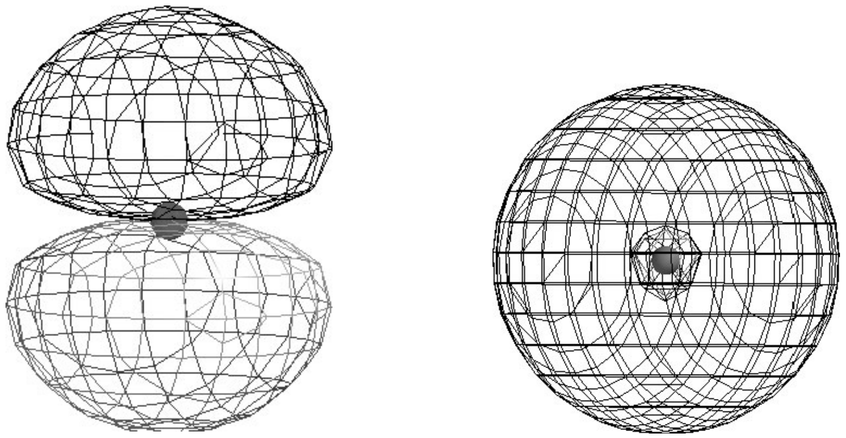
Any nodal surface divides the orbital region into discrete subregions, which we call *lobes*. It is usually possible to sketch an orbital region by first determining the nodal surfaces and then sketching lobes between the nodal surfaces. The wave function always has opposite signs in two lobes that are separated by a nodal surface, so it is not difficult to assign the sign for each lobe of a real orbital. Remember that any wave function can be multiplied by a constant, so that if we change all the signs of the lobes (multiplying by -1) no physical change is made.

Figure 17.9 schematically depicts several orbital regions of real orbitals. The sign of the orbital function is indicated by showing one sign in color and the other in black. The orbital regions of complex orbitals differ from those of real orbitals. The magnitude of the complex exponential $e^{im\phi}$ or $e^{-im\phi}$ is equal to unity, so that the magnitude of the complex orbital does not depend on ϕ. We say that these orbital regions are *cylindrically symmetric*. The vertical nodal planes that occur in the real and imaginary parts do not occur in the probability density. The real orbitals have orbital regions with lobes that lie between their vertical nodal planes. The compactness of the lobes of the orbital regions of the real p and d functions often makes them more useful than the complex p and d orbitals in discussing chemical bonding.

A wave function with more nodes has a higher energy because it corresponds to a shorter de Broglie wavelength and a larger electron speed. With a particle in a one-dimensional box, the number of nodes was (in addition to the nodes at the ends of the box) equal to $n - 1$, where n was the quantum number, and the energy was proportional to n^2. With the harmonic oscillator, the number of nodes (in addition to the nodes at $|x| \to \infty$) was equal to v, the quantum number, and the energy was proportional to $v + 1/2$. In the hydrogen-like orbitals the number of nodal surfaces is equal to the quantum number n and the energy is proportional to $-1/n^2$.



The $3d_z^2$ Orbital Region The $3p_z$ Orbital Region The $3s$ Orbital Region



The $2p_z$ Orbital Region The $2s$ Orbital Region

Figure 17.9 Some Orbital Regions of Hydrogen-Like Orbitals. Positive regions are in black and negative regions are in gray.

Pictures of orbital regions are included in elementary chemistry and organic chemistry textbooks, but sometimes the distinction between the orbital and the orbital region is not emphasized. The orbital is a wave function, whereas the orbital region is a three-dimensional region in space, inside which the magnitude of the orbital function is larger than some specified small value.

PROBLEMS

Section 17.4: The Orbitals of the Hydrogen-Like Atom

17.27 **a.** Sketch the nodal surfaces for the first five energy eigenfunctions for a particle in a three-dimensional spherical box. *Hint:* The spherical harmonic functions are the same as with the hydrogen atom, and the pattern of nodes in the radial function is the same as with the hydrogen atom, except that the nodal sphere at infinity is replaced by a nodal sphere at the surface of the box.

b. Sketch the orbital regions for the first few energy eigenfunctions for a particle in a three-dimensional spherical box.

c. Sketch the orbital regions for the first few energy eigenfunctions for a particle in a three-dimensional rectangular box. Compare them with the orbital regions in part b.

17.28 Sketch the nodal surfaces (cones and planes) for the real and imaginary parts of the spherical harmonic functions:

a. $Y_{10}(\Theta, \phi)$

b. $Y_{22}(\Theta, \phi)$

c. $Y_{31}(\Theta, \phi)$

d. $Y_{21}(\Theta, \phi)$

17.29 Sketch the nodal surfaces (cones and planes) for the real and imaginary parts of the spherical harmonic functions:

a. $Y_{32}(\Theta, \phi)$

b. $Y_{40}(\Theta, \phi)$

c. $Y_{33}(\Theta, \phi)$

d. $Y_{20}(\Theta, \phi)$

17.30 Transform the expression for $\Theta_{11}\Phi_{1y}$ to Cartesian coordinates. Show that this function is an eigenfunction of the operator $\widehat{L}_y$ and find its eigenvalue.

17.31 Draw rough graphs of the following pairs of functions and argue from the graphs that the functions are orthogonal to each other:

a. $\Theta_{00}(\theta)$ and $\Theta_{10}(\theta)$

b. $\Theta_{11}(\theta)$ and $\Theta_{21}(\theta)$

c. Φ_{2x} and Φ_{3y}

17.32 Calculate the angle between the z axis and each of the cones of possible directions of the orbital angular momentum for $l = 2$.

17.33 Find the ratio of the magnitude of the orbital angular momentum to the maximum value of its z component for each of the cases $l = 1, 2, 3$, and 4.

17.34 **a.** Draw a rough picture of the nodal surfaces of each of the real $3d$ orbitals. From these, draw rough pictures of the orbital regions.

b. Do the same for the complex $3d$ orbitals (eigenfunctions of $\widehat{L}_z$).

17.5 Expectation Values in the Hydrogen Atom

For stationary states the expectation value for an error-free measurement of a mechanical variable A is given by Eq. (16.4-4)

$$\langle A \rangle = \frac{\displaystyle\int \psi^* \widehat{A} \psi \, dq}{\displaystyle\int \psi^* \psi \, dq} \tag{17.5-1}$$

If the wave function is normalized, the denominator in this equation is equal to unity and can be omitted.

Normalization of the Hydrogen Atom Orbitals

For motion of one particle in three dimensions, normalization in Cartesian coordinates means that

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi(x, y, z)^* \psi(x, y, z) dxdydz = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\psi(x, y, z)|^2 d^3\mathbf{r} = 1 \tag{17.5-2}$$

where

$$d^3\mathbf{r} = dxdydz \quad \text{(Cartesian coordinates)} \tag{17.5-3}$$

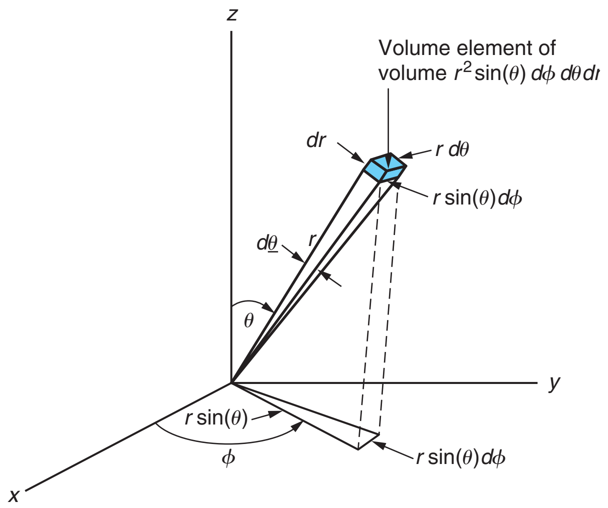


Figure 17.10 The Volume Element in Spherical Polar Coordinates.

In spherical polar coordinates,

$$\int_0^\infty\int_0^\pi\int_0^{2\pi}\psi(r,\theta,\phi)|^2r^2\sin(\theta)d\phi d\theta dr=\int_0^\infty\int_0^\pi\int_0^{2\pi}|\psi(r,\theta,\phi)|^2d^3\mathbf{r}=1 \qquad (17.5\text{-}4)$$

where

$$d^3\mathbf{r}=r^2\sin(\theta)d\phi d\theta dr \quad \text{(spherical polar coordinates)} \qquad (17.5\text{-}5)$$

The Jacobian is named for Carl Gustav Jacob Jacobi, 1804–1851, a great German mathematician who made numerous contributions to mathematics.

The factor $r^2\sin(\theta)$, which is called a *Jacobian*, is required to complete the element of volume in spherical polar coordinates. The form of this Jacobian can be deduced from the fact that an infinitesimal length in the r direction is dr, an infinitesimal arc length in the θ direction is $rd\theta$, and an infinitesimal arc length in the ϕ direction is $r\sin(\theta)$, $d\phi$ if the angles are measured in radians. The element of volume is the product of these mutually perpendicular infinitesimal lengths. Spherical polar coordinates were depicted in Figure 17.3. The volume element is crudely depicted by finite increments in Figure 17.10.

The normalization integral for the hydrogen atom orbitals can be factored in spherical polar coordinates:

$$\int_0^\infty R^*Rr^2dr\int_0^\pi\Theta^*\Theta\sin(\theta)d\theta\int_0^{2\pi}\Phi^*\Phi d\phi=1 \qquad (17.5\text{-}6)$$

We make the additional normalization requirement that each of the three integrals in this equation equals unity. The constants in the formulas for the R, Θ, and Φ factors that we have introduced correspond to this requirement. These separate normalizations in Eq. (17.5-6) simplify the calculation of many expectation values.

EXAMPLE 17.7

Calculate the expectation values $\langle 1/r\rangle$ and $\langle\mathcal{V}\rangle$ for a hydrogen-like atom in the 1s state.

Solution

Since the wave function is normalized we can omit the denominator in the formula for the expectation value shown in Eq. (16.4-1). We can factor the integral:

$$\left\langle \frac{1}{r} \right\rangle = \int_0^\infty R_{10}^* \frac{1}{r} R_{10} r^2 dr \int_0^\pi \Theta_{00}^* \Theta_{00} \sin(\theta) d\theta \int_0^{2\pi} \Phi_0^* \Phi_0 d\phi \tag{17.5-7}$$

By our separate normalizations, the second and third integrals both equal unity, so that

$$\left\langle \frac{1}{r} \right\rangle = \int_0^\infty R_{10}^* \frac{1}{r} R_{10} r^2 dr = 4\left(\frac{Z}{a}\right)^3 \int_0^\infty e^{-2Zr/a} r dr = 4\left(\frac{Z}{a}\right)^3 \left(\frac{a}{2Z}\right)^2 \int_0^\infty e^{-u} u du$$
$$= 4\left(\frac{Z}{a}\right)^3 \left(\frac{a}{2Z}\right)^2 (1) = \frac{Z}{a} \tag{17.5-8}$$

where we looked up the integral in Appendix C. Since the θ and the ϕ functions are both separately normalized, we could have omitted them from the outset and used only the radial factor R in calculating $\langle 1/r \rangle$. The same thing is true for the expectation value of any function of r.

We can use the result for $\langle 1/r \rangle$ to calculate $\langle \mathcal{V} \rangle$:

$$\langle \mathcal{V} \rangle = -\frac{Z e^2}{4\pi\varepsilon_0} \left\langle \frac{1}{r} \right\rangle = -\frac{Z^2 e^2}{4\pi\varepsilon_0 a} = 2E_{1s} \tag{17.5-9}$$

Note that $\langle 1/r \rangle$ is proportional to Z and $\langle \mathcal{V} \rangle$ is proportional to Z^2.

Exercise 17.13

Obtain numerical values for $\langle 1/r \rangle$ and $\langle \mathcal{V} \rangle$ for a hydrogen atom ($Z = 1$) in the $1s$ state.

The expectation value of the potential energy of a hydrogen-like atom equals twice the total energy. Therefore, the kinetic energy is half as large as the magnitude of the potential energy, and is equal in magnitude to the total energy (the kinetic energy must be positive while the total energy and the potential energy are negative). This behavior occurs in all systems of particles interacting only with the Coulomb potential energy, and is a consequence of the *virial theorem* of mechanics.[4]

The Radial Distribution Function

The radial distribution function, $f_r(r)$, is defined as the probability per unit value of r for finding the electron at a given distance from the nucleus. If r' is a particular value of r, then

$$\begin{pmatrix}\text{probability that the distance} \\ \text{from the nucleus to the electron} \\ \text{lies between } r' \text{ and } r' + dr\end{pmatrix} = f_r(r')dr \tag{17.5-10}$$

---

[4] I. N. Levine, *op. cit.*, p. 459ff (note 2).

The locations that lie at distances from the nucleus between r' and $r' + dr$ constitute a spherical shell of radius r' and thickness dr, as shown crudely in Figure 17.11a. The probability of finding the electron in this shell is obtained by integrating over θ and ϕ:

$$f_r(r)dr = \left(\int_0^{\pi}\int_0^{2\pi} |\psi(r,\theta,\phi)|^2 r^2 \sin(\theta)\phi d\theta\right)dr \tag{17.5-11}$$

The integral can be factored, and the θ and ϕ integrals give factors of unity due to the separate normalizations of Θ and Φ:

$$f_r(r)dr = R(r)^* R(r)\left(\int_0^{\pi} |\Theta|^2 \sin(\theta)d\theta \int_0^{2\pi} |\Phi|^2 d\phi\right)r^2 dr = R(r)^* R(r) r^2 dr \tag{17.5-12}$$

so that

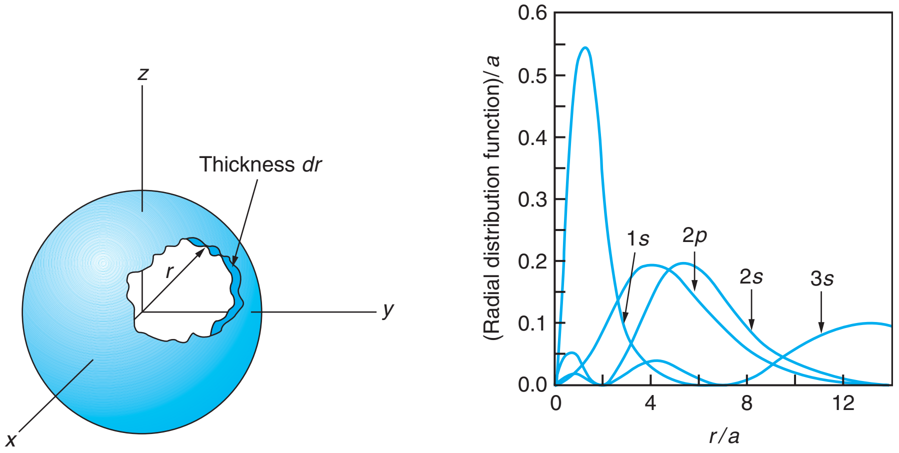
$$f_r(r) = r^2 R(r)^* R(r) = r^2 R(r)^2 \tag{17.5-13}$$

where we used the fact that the R function is real so that it equals its complex conjugate.

The expectation value of a quantity depending only on r can be computed using the radial distribution function. For example, the result of Example 17.7 can also be obtained from

$$\left\langle \frac{1}{r} \right\rangle = \int_0^{\infty} \frac{1}{r} R(r)^2 r^2 dr = \int_0^{\infty} \frac{1}{r} f_r(r)dr \tag{17.5-14}$$

Figure 17.11b shows graphs of the radial distribution function for several states. All of the states of a given subshell have the same radial distribution function because they have the same radial factor in their wave functions. A graph of a given radial distribution function can be sketched from the properties of the R function. All radial distribution functions vanish at $r = 0$ because of the r^2 factor and vanish at $r \to \infty$ because the exponential factor in R overwhelms any finite power of r as $r \to \infty$.



(a) (b)

Figure 17.11 The Probability Distribution for Electron-Nucleus Distances. (a) A spherical shell of radius r, and thickness dr. (b) Radial distribution functions for hydrogen orbitals.

Exercise 17.14

Sketch rough graphs of the radial distribution function for the following:

a. R_{43}

b. R_{75}

c. R_{50}

PROBLEMS

Section 17.5: Expectation Values in the Hydrogen Atom

17.35 Calculate $\langle r\rangle$, the expectation value of the distance from the nucleus for the $1s$ state of a hydrogen-like atom for $Z = 1$, $Z = 2$, and $Z = 3$.

17.36 **a.** Calculate the expectation value $\langle r\rangle$ for a hydrogen-like atom in the $1s$ state. Why is this not equal to $\langle 1/r\rangle^{-1}$?

b. Calculate $\langle r^2\rangle$ for a hydrogen-like atom in the $1s$ state. Why is this not equal to $\langle r\rangle^2$?

c. Find the most probable value of r for a hydrogen-like atom in the $1s$ state. Why is this not equal to $\langle r\rangle$?

17.37 Find the most probable distance of the electron from the nucleus for a hydrogen atom in the 211 ($2p1$) state.

17.6 The Time-Dependent Wave Functions of the Hydrogen Atom

We can write a time-dependent hydrogen atom wave function from our orbitals, using Eq. (15.2-18):

$$\Psi_{nlm}(r,\theta,\phi,t) = \psi_{nlm}(r,\theta,\phi)e^{-iE_nt/\hbar} \tag{17.6-1}$$

The probability density $\Psi^*\Psi$ is time-independent since the complex exponential and its complex conjugate cancel each other.

$$|\Psi_{nlm}(r,\theta,\phi,t)|^2 = \psi^*_{nlm}(r,\theta,\phi)e^{iE_nt/\hbar}\psi_{nlm}(r,\theta,\phi)e^{-iE_nt/\hbar} = \psi^*\psi \tag{17.6-2}$$

Our hydrogen atom orbitals correspond to stationary states, as do all wave functions that are products of a coordinate factor and a time factor. The expectation value of any time-independent variable in a stationary state is time-independent, and can be calculated from the coordinate wave function, as shown in Eq. (16.4-4).

The real orbitals correspond to standing waves, with stationary nodes. The complex orbitals with $m \neq 0$ do not represent standing waves, even though they correspond to stationary states. The Φ_m factor gives the following complex exponential factor in the time-dependent wave function:

$$\exp(im\phi - iEt/\hbar) = \cos(m\phi - Et/\hbar) + i\sin(m\phi - Et/\hbar) \tag{17.6-3}$$

For $m \neq 0$, this corresponds to a motion of the nodal planes of the real and imaginary parts around the z axis, and constitutes a traveling wave moving around the nucleus. It is easy to visualize an electron orbiting around the z axis like a classical particle, producing the angular momentum values that we have obtained. However, if we take E as negative, the motion is clockwise for $m > 0$ and counterclockwise for $m < 0$ when viewed from the positive end of the z axis. This direction of motion is opposite to the motion of a classical particle orbiting the nucleus with positive values of L_z. Since a constant can be added to the energy without effect, as discussed in Chapter 15, we can add a constant to E and make the frequency of oscillation equal to any value whatsoever, as mentioned in Example 15.6. Only the differences in the frequencies of oscillation have meaning. It appears that a positive value of E is required to make the nodes of the de Broglie wave move around the nucleus in the "correct" direction.

EXAMPLE 17.8

a. Calculate the frequency of oscillation of the 1*s* orbital of a hydrogen atom. Take the zero of energy as the value of $\langle \mathscr{V} \rangle$ for the 1*s* state, equal to $2E_{1s}$ (an arbitrary choice).

b. Calculate the frequency of oscillation of the 211 orbital of a hydrogen atom, using this zero of energy.

c. Calculate the frequency of a photon given off if a hydrogen atom makes a transition from the $n = 2$ to the $n = 1$ energy level of a hydrogen atom. Compare this frequency with the frequency of the 211 orbital oscillation, with the frequency of oscillation of the 1*s* orbital, and the difference between these two frequencies.

Solution

a. Relative to this zero of energy, the energy of the 1*s* state is $-E_1$, equal to 2.179×10^{-18} J. The frequency is given by Eq. (15.2-23)

$$\nu = \frac{E}{h} = \frac{2.179 \times 10^{-18}\ \mathrm{J}}{6.6261 \times 10^{-34}\ \mathrm{J\,s}} = 3.289 \times 10^{-15}\ \mathrm{s}^{-1}$$

b. Relative to this zero of energy, the energy of this state is

$$E_2 = -\frac{2.179 \times 10^{-18}\ \mathrm{J}}{2^2} - (-2(2.179 \times 10^{-18}\ \mathrm{J})) = 3.183 \times 10^{-18}\ \mathrm{J}$$

$$\nu_2 = \frac{3.183 \times 10^{-18}\ \mathrm{J}}{6.6261 \times 10^{-34}\ \mathrm{J\,s}} = 5.755 \times 10^{15}\ \mathrm{s}^{-1}$$

c.

$$\nu(\text{photon}) = \frac{E_2 - E_1}{h} = \frac{3.183 \times 10^{-18}\ \mathrm{J} - 2.179 \times 10^{-18}\ \mathrm{J}}{6.6261 \times 10^{-34}\ \mathrm{J\,s}}$$

$$= 2.466 \times 10^{15}\ \mathrm{s}^{-1}$$

This frequency does not match either ν_1 or ν_2, but it does match $\nu_1 - \nu_2$.

$$\nu_1 - \nu_2 = 5.755 \times 10^{15}\ \mathrm{s}^{-1} - 3.289 \times 10^{15}\ \mathrm{s}^{-1} = 2.466 \times 10^{15}\ \mathrm{s}^{-1}$$

The values of the frequencies of oscillation of the wave functions do not have any physical meaning, but the differences in the frequencies do have meaning.

From this example we can deduce the same thing that we deduced in Example 15.6. Only the difference in de Broglie frequencies is meaningful.

If we visualize an electron orbiting around the z axis like a classical particle, it is difficult to picture the motion of an electron in an orbital with $m = 0$, since there are no nodal planes and L_z has the predictable value of zero. We can only visualize the wave pulsating without nodes, and try to visualize the electron moving out from the nucleus, then moving toward the nucleus, passing through the nucleus and repeating the motion on the other side of the nucleus. Sometimes it is best not to visualize things classically.

PROBLEMS

Section 17.6: The Time-Dependent Wave Functions of the Hydrogen Atom

17.38 Describe verbally the how an electron appears to move around the nucleus in the 211 state and in the 21, −1 state.

17.39 **a.** The energy of the 211 state of the hydrogen atom relative to the ground-state energy is equal to $10.20\ \text{eV} = 1.6340 \times 10^{-18}$ J. Find the frequency of oscillation of the orbital using this energy. Remember that the frequency of oscillation of a de Broglie wave depends on the choice of the zero of energy. Only differences in frequencies are meaningful.

b. Find the angular speed around the z axis of the angular nodes of the wave function in radians per second for the 211 state of the hydrogen atom. Convert this to revolutions per second.

c. Assume that the electron is orbiting around the z axis at a distance equal to $4a$ where a is the Bohr radius. This distance is equal to the most probable distance for the 211 state of the hydrogen atom. Assume that $L_z = \hbar$ and calculate the angular speed using the classical formula

$$L_z = mr\omega^2$$

where ω is the angular speed in radians per second. Compare this result with the angular speed of the nodes in parts a and b.

d. Calculate the speed of the electron with the same assumptions as in part c.

17.7 The Intrinsic Angular Momentum of the Electron. "Spin"

The complex orbitals with $m \neq 0$ correspond to revolution of the electron around the nucleus. The angular momentum of this motion is called the *orbital angular momentum*. Electrons are found experimentally to have an additional angular momentum that is not included in the Schrödinger theory. To obtain adequate agreement with experiment this feature must be added to the Schrödinger theory. We call it the *intrinsic angular momentum* or the *spin angular momentum*. There is a version of quantum mechanics that is compatible with special relativity, based on the Dirac equation. The intrinsic angular momentum occurs naturally in this theory, which we do not discuss.[5]

The Dirac equation is named for P. A. M. Dirac, 1902–1984, a famous British mathematician and physicist who shared the 1933 Nobel Prize in physics with Schrödinger.

EXAMPLE 17.9

Calculate the expectation value of the square of the speed of the electron in a hydrogen atom in the 1s state, and from this calculate the root-mean-square speed. Compare this speed with the speed of light.

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[5] F. Mandl, *Quantum Mechanics*, Butterworths Scientific Publications, London, 1957, p. 203ff.

Solution

We can obtain this quantity from the expectation value of the kinetic energy:

$$\langle \mathscr{K} \rangle = -E_1 = 2.18 \times 10^{-18}\,\mathrm{J}$$

$$\langle v^2 \rangle = \frac{2\langle \mathscr{K} \rangle}{m} = \frac{2(2.18 \times 10^{-18}\,\mathrm{kg\,m^2\,s^{-2}})}{9.11 \times 10^{-31}\,\mathrm{kg}} = 4.69 \times 10^{12}\,\mathrm{m^2\,s^{-2}}$$

$$v_{\mathrm{rms}} = \langle v^2 \rangle^{\{1/2\}} = 2.16 \times 10^{6}\,\mathrm{m\,s^{-1}}$$

which is smaller than the speed of light by a factor of roughly 1/100. For elements past the middle of the periodic table, the electron speeds approach the speed of light. For accurate work with these elements, relativistic corrections must be included or the Dirac equation must be used.

Exercise 17.15

The kinetic energy of $1s$ electron in a hydrogen-like atom is proportional to Z^2. Find the root-mean-square speed of a $1s$ electron in a uranium atom with $Z = 92$. Compare this with the speed of light.

The z component of the intrinsic angular momentum is found experimentally to have one of only two possible values, $\hbar/2$ and $-\hbar/2$. We denote the intrinsic angular momentum by **S** and write

$$S_z = \pm\frac{\hbar}{2} \tag{17.7-1}$$

We assign a new quantum number, m_s, for the z component of the intrinsic angular momentum, with the values

$$m_s = \pm\frac{1}{2} \tag{17.7-2}$$

so that:

$$S_z = m_s\hbar \tag{17.7-3}$$

The values of m_s follow the standard pattern of angular momentum quantum numbers if we assign a quantum number $s = 1/2$ for the square of the intrinsic angular momentum. The square of the intrinsic angular momentum has the fixed value

$$S^2 = \hbar^2\frac{1}{2}\left(\frac{1}{2} + 1\right) = \frac{3}{4}\hbar^2 \tag{17.7-4}$$

The orbital angular momentum and the intrinsic angular momentum are different from each other in three ways. First, the orbital angular momentum occurred naturally in the solution of the Schrödinger equation, whereas the intrinsic angular momentum is arbitrarily added to the Schrödinger theory. Second, the magnitude of the orbital angular momentum takes on various quantized magnitudes, whereas the intrinsic angular momentum has only one fixed magnitude. Third, the intrinsic angular momentum corresponds to quantum numbers that are half-integers instead of integers.

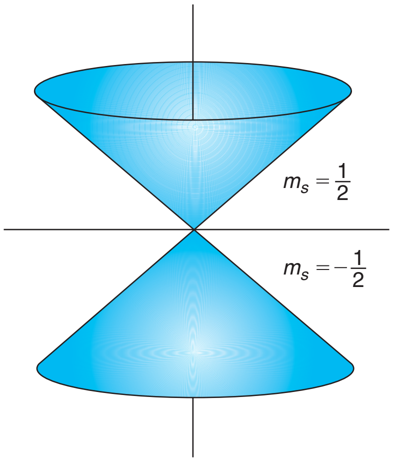

Figure 17.12 Cones of Possible Spin Angular Momentum Directions for One Electron.

EXAMPLE 17.10

Figure 17.12 shows the two cones of possible directions of the intrinsic angular momentum. Find the angle between the z axis and the intrinsic angular momentum for $m_s = +1/2$.

Solution

$$\theta = \arccos\left(\frac{\hbar/2}{\hbar\sqrt{(1/2)(3/2)}}\right) = \arccos\left(\frac{1/2}{\sqrt{3/4}}\right)$$

$$= \arccos(0.57735) = 54.7356\ldots\text{degrees} = 0.9553166\ldots\text{radians}$$

The total angular momentum of an electron is the vector sum of the orbital and intrinsic angular momenta and is denoted by **J**

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \tag{17.7-5}$$

Vector addition is described in Appendix B. The z component of **J** is the algebraic sum of L_z and S_z:

$$J_z = L_z + S_z = m\hbar + m_s\hbar = m\hbar \pm \frac{1}{2}\hbar \tag{17.7-6}$$

Although it is not known what the electron's internal structure is (if any), it is customary to ascribe the intrinsic angular momentum to rotation of the electron about its own axis, calling it the *spin angular momentum*.[6] The assumed spinning motion is analogous to the rotation of the earth on its axis, and the orbital motion is analogous to the earth's revolution about the sun. We will use this spin interpretation, although there is no guarantee that this picture is physically accurate. We will call the state for $m_s = +1/2$ the "spin up" state, and the state for $m_s = -1/2$ the "spin down" state, corresponding to the direction of the intrinsic angular momentum vector.

We have now twice as many possible states of electronic motion in a hydrogen-like atom as we did before, because for every set of values of the quantum numbers n, l, and m, m_s can equal either $1/2$ or $-1/2$. There are two ways to include spin in our notation. The first is to attach the value of m_s as another subscript on the orbital symbol, replacing nlm by $nlm\,m_s$. There is no need to include the value of s since it is fixed at $s = 1/2$. The orbital is now called a *spin orbital*. The second way, which we will usually use, is to multiply the original orbital by a *spin function* that is called α for $m_s = +1/2$ and β for $m_s = -1/2$. The original orbital is now called a *space orbital*, and the product of the space orbital and the spin function represents the spin orbital. The two ways of writing a spin orbital are equivalent:

$$\psi_{nlm,1/2} = \psi_{nlm}\alpha, \quad \psi_{nlm,-1/2} = \psi_{nlm}\beta \tag{17.7-7}$$

The spin functions are thought of as being functions of some spin coordinates that are not explicitly represented. We define operators for the spin angular momentum that are analogous to the orbital angular momentum operators. Since we do not have any

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[6] Superstring theory pictures the electron and other elementary particles as vibrations in 10 or 11 dimensions of tiny strings with physical dimensions around 10^{-35} m. For an introduction, see B. Greene, *The Elegant Universe*, Vintage Books, New York, 2003.

representation of the spin coordinates, we cannot write any mathematical formulas for the functions or for the operators, but assign their properties to conform to the standard pattern of angular momentum eigenvalues for $s = 1/2$. The spin functions α and β are defined to be eigenfunctions of $\widehat{S}^2$, the operator for the square of the spin angular momentum:

$$\widehat{S}^2\alpha = \hbar^2(1/2)(3/2)\alpha = \hbar^2\frac{3}{4}\alpha \tag{17.7-8}$$

$$\widehat{S}^2\beta = \hbar^2(1/2)(3/2)\beta = \hbar^2\frac{3}{4}\beta \tag{17.7-9}$$

The spin functions are also defined to be eigenfunctions of $\widehat{S}_z$, the operator for the z component of the spin angular momentum:

$$\widehat{S}_z\alpha = m_s\hbar\alpha = +\frac{\hbar}{2}\alpha \tag{17.7-10}$$

$$\widehat{S}_z\beta = m_s\hbar\beta = -\frac{\hbar}{2}\beta \tag{17.7-11}$$

The spin functions are defined to be normalized and orthogonal to each other. Since we do not have an explicit representation of any independent variables, we simply write the equations

$$\int \alpha(1)^*\alpha(1)\,d^s(1) = \int \beta(1)^*\beta(1)\,d^s(1) = 1 \quad \text{(by definition)} \tag{17.7-12}$$

and

$$\int \beta(1)^*\alpha(1)\,d^s(1) = \int \alpha(1)^*\beta(1)\,d^s(1) = 0 \quad \text{(by definition)} \tag{17.7-13}$$

We interpret the probability density for one electron as follows. If an electron in a hydrogen atom occupies the spin orbital $\psi_{nlm}(r_1, \theta_1, \phi_1)\alpha(1)$, then we assert that the probability of finding it in the volume element $r_1^2\sin(\theta_1)dr_1d\theta_1d\phi_1 = d^3\mathbf{r}_1$ with spin up is $|\psi_{nlm}(r_1, \theta_1, \phi_1)|^2d^3\mathbf{r}_1$ and the probability of finding it with spin down is zero. If an electron in a hydrogen atom occupies the spin orbital $\psi_{nlm}(r_1, \theta_1, \phi_1)\beta(1)$, then we assert that the probability of finding it in the volume element $d^3\mathbf{r}_1$ with spin down is $|\psi_{nlm}(r_1, \theta_1, \phi_1)|^2d^3\mathbf{r}_1$ and the probability of finding it with spin up is zero.

Inclusion of the intrinsic angular momentum modifies the Schrödinger theory of the electron so that it agrees adequately with experiment for most purposes. Further modifications can be made to include additional aspects of relativistic quantum mechanics, such as differences between the energies of "spin up" and "spin down" states for states of nonzero orbital angular momentum. We will not discuss the *spin–orbit coupling* that produces this effect. It is numerically unimportant for atoms in the first part of the periodic table, but it is important in heavy atoms.[7]

We are now able to apply the concept of a complete set of commuting observables to the hydrogen atom. As explained in Chapter 16, measurement of a complete set of

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[7] Pilar, *op. cit.*, p. 301ff (note 1); K. Balasubramanian, *J. Phys. Chem.*, **93**, 6585 (1989).

commuting observables can put a system into a known state. The four observables, E, L^2, L_z, and S_z, form a complete set of commuting observables for the hydrogen atom. Assume that we can measure the energy without any experimental error. The outcome must be an eigenvalue of $\widehat{H}$, and let us assume that the outcome is E_3, equal to $(-13.6\,\text{eV})/3^2 = -1.511$ eV. After the measurement, the wave function must be a linear combination of all of the energy eigenfunctions in the $3s$, $3p$, and $3d$ subshells, all of which correspond to the correct energy eigenvalue. There are 18 such wave functions.

Assume that we now measure L^2 and that the outcome is $6\hbar^2$, which means that after the measurement the wave function is a linear combination of all energy eigenfunctions with $n = 3$ and $l = 2$ (all of the states in the $3d$ subshell). There are 10 spin orbitals in the $3d$ subshell. Now assume that we measure L_z and obtain the value $2\hbar$, corresponding to $m = 2$. This means that the wave function is now a linear combination of $\psi_{322}\alpha$ and $\psi_{322}\beta$. Now assume that we measure S_z and obtain the result $\hbar/2$. This means that we have put the hydrogen atom into the state corresponding to $\psi_{322}\alpha$. Since there were four quantum numbers to be determined, we needed four commuting operators to put the hydrogen atom into a known state. We do not have any information about the state before the measurements, except that it could be represented by a linear combination in which the coefficient of the $\psi_{322}\alpha$ state is nonzero.

PROBLEMS

Section 17.7: The Intrinsic Angular Momentum of the Electron. “Spin”

17.40 Calculate the expectation value of the square of the speed of the electron in a hydrogen-like atom with $Z = 26$ (an Fe^{25+} ion) in the $1s$ state, and from this calculate the root-mean-square speed. Compare this speed with the speed of light and with the root-mean-square speed of the electron in a hydrogen atom from Example 17.9.

17.41 If the spin angular momentum is known to lie somewhere in the cone of possible directions for $m_s = 1/2$, and the orbital angular momentum is known to lie somewhere in the cone of possible directions for $m = 1$, what is the largest angle possible between the two angular momentum vectors? What is the smallest angle?

17.42 The standard model of subatomic particles does not ascribe any internal structure to the electron. The “string theory” asserts that all fundamental particles consist of patterns of vibration of tiny string-like objects that are the true fundamental particles. These strings have size in the range of 10^{-35} m. Pretend that the electron is an object of mass equal to the mass of an electron moving in a circular orbit of radius 1×10^{-35} m. Find its apparent speed in this orbit, given the magnitude of the spin angular momentum. Compare this apparent speed with the speed of light.

Summary of the Chapter

The time-independent Schrödinger equation for a hydrogen atom was separated into a one-particle Schrödinger equation for the motion of the center of mass of the two particles and a one-particle Schrödinger equation for the motion of the electron relative to the nucleus. The motion of the center of mass is the same as that of a free particle. The Schrödinger equation for the relative motion was solved by separation of variables in spherical polar coordinates, assuming the trial function

$$\psi_{nlm}(r, \theta, \phi) = R_{nl}(r)Y_{lm}(\theta, \phi) = R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\phi)$$

The angular functions $Y_{lm}(\theta, \phi)$ are called spherical harmonic functions. These functions are eigenfunctions of the operator for the square of the orbital angular momentum and its z component, with eigenvalues given by

$$\widehat{L}^2 Y_{lm} = \hbar l(l+1) Y_{lm}$$

and

$$\widehat{L}_z Y_{lm} = \hbar m Y_{lm}$$

The radial factors are a set of functions with two quantum numbers: n, the principal quantum number, and l, the same quantum number as in the spherical harmonic functions. The hydrogen-like atom has a single electron and Z protons in the nucleus. The energy eigenvalues of the hydrogen-like atom depend only on the principal quantum number:

$$E = E_n = -\frac{(13.60\text{ eV})\, Z^2}{n^2}$$

The intrinsic electronic angular momentum of the electron was introduced. It corresponds to fixed magnitude and two possible z projections, $\hbar/2$ and $-\hbar/2$. It is commonly visualized as due to a spinning motion of the electron in addition to its orbital motion.

ADDITIONAL PROBLEMS

17.43 **a.** Calculate the de Broglie wavelength for an electron moving with the speed found in Example 17.9.

b. Compare your result in part a with the circumference of the first Bohr orbit for the hydrogen atom.

17.44 Consider a three-dimensional harmonic oscillator, with the potential energy function

$$\mathcal{V} = \frac{k}{2}(x^2 + y^2 + z^2)$$

where k is the force constant.

a. Using the solution for a one-dimensional oscillator, write the formula representing the ground-state wave function in Cartesian coordinates.

b. Using the solution for a one-dimensional oscillator write the formula representing the energy eigenvalues. Give the degeneracy of each of the first three energy levels. Draw an energy level diagram for these energy levels.

c. Draw a sketch of the orbital region for the ground state and one of the states of the first excited level (specify the state).

d. Explain why the solution could also be carried out in spherical polar coordinates. Do not carry out the solution. What can you say about the functions of θ and ϕ that occur in the solution? What can you say about the quantum numbers that would occur? What can you say about the energy levels? What can you say about the degeneracies of the first three energy levels? What other variables other than the energy will have predictable values for the states corresponding to the solutions in spherical polar coordinates?

17.45 Calculate the expectation value and the standard deviation of L_z for a hydrogen atom in the $2p_x$ state. Explain what the values mean.

17.46 **a.** For a hydrogen atom in the $2p_z$ state, give the value of $\langle L_z \rangle$ and $\langle L_z^2 \rangle$.

b. From your result of part a, give the value of $\langle L_x \rangle$, $\langle L_x^2 \rangle$, $\langle L_y \rangle$, and $\langle L_y^2 \rangle$.

17.47 For a hydrogen atom in the $2p_x$ state, give the value of $\langle L_x \rangle$ and $\langle L_x^2 \rangle$. What can you say about the value of $\langle L_y^2 \rangle$ for this state?

17.48 Give the numerical value of each of the following:

a. The reduced mass of the two particles in a hydrogen atom.

b. The reduced mass of the nuclei in a CO molecule.

c. The magnitude of the orbital angular momentum of an electron in a hydrogen atom in a state with $n = 3$, $l = 2$, $m = 1$.

d. The z component of the orbital angular momentum in part c.

e. The z component of the spin angular momentum of an electron with “spin up.”

f. The magnitude of the spin angular momentum of an electron.

g. The energy in electron volts of a hydrogen atom in the $n = 3$ energy level.

h. The degeneracy of the $n = 3$ energy level of a hydrogen atom.

17.49 From the pattern of nodal surfaces observed in the subshells that we have discussed, predict the following, excluding the nodal sphere at $r \rightarrow \infty$:

a. The number of nodal spheres in the 6s wave function.

b. The number of nodal spheres in a 6p wave function.

c. The number of nodal planes containing the z axis in the real part of the $\psi_{6d0}(\psi_{620})$ wave function.

d. The number of nodal cones in the real part of the $\psi_{6p1}(\psi_{611})$ wave function.

17.50 Use the expression for the time-dependent wave function to show that the real hydrogen-like energy eigenfunctions correspond to standing waves, whereas the complex hydrogen-like energy eigenfunctions correspond to traveling waves. Tell how the traveling waves move. Show that both types of energy eigenfunctions correspond to stationary states.

17.51 Identify the following statements as either true or false. If a statement is true only under special circumstances, label it as false.

a. The angular factors Θ and Φ are the same functions for the hydrogen atom wave functions and those of any other central-force problem.

b. In a central-force problem, the motion of the center of mass and the relative motion can be treated separately only to a good approximation.

c. Every atom is spherical in shape.

d. The x or y axis could be chosen as the unique direction for angular momentum components instead of the z axis.

e. The energy eigenvalues for the H atom in the Schrödinger equation are identical with those in the Bohr theory.

f. The angular momentum eigenvalues for the H atom in the Schrödinger equation are identical with those in the Bohr theory.

g. There is a one-to-one correspondence between the states of the H atom in the Bohr theory and the states of the H atom in quantum mechanics.

18

The Electronic States of Atoms. II. The Zero-Order Approximation for Multielectron Atoms

PRINCIPAL FACTS AND IDEAS

1. The zero-order approximation for a multielectron atom ignores the electron–electron repulsion, so that each electron occupies a hydrogen-like spin orbital.
2. The electronic wave function for a multielectron atom must be antisymmetric. That is, the wave function must change sign if the coordinates of two electrons are exchanged.
3. In an antisymmetrized orbital wave function, every electron must occupy a different spin orbital (the Pauli exclusion principle).
4. In the Russell–Saunders approximation, the total orbital angular momentum and the total spin angular momentum of a multielectron atom can have predictable values that follow the same pattern as other angular momenta.

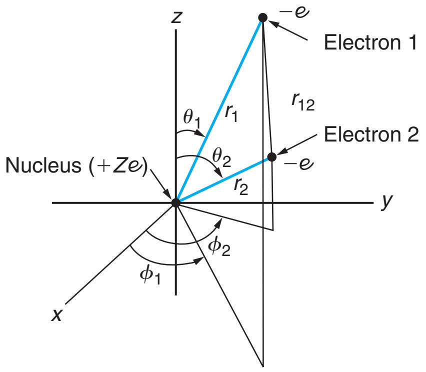

Figure 18.1 The Helium Atom System.

18.1 The Helium-Like Atom

The helium atom contains two electrons and a nucleus containing two protons. We define a *helium-like atom* to have two electrons and a nucleus with Z protons, so that $Z = 2$ represents the He atom, $Z = 3$ represents the Li^+ ion, and so on. The helium-like atom is shown in Figure 18.1. Our treatment will apply to any value of Z. With the hydrogen-like atom, the motion of the electron relative to the nucleus was equivalent to the motion of a fictitious particle with mass equal to the reduced mass of the electron and the nucleus. Replacing the reduced mass by the mass of the electron in our formulas was equivalent to assuming a stationary nucleus. This was a good approximation, because the mass of the nucleus is large compared to mass of the electron, which means that the nucleus remains close to the center of mass.

The helium nucleus is even more massive than the hydrogen nucleus, and we will assume that the nucleus is stationary while studying the motion of the electrons. Of course, the nucleus can move, but as it moves, the electrons follow along, adapting to a new location of the nucleus almost as though it had always been there. This is similar to ignoring the motion of the earth around the sun when we describe the motion of the moon relative to the earth.

Assuming a stationary nucleus, the classical Hamiltonian function of the electrons in a helium-like atom with Z protons in the nucleus is

$$\mathscr{H}_{\mathrm{cl}} = \frac{1}{2m}p_1^2 + \frac{1}{2m}p_2^2 + \frac{1}{4\pi\varepsilon_0}\left(-\frac{Ze^2}{r_2} - \frac{Ze^2}{r_1} + \frac{e^2}{r_{12}}\right) \tag{18.1-1}$$

where m is the mass of an electron, $-e$ is the charge of the electron, p_1^2 is the square of the momentum of electron 1, p_2^2 is the square of the momentum of electron 2, and the distances are as labeled in Figure 18.1. The Hamiltonian operator is obtained by making the replacements shown in Eq. (16.3-8) and its analogues:

$$\widehat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) + \frac{1}{4\pi\varepsilon_0}\left(-\frac{Ze^2}{r_2} - \frac{Ze^2}{r_1} + \frac{e^2}{r_{12}}\right) \tag{18.1-2}$$

where ∇_1^2 and ∇_2^2 are the Laplacian operators for the coordinates of electrons 1 and 2 as defined in Eq. (15.2-26) and Eq. (B-45).

The Hamiltonian operator of Eq. (18.1-2) gives a Schrödinger equation that cannot be solved exactly. No three-body system can be solved exactly, either classically or quantum mechanically, so we must work with approximations. We begin with the *zero-order approximation*, which corresponds to ignoring the term that depends on r_{12}. This is not a good approximation, but it is a starting point for better approximations. The zero-order Hamiltonian operator is a sum of two hydrogen-like Hamiltonians:

$$\widehat{H}^{(0)} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_2} \tag{18.1-3}$$

$$= \widehat{H}_{\mathrm{HL}}(r_1,\theta_1,\phi_1) + \widehat{H}_{\mathrm{HL}}(r_2,\theta_2,\phi_2) = \widehat{H}_{\mathrm{HL}}(1) + \widehat{H}_{\mathrm{HL}}(2) \tag{18.1-4}$$

where $\widehat{H}_{\mathrm{HL}}(1)$ and $\widehat{H}_{\mathrm{HL}}(2)$ are hydrogen-like Hamiltonians. In the last equality we abbreviate the coordinates of a particle by writing only the particle index. These hydrogen-like Hamiltonians must correspond to $Z = 2$ for the helium atom, or $Z = 3$ for the Li^+ ion, and so on. The zero-order time-independent Schrödinger equation is

$$\widehat{H}^{(0)}\Psi^{(0)}(1,2) = \left[\widehat{H}_{\mathrm{HL}}(1) + \widehat{H}_{\mathrm{HL}}(2)\right]\Psi^{(0)}(1,2) = E^{(0)}\Psi^{(0)}(1,2) \tag{18.1-5}$$

where we continue our practice of the last chapter, using a capital Ψ for a multielectron wave function and a lower-case ψ for a one-electron wave function. Equation (18.1-5) can be solved by separation of variables, using the trial solution:

$$\Psi^{(0)}(1,2) = \psi_1(r_1,\theta_1,\phi_1)\psi_2(r_2,\theta_2,\phi_2) = \psi_1(1)\psi_2(2) \tag{18.1-6}$$

where ψ_1 and ψ_2 are two orbitals. In the second equality we abbreviate the coordinates by writing only the subscript specifying the electron. A multielectron wave function that is a product of orbitals is called an *orbital wave function*.

We substitute the trial solution of Eq. (18.1-6) into Eq. (18.1-5) and use the fact that $\psi_1(1)$ is treated as a constant when $\widehat{H}_{\mathrm{HL}}(2)$ operates and $\psi_2(2)$ is treated as a constant when $\widehat{H}_{\mathrm{HL}}(1)$ operates. The result is:

$$\psi_2(2)\widehat{H}_{\mathrm{HL}}(1)\psi_1(1) + \psi_1(1)\widehat{H}_{\mathrm{HL}}(2)\psi_2(2) = E^{(0)}\psi_1(1)\psi_2(2) \tag{18.1-7}$$

We divide by $\psi_1(1)\psi_2(2)$:

$$\frac{1}{\psi_1(1)}\widehat{H}_{\mathrm{HL}}(1)\psi_1(1) + \frac{1}{\psi_2(2)}\widehat{H}_{\mathrm{HL}}(2)\psi_2(2) = E^{(0)} \tag{18.1-8}$$

The variables are now separated. That is, each of the terms on the left-hand side of the equation depends only on a set of variables not occurring in the other term. Because each set of variables can be allowed to range while the other is fixed, the first term must equal a constant, which we call E_1, and the second term must equal a constant, E_2. These constants must add to the approximate energy eigenvalue $E^{(0)}$:

$$E_1 + E_2 = E^{(0)} \tag{18.1-9}$$

We set the first term in Eq. (18.1-8) equal to E_1 and multiply by $\psi_1(1)$ and carry out the analogous operations on the second term. We now have two equations:

$$\widehat{H}_{\mathrm{HL}}(1)\psi_1(1) = E_1\psi_1(1) \tag{18.1-10}$$

$$\widehat{H}_{\mathrm{HL}}(2)\psi_2(2) = E_2\psi_2(2) \tag{18.1-11}$$

These are two hydrogen-like Schrödinger equations. The eigenvalues E_1 and E_2 are hydrogen-like orbital energies. The total electronic energy in the zero-order approximation is

$$E^{(0)}_{n_1n_2} = E_{n_1}(\text{HL}) + E_{n_2}(\text{HL}) = -(13.60\,\text{eV})\left[\frac{Z^2}{n_1^2} + \frac{Z^2}{n_2^2}\right] \tag{18.1-12}$$

where n_1 and n_2 are two values of the principal quantum number for a hydrogen-like atom.

The orbitals $\psi_1(1)$ and $\psi_2(2)$ are hydrogen-like orbitals:

$$\Psi^{(0)}(1,2) = \psi_1(1)\psi_2(2) = \psi_{n_1l_1m_1}(1)\,\psi_{n_2l_2m_2}(2) \tag{18.1-13}$$

The function in Eq. (18.1-13) satisfies the zero-order Schrödinger equation, but does not include the spin angular momentum, which can be included by replacing the space orbitals by spin orbitals:

$$\Psi^{(0)}(1,2) = \psi_1(1)\psi_2(2) = \psi_{n_1l_1m_1,m_{s1}}(1)\,\psi_{n_2l_2m_2,m_{s2}}(2) \tag{18.1-14}$$

We can also represent the spin orbitals as products of space orbitals and spin functions. One of several possible orbital wave functions would then be

$$\Psi^{(0)}(1,2) = \psi_1(1)\psi_2(2) = \psi_{n_1l_1m_1}(1)\alpha(1)\,\psi_{n_2l_2m_2}(2)\beta(2) \tag{18.1-15}$$

PROBLEMS

Section 18.1: The Helium-Like Atom

18.1 Assume that each of the two electrons in a helium atom is 50.0 pm (5.00×10^{-11} m) from the nucleus.

a. If the two electrons lie on a line passing through the nucleus and are on opposite sides of the nucleus, calculate the potential energy of the electron–electron repulsion. Compare it with the potential energy of the electron–nucleus attraction.

b. Repeat the calculation of part a assuming that the two electrons and the nucleus are at the corners of an equilateral triangle, 50.0 pm from each other.

18.2 It has been proposed that much of the error due to assuming a stationary nucleus for the helium atom can be removed by replacing the mass of each electron by the reduced mass of an electron and the helium nucleus. Assume that the helium nucleus is a ^{4}He nucleus with a mass of 4.00141 atomic mass units, and calculate the reduced mass. Compare it with the mass of an electron. Calculate the effect that inclusion of this would have on the zero-order ground-state energy of a helium atom.

18.2

The Indistinguishability of Electrons and the Pauli Exclusion Principle

If a two-electron wave function is denoted by $\Psi(1,2)$, the probability of finding electron 1 in the volume element $d^3\mathbf{r}_1$ and simultaneously finding electron 2 in the volume element $d^3\mathbf{r}_2$ is given by

$$(\text{Probability}) = |\Psi(1,2)|^2\, d^3\mathbf{r}_1 d^3\mathbf{r}_2 = \Psi^*(1,2)\Psi(1,2) d^3\mathbf{r}_1 d^3\mathbf{r}_2 \tag{18.2-1}$$

If the wave function is a product of two orbitals as in Eq. (18.1-6) the probability density for two particles is the product of two one-particle probability densities:

$$|\Psi(1,2)|^2 = |\psi_1(1)|^2|\psi_2(2)|^2 \tag{18.2-2}$$

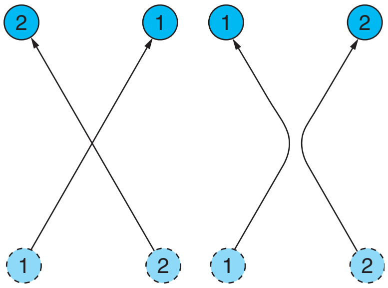

Figure 18.2 Two Encounters of Classical Particles.

Although we have obtained a wave function that satisfies our zero-order Schrödinger equation and the appropriate boundary conditions, it must be modified to conform to a new condition, which is required to obtain adequate agreement with experiment: *Identical particles are inherently indistinguishable from each other.* This condition is plausible because of the uncertainty principle, which makes exact trajectories impossible to specify. If two identical particles approach each other closely it might not be possible to tell which is which after the encounter. Figure 18.2 shows two encounters that could be distinguished from each other if classical mechanics were valid, but which might not be distinguished according to quantum mechanics, because of the combined uncertainties of position and momentum.

Our theory must not include anything that would allow us to distinguish one particle from another of the same kind. In a helium atom the probability of finding electron 1 at location 1 and finding electron 2 at location 2 must equal the probability of finding electron 1 at location 2 and finding electron 2 at location 1. Any difference in these two probabilities could give an illusory means of distinguishing the particles. We say that the probability density $\Psi^*\Psi$ must be *symmetric* with respect to interchange of the two particles' coordinates:

$$\Psi(1,2)^*\Psi(1,2) = \Psi(2,1)^*\Psi(2,1) \tag{18.2-3}$$

The labels in this equation mean that in the function on the right-hand side r_2, θ_2, and ϕ_2 are placed in the formula for the wave function where r_1, θ_1, and ϕ_1 were in the formula on the left-hand side, and vice versa.

There are two ways to satisfy Eq. (18.2-3). Either the wave function can be *symmetric* with respect to interchange of the particles:

$$\Psi(1,2) = \Psi(2,1) \quad \text{(symmetric wave function)} \tag{18.2-4}$$

or the wave function can be *antisymmetric* with respect to interchange of the particles:

$$\Psi(1,2) = -\Psi(2,1) \quad \text{(antisymmetric wave function)} \tag{18.2-5}$$

Bosons are named for Satyendra Nath Bose, 1894–1974, an Indian physicist who gained early recognition for deriving Planck's black-body radiation by assuming that photons are bosons. Fermions are named for Enrico Fermi, 1901–1954, an Italian-American physicist who was well known for his work on nuclear fission and who received the 1938 Nobel Prize in physics for his work on neutron bombardment.

Particles that require symmetric wave functions as in Eq. (18.2-4) are called *bosons*, and particles that require antisymmetric wave functions as in Eq. (18.2-5) are called *fermions*. Electrons are experimentally found to be fermions, as are protons and neutrons. Photons are bosons, as are nuclei containing an even number of nucleons (protons and neutrons). All fermions have spin quantum numbers that are equal to half-integers, whereas bosons have spin quantum numbers equal to integers.

The simplest way to make a two-electron orbital wave function satisfy the antisymmetrization requirement is to add a second term that is the negative of the first term with the coordinate labels interchanged, giving

$$\Psi(1,2) = C[\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2)] \tag{18.2-6}$$

where the ψ functions are spin orbitals and where C is a constant that can be chosen to normalize the function. By writing Eq. (18.2-6) we have **antisymmetrized** the wave function. We do not now specify which electron occupies which spin orbital.

Exercise 18.1

By explicit manipulation, show that the function of Eq. (18.2-6) obeys Eq. (18.2-5).

The Pauli exclusion principle is named for Wolfgang Pauli, 1900–1958, an Italian-American physicist who received the 1945 Nobel Prize in physics for his contributions to quantum mechanics.

There is an important fact about electrons that we can see in Eq. (18.2-6). If the spin orbitals ψ_1 and ψ_2 are the same function, the antisymmetric wave function is the difference of two identical terms and vanishes. Therefore, a given spin orbital cannot occur more than once in any term of an antisymmetrized two-electron orbital wave function. This is an example of the *Pauli exclusion principle*, which applies to orbital wave functions for any number of electrons: *In an antisymmetrized orbital wave function, the same spin orbital cannot occur more than once in each term.* Another statement of the Pauli exclusion principle is: *In an antisymmetrized orbital wave function, no two electrons can occupy the same spin orbital.*

The probability density for the antisymmetrized wave function of Eq. (18.2-6) is

$$\begin{aligned}\Psi(1,2)^*\Psi(1,2) = |C|^2\Big[&|\psi_1(1)|^2|\psi_2(2)|^2 - \psi_1(1)^*\psi_2(2)^*\psi_1(2)\\ &- \psi_2(1)^*\psi_1(1)\psi_1(2)^*\psi_2(2) + |\psi_2(1)|^2|\psi_1(2)|^2\Big]\end{aligned} \tag{18.2-7}$$

To normalize the wave function, we integrate the function of Eq. (18.2-7) over the space coordinates and spin coordinates of both particles and set the result equal to unity. If the orbitals are normalized the first term and the fourth term both give unity after integration. Because the hydrogen-like spin orbitals are orthogonal to each other, the second and third terms give zero after integration. The result is

$$1 = |C|^2[1 + 1] = 2|C|^2 \tag{18.2-8}$$

If C is taken to be real and positive,

$$C = \sqrt{\frac{1}{2}} \tag{18.2-9}$$

PROBLEMS

Section 18.2: The Indistinguishability of Electrons and the Pauli Exclusion Principle

18.3 Pretend that electrons are bosons with zero spin. Describe how the ground state of the helium atom would differ from the actual ground state in the orbital approximation.

18.4 Pretend that electrons are bosons with zero spin. Describe how the excited states of the helium atom would differ from the actual excited states in the orbital approximation.

18.3 The Ground State of the Helium Atom in Zero Order

The lowest-energy state of a system is called its *ground state*. The lowest zero-order energy of the helium atom corresponds to both electrons occupying $1s$ hydrogen-like orbitals with different spins. The antisymmetrized zero-order ground-state wave function can be written as

$$\begin{aligned}\Psi_{\text{gs}}^{(0)}(1,2) &= \Psi_{1s1s}^{(0)}(1,2)\\ &= \sqrt{\frac{1}{2}}\left[\psi_{100,1/2}(1)\psi_{100,-1/2}(2) - \psi_{100,-1/2}(1)\psi_{100,1/2}(2)\right]\end{aligned} \tag{18.3-1}$$

or

$$\begin{aligned}\Psi_{1s1s}^{(0)}(1,2) &= \sqrt{\frac{1}{2}}[\psi_{100}(1)\alpha(1)\psi_{100}(2)\beta(2) - \psi_{100}(1)\beta(1)\psi_{100}(2)\alpha(2)]\\ &= \sqrt{\frac{1}{2}}\psi_{100}(1)\psi_{100}(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)]\end{aligned} \tag{18.3-2}$$

where the ψ_{100} orbitals are hydrogen-like orbitals with $Z = 2$.

EXAMPLE 18.1

Show that the function in Eq. (18.3-2) is normalized. Both the space and the spin coordinates must be integrated.

Solution

$$\begin{aligned}&\int \Psi^{(0)*}(1,2)\Psi^{(0)}(1,2)d^3\mathbf{r}_1 d^s(1)d^3\mathbf{r}_2 d^s(2)\\ &= \frac{1}{2}\int \psi_{100}^*(1)\psi_{100}^*(2)[\alpha^*(1)\beta^*(2) - \beta^*(1)\alpha^*(2)]\\ &\quad \times \psi_{100}(1)\psi_{100}(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)]d^3\mathbf{r}_1 d^s(1)d^3\mathbf{r}_2 d^s(2)\\ &= \frac{1}{2}\int \psi_{100}^*(1)\psi_{100}^*(2)\psi_{100}(1)\psi_{100}(2)d^3\mathbf{r}_1 d^3\mathbf{r}_2\\ &\quad \times \int [\alpha^*(1)\beta^*(2) - \beta^*(1)\alpha^*(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)]d^s(1)d^s(2)\end{aligned} \tag{18.3-3}$$

The integral over the space coordinates is equal to unity if the space orbitals are normalized. The integral over the spin coordinates is equal to

$$\begin{aligned}&\int [\alpha^*(1)\alpha(1)\beta^*(2)\beta^*(2) - \alpha^*(1)\beta(1)\beta^*(2)\alpha(2)\\ &\quad - \beta^*(1)\alpha(1)\alpha^*(2)\beta(2) + \beta^*(1)\beta(1)\alpha^*(2)\alpha(2)]d^s(1)d^s(2)\end{aligned} \tag{18.3-4}$$

The first term and the last term equal unity after integration. The second and third terms vanish after integration, so that this integral is equal to 2, which cancels the factor of 1/2 and the function is normalized.

Probability Densities for Two Particles

The probability of finding electron 1 in volume element $d^3\mathbf{r}_1$ and electron 2 in volume element $d^3\mathbf{r}_2$, irrespective of the spins of the electrons, is obtained by integrating the square of the wave function over the spin coordinates of both electrons. For the zero-order wave function of a helium atom in its ground state

$$\begin{aligned}\text{Probability} &= \frac{1}{2}\psi_{100}{}^{*}(1)\psi_{100}{}^{*}(2)\psi_{100}(1)\psi_{100}(2)d^{3}\mathbf{r}_{1}d^{3}\mathbf{r}_{2}\\ &\quad\times\int[\alpha^{*}(1)\beta^{*}(2)-\beta^{*}(1)\alpha^{*}(2)][\alpha(1)\beta(2)-\beta(1)\alpha(2)]d^{s}(1)d^{s}(2)\\ &= \psi_{100}{}^{*}(1)\psi_{100}{}^{*}(2)\psi_{100}(1)\psi_{100}(2)d^{3}\mathbf{r}_{1}d^{3}\mathbf{r}_{2}\end{aligned}\tag{18.3-5}$$

The second equality follows from Example 18.1. The two-electron probability density irrespective of spin is

$$\begin{aligned}\begin{pmatrix}\text{Probability}\\ \text{density}\end{pmatrix} &= \psi_{100}{}^{*}(1)\psi_{100}(1)\psi_{100}{}^{*}(2)\psi_{100}(2)\\ &= |\psi_{100}(r_1,\theta_1,\phi_1)|^2|\psi_{100}(r_2,\theta_2,\phi_2)|^2\end{aligned}\tag{18.3-6}$$

The probability of finding electron 1 in the volume element $d^3\mathbf{r}_1$ is given by integrating the two-electron probability density over all positions of particle 2:

$$\begin{aligned}\begin{pmatrix}\text{Probability of finding}\\ \text{particle 1 in } d^3\mathbf{r}_1\end{pmatrix} &= [\int|\psi_{100}(1)|^2\psi_{100}(2)|^2 d^3\mathbf{r}_2]d^3\mathbf{r}_1\\ &= |\psi_{100}(r_1,\theta_1,\phi_1)|^2 d^3\mathbf{r}_1\\ &= |\psi_{100}(r_1,\theta_1,\phi_1)|^2 r_1^2\sin(\theta_1)dr_1d\theta_1d\phi_1\end{aligned}\tag{18.3-7}$$

The probability for the second electron is the same function. The total density of electrons is

$$(\text{Total electron density}) = 2|\psi_{100}(r,\theta,\phi)|^2 \tag{18.3-8}$$

The density of electric charge due to the electrons is

$$(\text{Total electron charge density}) = -2e|\psi_{100}(r,\theta,\phi)|^2 \tag{18.3-9}$$

where $-e$ is the electron's charge.

Now consider the spins of the electrons. We take the wave function in Eq. (18.3-5) before the spin integrations were carried out. Multiplying out the spin factors, we obtain

$$\begin{aligned}\text{Probability} &= \frac{1}{2}\psi_{100}{}^{*}(1)\psi_{100}{}^{*}(2)\psi_{100}(1)\psi_{100}(2)d^{3}\mathbf{r}_{1}d^{3}\mathbf{r}_{2}\\ &\quad\times[\alpha^{*}(1)\alpha(1)\beta^{*}(2)\beta(2)-\beta^{*}(1)\alpha(1)\alpha^{*}(2)\beta(2)\\ &\quad-\alpha^{*}(1)\beta(1)\beta^{*}(2)\alpha(2)+\beta^{*}(1)\beta(1)\alpha^{*}(2)\alpha(2)]\end{aligned}\tag{18.3-10}$$

The first term in the sum of products of spin functions corresponds to electron 1 with spin up and electron 2 with spin down. The fourth term corresponds to electron 1 with spin down and electron 2 with spin up. The second and third terms are *exchange terms* with no classical interpretation.

We now integrate this function over the space and spin coordinates of particle 2 to find the probability of finding particle 1. The space integration yields unity by the normalization of the space orbital $\psi_{100}(2)$. Integrating the spin coordinates of particle 2 gives zero for the second and third terms in the sum of spin functions by the orthogonality of the spin functions and gives unity for the first and fourth terms by the normalization of the spin functions. We obtain

$$\begin{pmatrix}\text{Probability of finding}\\ \text{electron 1 in } d^3\mathbf{r}_1\end{pmatrix} = \frac{1}{2}|\psi_{100}{}^*(1)|^2[\alpha^*(1)\alpha(1) + \beta^*(1)\beta(1)]d^3\mathbf{r}_1 \quad (18.3\text{-}11)$$

We interpret this to mean that the probability of finding the particle in the volume element $d^3\mathbf{r}_1$ with spin up is the factor multiplying the term $\alpha^*(1)\alpha(1)$:

$$\begin{pmatrix}\text{Probability of finding electron 1}\\ \text{in } d^3\mathbf{r}_1 \text{ with spin up}\end{pmatrix} = \frac{1}{2}|\psi_{100}{}^*(1)|^2 d^3\mathbf{r}_1 \quad (18.3\text{-}12)$$

The probability of finding the particle in this volume element $d^3\mathbf{r}_1$ with spin down is the factor multiplying the term $\beta^*(1)\beta(1)$. It has the same value as the result in Eq. (18.3-12). The probability of finding either spin irrespective of location is equal to 1/2. For much of our work with probability densities we can ignore the spins of the particles.

The energy eigenvalue for our zero-order ground-state wave function is the sum of two hydrogen-like orbital energies for $n = 1$:

$$E_{1s1s}^{(0)} = E_1(\text{HL}) + E_1(\text{HL}) = 2(-13.60\,\text{eV})Z^2 \quad (18.3\text{-}13)$$

where we use a double 1s subscript to denote that both electrons occupy 1s space orbitals. For helium $Z = 2$, so that

$$E_{1s1s}^{(0)} = -108.8\,\text{eV} \quad (18.3\text{-}14)$$

This approximate energy eigenvalue is seriously in error, since the experimental value is −79.0 eV. We discuss better approximations in the next chapter.

PROBLEMS

Section 18.3: The Ground State of the Helium Atom

18.5 **a.** Calculate the expectation value of the kinetic energy of the electrons in a helium atom in the ground state in the zero-order approximation.

b. Calculate the expectation value of the potential energy of a helium atom in the ground state in the zero-order approximation.

c. Calculate the expectation value of the energy of a helium atom in the ground state in the zero-order approximation.

d. Specify which of the values calculated in parts a–c belong to the predictable case and which belong to the statistical case as defined in Chapter 16.

18.6 **a.** Calculate the expectation value of the kinetic energy of the electrons in a helium atom in the excited state corresponding to the configuration (1s)(2s) in the zero-order approximation.

b. Calculate the expectation value of the potential energy of the electrons in a helium atom in the excited state corresponding to the configuration (1s)(2s) in the zero-order approximation.

18.7 **a.** Use the identity

$$\widehat{S}^2 = \widehat{S}_1^2 + \widehat{S}_2^2 + 2(\widehat{S}_{x1}\widehat{S}_{x2} + \widehat{S}_{y1}\widehat{S}_{y2} + \widehat{S}_{z1}\widehat{S}_{z2})$$

and the facts[1]

$$\widehat{S}_x\alpha = \frac{\hbar}{2}\beta \quad \widehat{S}_y\alpha = \frac{i\hbar}{2}\beta$$

$$\widehat{S}_x\beta = \frac{\hbar}{2}\alpha \quad \widehat{S}_y\beta = \frac{-i\hbar}{2}\alpha$$

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[1] I. N. Levine, *Quantum Chemistry*, 6th ed., Prentice-Hall, Upper Saddle River, NJ, 2000, p. 301.

to show that

$$\widehat{S}^2[\alpha(1)\beta(2)+\beta(1)\alpha(2)] = 2\hbar^2[\alpha(1)\beta(2)+\beta(1)\alpha(2)]$$

b. Show that for a two-electron system

$$\widehat{S}^2[\alpha(1)\beta(2)-\beta(1)\alpha(2)] = 0$$

18.4 Excited States of the Helium Atom

States of higher energy than the ground state are called *excited states*. For orbital wave functions there are two cases: (1) both electrons occupy the same space orbital with different spin functions, as is the case with the ground state; (2) the two electrons occupy different space orbitals, either with the same or different spin functions. A statement of which space orbitals are occupied is called the *electron configuration*. The *detailed configuration* is specified by writing the designation of each occupied space orbital with a right superscript giving the number of electrons occupying that space orbital (either 1 or 2). The *subshell configuration* is specified by writing the designation of each occupied subshell with a right superscript giving the number of electrons occupying orbitals of that subshell. Unoccupied space orbitals or subshells are omitted from the configuration. The maximum value of this superscript is 2 for an s subshell, 6 for a p subshell, 10 for a d subshell, and 14 for an f subshell. A superscript equal to unity is usually omitted, so that $(1s)(2s)$ is the same as $(1s)^1(2s)^1$.

If both electrons occupy the same space orbital, the wave function for an excited state is similar to that of the ground state. For the configuration $(2s)^2$:

$$\Psi_{2s2s} = \frac{1}{\sqrt{2}}\psi_{2s}(1)\psi_{2s}(2)[\alpha(1)\beta(2)-\beta(1)\alpha(2)] \tag{18.4-1}$$

The probability density for two electrons and the electric charge density are analogous to those of the ground state.

If the electrons occupy different space orbitals there are four possible states for each pair of space orbitals. For the $(1s)(2s)$ configuration we can write four antisymmetric wave functions that are products of a space factor and a spin factor:

$$\Psi_1 = \frac{1}{\sqrt{2}}[\psi_{1s}(1)\psi_{2s}(2)-\psi_{2s}(1)\psi_{1s}(2)]\alpha(1)\alpha(2) \tag{18.4-2a}$$

$$\Psi_2 = \frac{1}{\sqrt{2}}[\psi_{1s}(1)\psi_{2s}(2)-\psi_{2s}(1)\psi_{1s}(2)]\beta(1)\beta(2) \tag{18.4-2b}$$

$$\Psi_3 = \frac{1}{\sqrt{2}}[\psi_{1s}(1)\psi_{2s}(2)-\psi_{2s}(1)\psi_{1s}(2)]\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)+\beta(1)\alpha(2)] \tag{18.4-2c}$$

$$\Psi_4 = \frac{1}{\sqrt{2}}[\psi_{1s}(1)\psi_{2s}(2)+\psi_{2s}(1)\psi_{1s}(2)]\frac{1}{\sqrt{2}}[\alpha(1)\beta(2)-\beta(1)\alpha(2)] \tag{18.4-2d}$$

The number of states can be determined by counting the number of ways of arranging two spins: up–up, down–down, up–down, and down–up. As shown in Eq. (18.4-2), the up–down and down–up arrangements combine in two ways, corresponding to symmetric and antisymmetric spin factors.

Exercise 18.2

a. Show that Ψ_3 and Ψ_4 satisfy the zero-order Schrödinger equation and find the energy eigenvalue.

b. Show that these functions are normalized if the orbitals are normalized.

Probability Densities for Excited States

The probability density for finding the two electrons irrespective of spins is obtained by integrating the square of the wave function over the spin coordinates. Consider the state corresponding to Ψ_1 in Eq. (18.4-2a). The probability of finding electron 1 in the volume element $d^3\mathbf{r}_1$ and electron 2 in the volume element $d^3\mathbf{r}_2$ irrespective of spins is

$$\begin{aligned}
(\text{Probability}) &= \frac{1}{2}([\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)])d^3\mathbf{r}_1 d^3\mathbf{r}_2 \\
&\quad \times \int \alpha(1)^*\alpha(2)^*\alpha(1)\alpha(2)d^s(1)d^s2 \\
&= \frac{1}{2}\,[\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)]^2\, d^3\mathbf{r}_1 d^3\mathbf{r}_2 \\
&= \frac{1}{2}[\psi_{1s}(1)^2\psi_{2s}(2)^2 - \psi_{1s}(1)\psi_{2s}(2)\psi_{2s}(1)\psi_{1s}(2) \\
&\quad - (\psi_{2s}(1)\psi_{1s}(2)\psi_{1s}(1)\psi_{2s}(2) + \psi_{2s}(1)^2\psi_{1s}(2)^2]d^3\mathbf{r}_1)d^3\mathbf{r}_2 \qquad (18.4\text{-}3)
\end{aligned}$$

where we have used the fact that the $1s$ and $2s$ space orbitals are real and the fact that the spin functions are normalized. The probability of finding electron 1 in the volume element $d^3\mathbf{r}_1$ is obtained by integrating over the coordinates of particle 2:

$$\begin{aligned}
\begin{pmatrix}\text{Probability of finding} \\ \text{particle 1 in } d^3\mathbf{r}_1\end{pmatrix} &= \frac{1}{2}\int [\psi_{1s}(1)^2\psi_{2s}(2)^2 - \psi_{1s}(1)\psi_{2s}(2)\psi_{2s}(1)\psi_{1s}(2) \\
&\quad - (\psi_{2s}(1)\psi_{1s}(2)\psi_{1s}(1)\psi_{2s}(2) + \psi_{2s}(1)^2\psi_{1s}(2)^2]d^3\mathbf{r}_2)d^3\mathbf{r}_2 \\
&= \frac{1}{2}(\psi_{1s}(1)^2 + \psi_{2s}(1)^2)d^3\mathbf{r}_1 \qquad (18.4\text{-}4)
\end{aligned}$$

The second and third terms in Eq. (18.4-3) vanish because of orthogonality when the coordinates of particle 2 are integrated. This probability is the average of what would occur if electron 1 occupied orbital 1 and what would occur if it occupied orbital 2, which is reasonable since we cannot say which electron occupies which orbital. The expression for electron 2 is the same function. For the two-electron system the total probability of finding some electron in a volume $d^3\mathbf{r}_1$ is the sum of the probabilities for the two electrons:

$$\begin{pmatrix}\text{Probability of finding} \\ \text{an electron in } d^3\mathbf{r}_1\end{pmatrix} = (\psi_{1s}(\mathbf{r}_1)^2 + \psi_{2s}(\mathbf{r}_1)^2)d^3\mathbf{r}_1 \qquad (18.4\text{-}5)$$

When this probability density is multiplied by $-e$, the electron charge, it is the charge density (charge per unit volume) due to the electrons. The other three wave functions represented in Eq. (18.4-2) give the same results.

Exercise 18.3

Show that the other three wave functions in Eq. (18.4-2) give the same result for the charge density.

PROBLEMS

Section 18.4: Excited States of the Helium Atom

18.8 Draw a graph of a probability density for finding any electron at a distance r from the nucleus of a helium atom in the $(1s)(2s)$ configuration, using the zero-order wave function of Eq. (18.4-2a).

18.5 Angular Momentum in the Helium Atom

In any set of interacting particles the total angular momentum is the vector sum of the angular momenta of all of the particles. The total angular momentum of an isolated system of interacting particles is *conserved*, both in classical mechanics and in quantum mechanics. That is, if the angular momentum of one particle in such a system changes, the angular momentum of other particles must change so that the vector sum does not change. A conserved quantity does not change in time and is called a *constant of the motion*. A quantum number determining the value of a conserved quantity is called a *good quantum number*, and the quantity itself is sometimes referred to by that name.

The total angular momentum of an atom includes the angular momentum of the nucleus and all electrons. We assume a stationary nucleus and assume also that the angular momentum of the nucleus does not change so that we can ignore it. The angular momentum of an electron is the vector sum of its orbital and spin angular momenta. The total electronic angular momentum of a multielectron atom is the vector sum of the angular momenta of all electrons. It can also be considered to be the sum of the total orbital angular momentum and the total spin angular momentum. For atoms in the first part of the periodic table the total orbital angular momentum and the total spin angular momentum can separately be assumed to be good quantum numbers to an adequate approximation. This assumption is called *Russell–Saunders coupling*, and we will now assume it to be an adequate approximation.

We now use lower-case letters for the angular momentum quantities of a single electron and use capital letters for the angular momentum quantities of an atom. Let $\mathbf{l}_1$ and $\mathbf{s}_1$ be the orbital and spin angular momenta of electron 1, let $\mathbf{l}_2$ and $\mathbf{s}_2$ be the orbital and spin angular momenta of electron 2, and so on. The total orbital angular momentum $\mathbf{L}$ and total spin angular momenta $\mathbf{S}$ of the electrons of the helium atom are vector sums of the contributions of the individual electrons:

$$\mathbf{L} = \mathbf{l}_1 + \mathbf{l}_2 + \cdots \tag{18.5-1}$$

$$\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 + \cdots \tag{18.5-2}$$

The total electronic angular momentum of the atom is denoted by $\mathbf{J}$:

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \tag{18.5-3}$$

There are operators for all of these quantities and their z components. The eigenvalues of the $\widehat{J}^2, \widehat{J}_z, \widehat{L}^2, \widehat{L}_z, \widehat{S}^2$, and $\widehat{S}_z$ operators follow the same pattern as other angular momenta, as follows:

$$\widehat{J}^2\Psi = \hbar^2 J(J+1)\Psi \tag{18.5-4}$$

$$\widehat{J}_z\Psi = \hbar M_J\Psi \tag{18.5-5}$$

$$\widehat{L}^2\Psi = \hbar^2 L(L+1)\Psi \tag{18.5-6}$$

$$\widehat{L}_z\Psi = \hbar M_L\Psi \tag{18.5-7}$$

$$\widehat{S}^2\Psi = \hbar^2 S(S+1)\Psi \tag{18.5-8}$$

$$\widehat{S}_z\Psi = \hbar M_S\Psi \tag{18.5-9}$$

The orbital angular momentum quantum number L is a non-negative integer. The total spin angular momentum quantum number S is a non-negative integer or half-integer, and the total angular momentum quantum number J is a non-negative integer or half-integer. Since **J** is the vector sum of **L** and **S**, the largest value that the quantum number J can have is $L + S$, and its smallest value is $|L - S|$. From the universal pattern of angular momentum quantum numbers, M_L ranges from L to $-L$, M_S ranges from S to $-S$, and M_J ranges from J to $-J$. Figure 18.3 illustrates how angular momentum vectors can add vectorially to produce some particular values of the quantum numbers L, M_L, S, and M_S. In each diagram, the tail of the second vector is placed at the head of the first vector, as is done in the geometric representation of vector addition.

In Russell–Saunders coupling, each energy level corresponds to a particular value of L and a particular value of S and is called a *term*. A *Russell–Saunders term symbol* is assigned to each term. The main part of the symbol is a letter giving the value of L, as follows:

Value of L	Symbol
0	S
1	P
2	D
3	F
4	G
etc.	

After F the symbols are in alphabetical order. Notice the similarity with the subshell designations for a hydrogen-like atom.

A left superscript with the value $2S+1$ is attached to the term symbol. For two electrons we can have $S = 0$, giving a superscript of 1 (a *singlet term*), or we can have $S = 1$, giving a superscript of 3 (a *triplet term*). For a single electron we can have only $S = 1/2$, giving a superscript of 2 (a *doublet term*). If $S = 3/2$, the superscript equals 4 (a *quartet term*), and so on. The value of the left superscript is called the *multiplicity* of the term. A right subscript can be attached to the term symbol to specify the value of J, but is sometimes omitted.

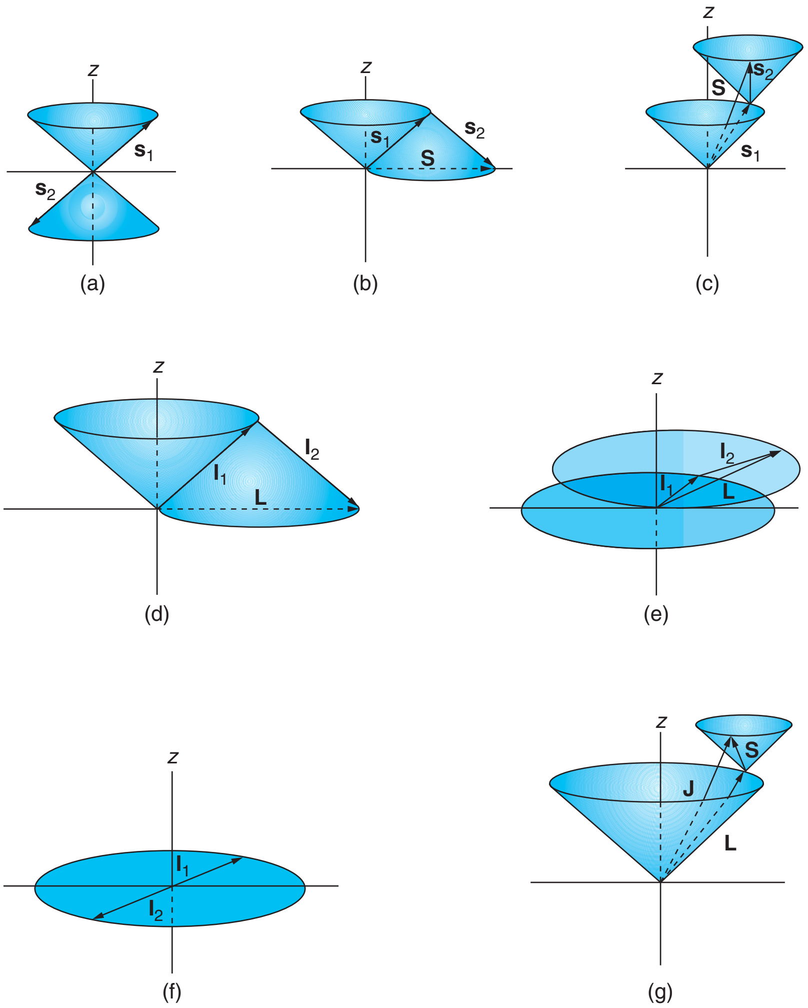

Figure 18.3 Examples of Vector Addition of Angular Momenta. (a) Two electron spins: $m_{s1} = 1/2$, $m_{s2} = -1/2$, $M_s = 0$, $S = 0$. (b) Two electron spins: $m_{s1} = 1/2$, $m_{s2} = -1/2$, $M_s = 0$, $S = 1$. (c) Two electron spins: $m_{s1} = 1/2$, $m_{s2} = 1/2$, $M_s = 1$, $S = 1$. (d) Two p electrons' orbital angular momenta: $l_1 = 1$, $m_l = 1$, $l_2 = 1$, $m_2 = -1$, $M_L = 0$, $L = 1$. (e) Two p electrons' orbital angular momenta: $l_1 = 1$, $m_1 = 0$, $l_2 = 1$, $m_2 = 0$, $M_L = 0$, $L = 2$. (f) Two p electrons' orbital angular momenta: $m_1 = 0$, $l_1 = 1$, $m_2 = 0$, $l_2 = 1$, $M_L = 0$, $L = 0$. (g) Total orbital and spin angular momenta: $L = 1$, $M_L = 1$, $S = 1/2$, $M_S = 1/2$, $M_J = 3/2$, $J = 3/2$.

For two electrons, we have the operators

$$\widehat{L}^2 = (\widehat{l}_{x1} + \widehat{l}_{x2})^2 + (\widehat{l}_{y1} + \widehat{l}_{y2})^2 + (\widehat{l}_{z1} + \widehat{l}_{z2})^2 \tag{18.5-10}$$

$$\widehat{L}_z = \widehat{l}_{z1} + \widehat{l}_{z2} \tag{18.5-11}$$

$$\widehat{S}^2 = (\widehat{s}_{x1} + \widehat{s}_{x2})^2 + (\widehat{s}_{y1} + \widehat{s}_{y2})^2 + (\widehat{s}_{z1} + \widehat{s}_{z2})^2 \tag{18.5-12}$$

$$\widehat{S}_z = \widehat{s}_{z1} + \widehat{s}_{z2} \tag{18.5-13}$$

The $\widehat{L}^2$ and $\widehat{S}^2$ operators are not easy to use, and we will not operate explicitly with them.[2] We will work with the $\widehat{L}_z$ and $\widehat{S}_z$ operators, and will deduce values of L and S from the M_L and M_S values. We can find the values of M_L and M_S since the z components of the one-electron operators add algebraically as in Eqs. (18.5-11) and (18.5-13). For two electrons

$$M_L = m_1 + m_2 \tag{18.5-14a}$$

and

$$M_S = m_{s1} + m_{s2} \tag{18.5-14b}$$

EXAMPLE 18.2

Find the values of the quantum numbers M_L and M_S for each of the wave functions in Eq. (18.4-2) for the $(1s)(2s)$ configuration of the helium atom.

Solution

$$\begin{aligned}\widehat{L}_z\Psi_1 &= (\widehat{l}_{z1} + \widehat{l}_{z2})\Psi_1 = \frac{1}{\sqrt{2}}[\widehat{l}_{z1}\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)(\widehat{l}_{z2}\psi_{1s}(2))]\alpha(1)\alpha(2)\\ &= 0 + 0 = 0\end{aligned} \tag{18.5-15}$$

so that $M_L = 0$. The other wave functions also contain only s orbitals, so that $M_L = 0$ for all of them. We operate with $\widehat{S}_z$ to find the value of M_S.

$$\begin{aligned}\widehat{S}_z\Psi_1 &= (\widehat{s}_{z1} + \widehat{s}_{z2})\Psi_1\\ &= \frac{1}{\sqrt{2}}\big(\psi_{1s}(1)\psi_{1s}(2) - \psi_{1s}(1)\psi_{1s}(2)\big)\big(\widehat{s}_{z1}\alpha(1)\alpha(2) + \alpha(1)\widehat{s}_{z2}\alpha(2)\big)\\ &= \frac{1}{\sqrt{2}}\big(\psi_{1s}(1)\psi_{1s}(2) - \psi_{1s}(1)\psi_{1s}(2)\big)\left(\frac{\hbar}{2}\alpha(1)\alpha(2) + \alpha(1)\frac{\hbar}{2}\alpha(2)\right)\\ &= \left(\frac{\hbar}{2} + \frac{\hbar}{2}\right)\Psi_1 = \hbar\Psi_1\end{aligned} \tag{18.5-16}$$

so that Ψ_1 corresponds to $M_S = 1$. Similarly,

$$\widehat{S}_z\Psi_2 = \left(-\frac{\hbar}{2} - \frac{\hbar}{2}\right)\Psi_2 = -\hbar\Psi_2 \tag{18.5-17}$$

so that $M_S = -1$ for Ψ_2.

$$\begin{aligned}\widehat{S}_z\Psi_3 &= \frac{1}{2}[\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)]\\ &\quad\times [\widehat{s}_{z1}\alpha(1)\beta(2) + \widehat{s}_{z1}\beta(1)\alpha(2) + \alpha(1)\widehat{s}_{z2}\beta(2) + \beta(1)\widehat{s}_{z2}\alpha(2)]\\ &= \frac{1}{2}[\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)]\\ &\quad\times \left[\left(\frac{\hbar}{2}\right)\alpha(1)\beta(2) + \left(\frac{-\hbar}{2}\right)\beta(1)\alpha(2) + \alpha(1)\left(\frac{-\hbar}{2}\right)\beta(2) + \beta(1)\left(\frac{\hbar}{2}\right)\alpha(2)\right]\\ &= 0\end{aligned} \tag{18.5-18}$$

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[2] I. N. Levine, *op. cit.*, p. 318ff (note 1).

so that $M_S = 0$ for Ψ_3. A similar calculation leads to the value $M_S = 0$ for Ψ_4. We wrote the operations and functions explicitly, but could simply have added the m values and the m_s values to obtain the same answers.

The wave functions in Eq. (18.4-2) are eigenfunctions of the $\widehat{S}^2$ operator, although we do not prove this. The eigenvalues are as follows. See Problem 18.9:

$$\widehat{S}^2\alpha(1)\alpha(2) = \hbar^2(1)(2)\alpha(1)\alpha(2) \tag{18.5-19}$$

$$\widehat{S}^2\beta(1)\beta(2) = \hbar^2(1)(2)\beta(1)\beta(2) \tag{18.5-20}$$

$$\widehat{S}^2[\alpha(1)\beta(2) + \beta(1)\alpha(2)] = \hbar^2(1)(2)[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \tag{18.5-21}$$

$$\widehat{S}^2[\alpha(1)\beta(2) - \beta(1)\alpha(2)] = 0 \tag{18.5-22}$$

The first three functions correspond to a triplet term ($S = 1$). The fourth corresponds to a singlet term ($S = 0$). The symmetric spin factors correspond to the triplet, and the antisymmetric spin factor corresponds to the singlet.

We can now infer the values of L and S from the pattern that M_L ranges from L to $-L$ and M_S ranges from S to $-S$. We always begin with the largest values of M_L and M_S and assign the states to the largest values of L and S first. Since the only value of M_L is zero for all four of these wave functions, the only value of L is zero. The largest value of M_S is 1. This means that the largest value of S is 1. A value of S equal to 1 requires values of M_S equal to $1, 0,$ and -1. We assign three states with these values to a ^3S (triplet S) term. There is only one state remaining, with $M_S = 0$. We assign it to a ^1S (singlet S) term. The only terms are a ^3S term and a ^1S. Since $L = 0$, the value of J for each term is equal to the value of S. Including the J values, the terms are $^3S_1$ and $^1S_0$.

EXAMPLE 18.3

Enumerate the states in the $(1s)(2p)$ configuration and assign the Russell–Saunders term symbols.

Solution

With the $1s$ orbital and one of the $2p$ orbitals we can make wave functions analogous to those from the $(1s)(2s)$ configuration. We use the complex Φ functions so that we have definite values of m. With the $1s$ space orbital and the $2p1$ space orbital we have a symmetric space factor

$$\Psi_s = \frac{1}{\sqrt{2}}[\psi_{1s}(1)\psi_{2p1}(2) + \psi_{2p1}(1)\psi_{1s}(2)] \tag{18.5-23}$$

and an antisymmetric space factor

$$\Psi_a = \frac{1}{\sqrt{2}}[\psi_{1s}(1)\psi_{2p1}(2) - \psi_{2p1}(1)\psi_{1s}(2)] \tag{18.5-24}$$

Both of these space factors correspond to $M_L = 1$. The symmetric space factor combines with the antisymmetric spin factor, leading to one state with $S = 0$. The three triplet spin factors are all symmetric, so the antisymmetric space factor can combine with any of these, leading to three states, with M_S equal to $1, 0,$ and -1, corresponding to $S = 1$. The $2p0$ orbital combines with the $1s$ orbital in exactly the same way as the $2p1$ orbital except that $M_L = 0$ for these wave functions. The $2p, -1$ orbital combines with the $1s$ orbital in exactly the same way as the $2p1$ orbital except that $M_L = -1$. This gives a total of 12 states.

The three values of M_L correspond to $L = 1$ with no states left over, so that only P terms occur. Each symmetric spin factor combines with each one of the three antisymmetric space factors to give the nine states of the ^3P term, and the antisymmetric spin factor combines with each one of the symmetric space factors to give the three states of the ^1P term.

The states in the previous example can be counted up more simply by listing all the possible combinations of m_1, m_2, m_{s1}, and m_{s2} that can occur, and then marking off the states for each possible term, starting with the largest possible value of L. For each value of L we then work through the possible values of S, starting with the largest. These entries are shown in Table 18.1. Some of the actual states are linear combinations of the wave functions corresponding to the entries in this list, but the number of them is correctly counted. For example, for each set of values of m_1 and m_2 there is an entry for $m_{s1} = 1/2$ and $m_{s2} = -1/2$ and another entry for $m_{s1} = -1/2$ and $m_{s2} = 1/2$. The actual states correspond to the symmetric spin factor and the antisymmetric spin factor, but the two states are correctly counted. It does not matter which of the two lines in the table we assign to the triplet and to the singlet if we are just counting up the states.

The process of assigning the terms used in Example 18.3 can be summarized as follows: The largest value of M_L is identified, which must be equal to the largest value of L. The largest value of M_S occurring with this value of M_L is identified, which must be equal to the largest value of S occurring with the largest value of L. The states with the appropriate values of M_L ranging from $+L$ to $-L$ for the largest value of L are found, as are the states with the appropriate values of M_S from $+S$ to $-S$. For this example, the maximum value of L is 1 and the maximum value of S occurring with it is 1, corresponding to a ^3P term. For each value of M_L, three states with M_S equal to $1, 0$, and -1 are found. The nine states with the appropriate values of M_L and M_S for this term are marked in the table. After the states for the largest value of L are found, the largest remaining value of M_L is identified and the next value of L is assigned to be equal to this value. The largest remaining value of M_S occurring with this value of M_L is identified and this value is set equal to the value of S that corresponds to this value of L. The states with the appropriate values of M_L and M_S are found. In the example, the largest remaining value of M_L is 1 and the only value of M_S occurring with it is 0,

Table 18.1 Terms for the $(1s)(2p)$ Configuration of the He Atom for Example 18.4

Values						Terms	
m_1	m_2	m_{s1}	m_{s2}	M_L	M_S	^3P	^1P
0	1	$+1/2$	$+1/2$	1	1	x	
0	1	$+1/2$	$-1/2$	1	0	x	
0	1	$-1/2$	$+1/2$	1	0		x
0	1	$-1/2$	$-1/2$	1	-1	x	
0	0	$+1/2$	$+1/2$	0	1	x	
0	0	$+1/2$	$-1/2$	0	0	x	
0	0	$-1/2$	$+1/2$	0	0		x
0	0	$-1/2$	$-1/2$	0	-1	x	
0	-1	$+1/2$	$+1/2$	-1	1	x	
0	-1	$+1/2$	$-1/2$	-1	0	x	
0	-1	$-1/2$	$+1/2$	-1	0		x
0	-1	$-1/2$	$-1/2$	-1	-1	x	

corresponding to a ^1P term. If there were more states remaining, the process would be continued until all states have been assigned to terms.

Exercise 18.4

By explicit operation with $\widehat{L}_z = \widehat{L}_{z1} + \widehat{L}_{z2}$, show that the eigenvalues of the two space factors in Eq. (18.5-23) and Eq. (18.5-24) both equal $\hbar$, corresponding to $M_L = 1$.

If we wish to include the values of J, we can determine the possible values from the values of M_J, the quantum number for its z component. Since **J** is the vector sum of **L** and **S**, the z components add algebraically:

$$\widehat{J}_z = \widehat{L}_z + \widehat{S}_z \tag{18.5-25}$$

Therefore,

$$M_J = M_L + M_S \tag{18.5-26}$$

The possible values of J can be deduced by using the rule that for each value of J, the values of M_J range from $+J$ to $-J$. Since the largest value of M_J equals the largest value of M_L plus the largest value of M_S, the largest value of J is

$$J_{\text{max}} = L + S \tag{18.5-27}$$

The smallest value of J is

$$J_{\text{min}} = |L - S| \tag{18.5-28}$$

J must be non-negative.

EXAMPLE 18.4

Assign the M_J values to the 12 states of Table 18.1. Show that the following terms occur:

$$^1P_1, {}^3P_2, {}^3P_1, {}^3P_0$$

Solution

We adopt the notation that the left factor in each product is for electron 1 and the other factor is for electron 2. The terms are counted by assigning the proper set of eigenvalues for each term.

	M_L	M_S	M_J	term
$(\psi_s\psi_{p1} + \psi_{p1}\psi_s)(\alpha\beta - \beta\alpha)$	1	0	1	$^1P_1$
$(\psi_s\psi_{p1} - \psi_{p1}\psi_s)\alpha\alpha$	1	1	2	$^3P_2$
$(\psi_s\psi_{p1} - \psi_{p1}\psi_s)(\alpha\beta + \beta\alpha)$	1	0	1	$^3P_2$
$(\psi_s\psi_{p1} - \psi_{p1}\psi_s)\beta\beta$	1	-1	0	$^3P_0$
$(\psi_s\psi_{p0} + \psi_{p0}\psi_s)(\alpha\beta - \beta\alpha)$	0	0	0	$^1P_1$
$(\psi_s\psi_{p0} - \psi_{p0}\psi_s)\alpha\alpha$	0	1	1	$^3P_1$
$(\psi_s\psi_{p0} - \psi_{p0}\psi_s)(\alpha\beta + \beta\alpha)$	0	0	0	$^3P_1$
$(\psi_s\psi_{p0} - \psi_{p0}\psi_s)\beta\beta$	0	-1	-1	$^3P_1$
$(\psi_s\psi_{p-1} + \psi_{p-1}\psi_s)(\alpha\beta - \beta\alpha)$	-1	0	-1	$^1P_1$
$(\psi_s\psi_{p-1} - \psi_{p-1}\psi_s)\alpha\alpha$	-1	1	0	$^3P_2$
$(\psi_s\psi_{p-1} - \psi_{p-1}\psi_s)(\alpha\beta + \beta\alpha)$	-1	0	-1	$^3P_2$
$(\psi_s\psi_{p-1} - \psi_{p-1}\psi_s)\beta\beta$	-1	-1	-2	$^3P_2$

PROBLEMS

Section 18.5: Angular Momentum in the Helium Atom

18.9 Find the possible term symbols for the excited configuration $(2p)(3d)$ of the helium atom.

18.10 Find the possible term symbols for the excited configuration $(1s)(3d)$ for the helium atom. Which will probably have the lowest energy?

18.11 Pretend that the direction of angular momentum vectors can be specified exactly. If the spin angular momentum vector for one electron with spin up lies in the yz plane, and the spin angular momentum vector for another electron with spin down also lies in the yz plane, find the possible magnitudes and directions of their vector sum. To what values of S and M_S (if any) do these values correspond?

18.12 Pretend that the direction of angular momentum vectors can be specified exactly. Assume an electron in a hydrogen atom is in a ψ_{322} orbital with spin up and pretend that both the orbital angular momentum vector and the spin angular momentum vector lie in the xz plane. Find the possible vector sums and the possible z projection of the sum. To what values of $J$and M_J (if any) do the sums correspond?

18.6 The Lithium Atom

A lithium atom has three electrons and a nucleus with $Z = 3$. The Hamiltonian operator for a lithium atom with a stationary nucleus is

$$\begin{aligned}\widehat{H} = &-\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2 + \nabla_3^2)\\ &+\frac{1}{4\pi\varepsilon_0}\left(-\frac{3e^2}{r_1} - \frac{3e^2}{r_2} - \frac{3e^2}{r_3} + \frac{e^2}{r_{12}} + \frac{e^2}{r_{13}} + \frac{e^2}{r_{23}}\right)\end{aligned} \tag{18.6-1}$$

The zero-order Hamiltonian omits the electron–electron repulsion terms and consists of three hydrogen-like Hamiltonians with $Z = 3$:

$$\widehat{H}^{(0)} = \widehat{H}_{\mathrm{HL}}(1) + \widehat{H}_{\mathrm{HL}}(2) + \widehat{H}_{\mathrm{HL}}(3) \tag{18.6-2}$$

where we as usual abbreviate the coordinates by giving only the subscript specifying which electron is meant.

Solution of the Schrödinger equation in the zero-order approximation leads to a wave function that is a product of hydrogen-like orbitals with $Z = 3$:

$$\begin{aligned}\Psi^{(0)} &= \psi_{n_1l_1m_1,m_{s1}}(1)\,\psi_{n_2l_2m_2,m_{s2}}(2)\,\psi_{n_1l_1m_1,m_{s1}}(3)\\ &= \psi_1(1)\psi_2(2)\psi_3(3)\end{aligned} \tag{18.6-3}$$

where we abbreviate the subscripts in the second version of this equation. The zero-order electronic energy of the atom is the sum of three hydrogen-like energy eigenvalues with $Z = 3$. From Eq. (17.3-19),

$$\begin{aligned}E^{(0)} = E^{(0)}_{n_1n_2n_3} &= E_{n_1}(\mathrm{HL}) + E_{n_2}(\mathrm{HL}) + E_{n_3}(\mathrm{HL})\\ &= -(13.60\,\mathrm{eV})\left(\frac{3^2}{n_1^2} + \frac{3^2}{n_2^2} + \frac{3^2}{n_3^2}\right)\end{aligned} \tag{18.6-4}$$

Exercise 18.5

Carry out the steps to obtain Eq. (18.6-4).

Antisymmetrization

The orbital wave function of Eq. (18.6-3) can be antisymmetrized by writing a sum of the six terms corresponding to each possible order of the spin orbitals, keeping the particle labels in a fixed order. Each term that is generated from the first term by one exchange ("permutation") of a pair of indexes must be given a negative sign, and each term that is generated by two permutations of pairs of indexes must be given a positive sign. The antisymmetrized function is

$$\Psi = \frac{1}{\sqrt{6}}\,[\psi_1(1)\psi_2(2)\psi_3(3) - \psi_2(1)\psi_1(2)\psi_3(3) - \psi_1(1)\psi_3(2)\psi_2(3) \\ -\psi_3(1)\psi_2(2)\psi_1(3) + \psi_3(1)\psi_1(2)\psi_2(3) + \psi_2(1)\psi_3(2)\psi_1(3)] \tag{18.6-5}$$

Exercise 18.6

Show that the function produced by exchanging particle labels 1 and 3 in Eq. (18.6-5) is the negative of the original function. Choose another permutation and show the same thing.

If a spin orbital occurs more than once in each term in the wave function, the wave function vanishes, in agreement with the Pauli exclusion principle.

EXAMPLE 18.5

If orbitals ψ_1 and ψ_3 are the same function, show that the wave function of Eq. (18.6-5) vanishes.

Solution

$$\Psi = \frac{1}{\sqrt{6}}[\psi_1(1)\psi_2(2)\psi_1(3) - \psi_2(1)\psi_1(2)\psi_1(3) - \psi_1(1)\psi_1(2)\psi_2(3) \\ - \psi_1(1)\psi_2(2)\psi_1(3) + \psi_1(1)\psi_1(2)\psi_2(3) + \psi_2(1)\psi_1(2)\psi_1(3)]$$

The first and fourth terms cancel, the third and fifth terms cancel, and the second and sixth terms cancel, so that the wave function vanishes.

Slater Determinants

The Slater determinant is named for John C. Slater, 1900–1976, a prominent American physicist who made various contributions to atomic and molecular quantum theory.

There is another notation that can be used to write the antisymmetrized wave function of Eq. (18.6-5). It is known as a *Slater determinant*. A determinant is a quantity derived from a square matrix by a certain set of multiplications, additions, and subtractions. There is a brief introduction to matrices and determinants in Appendix B. If the elements of the matrix are constants, the determinant is equal to a single constant. If the elements of the matrix are orbitals, the determinant of that matrix is a single function of all of the coordinates on which the orbitals depend. The wave function of Eq. (18.6-5) is equal to the determinant:

$$\Psi = \frac{1}{\sqrt{6}}\begin{vmatrix} \psi_1(1) & \psi_1(2) & \psi_1(3) \\ \psi_2(1) & \psi_2(2) & \psi_2(3) \\ \psi_3(1) & \psi_3(2) & \psi_3(3) \end{vmatrix} \tag{18.6-6}$$

Exercise 18.7

Use the rule of Eq. (B-99) of Appendix B for expanding a three-by-three determinant to show that the function of Eq. (18.6-6) is the same as that of Eq. (18.6-5):

Two properties of determinants presented in Appendix B relate to the properties of antisymmetrized orbital wave functions:

1. If one exchanges two columns or two rows of a determinant, the resulting determinant is the negative of the original determinant. Exchanging the locations of two particles is equivalent to exchanging two columns, so that the Slater determinant exhibits the necessary antisymmetry.
2. If two rows or two columns of a determinant are identical, the determinant vanishes. If two electrons occupy identical spin orbitals, two rows of the determinant in Eq. (18.6-6) are identical, and the determinant vanishes, in agreement with the Pauli exclusion principle.

For an antisymmetrized orbital wave function for the Li atom we must choose three different spin orbitals. For the ground state, we choose orbitals with the minimum possible sum of orbital energies. This practice is called the *Aufbau principle*, from the German word for "building up." We choose the two $1s$ spin orbitals and one spin orbital from the second shell. We anticipate the fact that higher-order calculations will give a lower energy for the $2s$ spin orbitals than for the $2p$ spin orbitals, and choose one of the $2s$ spin orbitals. It does not matter whether we choose the spin-up or the spin-down spin orbital. From Eq. (18.6-4) the zero-order energy of the ground state is

$$\begin{aligned} E_{\mathrm{gs}}^{(0)} = E_{1s1s2s}^{(0)} &= 2E_1(\mathrm{HL}) + E_2(\mathrm{HL}) \\ &= (-13.60\,\mathrm{eV})\left(2\frac{3^2}{1^2} + \frac{3^2}{2^2}\right) = -275.4\,\mathrm{eV} \end{aligned} \tag{18.6-7}$$

This value is seriously in error, as was the zero-order value for helium. It differs from the experimental value of -203.5 eV by 35%.

Using space orbitals and spin functions a zero-order Slater determinant for the ground state is

$$\Psi^{(0)} = \frac{1}{\sqrt{6}} \begin{vmatrix} \psi_{1s}(1)\alpha(1) & \psi_{1s}(2)\alpha(2) & \psi_{1s}(3)\alpha(3) \\ \psi_{1s}(1)\beta(1) & \psi_{1s}(2)\beta(2) & \psi_{1s}(3)\beta(3) \\ \psi_{2s}(1)\alpha(1) & \psi_{2s}(2)\alpha(2) & \psi_{2s}(3)\alpha(3) \end{vmatrix} \tag{18.6-8}$$

The spin orbital $\psi_{2s}\beta$ could have been chosen instead of $\psi_{2s}\alpha$. We therefore have two states of equal energy. This doubly degenerate ground level corresponds to $S = 1/2$ (a doublet term), since the possible values of M_S are $+1/2$ and $-1/2$. Since $M_L = 0$, the value of L is 0, the only value of J is 1/2, and the ground term symbol of lithium is ${}^2S_{1/2}$.

Excited states of the lithium atom can correspond to various choices of orbitals. The values of M_L and M_S for these excited states can be calculated by algebraic addition. Using the rules that M_L ranges from $+L$ to $-L$ and that M_S ranges from $+S$ to $-S$, one can deduce the values of L and S that occur and can assign term symbols. Higher-order calculations must be used to determine the order of the energies of the excited states.

PROBLEMS

Section 18.6: The Lithium Atom

18.13 Show that the wave function of Eq. (18.6-5) is normalized if the orbitals are normalized and orthogonal to each other. The normalization integral is an integral over the coordinates of all three electrons. There will be 36 terms in the integrand. Look for a way to write down the result of integrating each term without having to write all of the integrands, using the orthogonality and normalization of the orbitals.

18.14 Show that the following determinant vanishes:

$$\begin{vmatrix} 1 & 2 & 3 \\ 1 & 2 & 3 \\ 2 & 1 & 4 \end{vmatrix}$$

18.15 Show that the following determinant vanishes:

$$\begin{vmatrix} 1 & 2 & 1 \\ 2 & 2 & 2 \\ 3 & 1 & 3 \end{vmatrix}$$

18.16 Show that the following determinants are equal to the negative of each other:

$$\begin{vmatrix} 1 & 2 & 1 \\ 2 & 1 & 2 \\ 3 & 1 & 3 \end{vmatrix} \quad \text{and} \quad \begin{vmatrix} 2 & 1 & 2 \\ 1 & 2 & 1 \\ 3 & 1 & 3 \end{vmatrix}$$

18.17 Find and explain the relationship between the two determinants:

$$\begin{vmatrix} 1 & 2 & 1 \\ 2 & 1 & 2 \\ 3 & 1 & 0 \end{vmatrix} \quad \text{and} \quad \begin{vmatrix} 3 & 6 & 3 \\ 2 & 1 & 2 \\ 3 & 1 & 0 \end{vmatrix}$$

18.18 Find the possible term symbols for the excited configuration $(1s)^2(2p)$.

18.19 Find the possible term symbols for the excited configuration $(1s)(2s)(2p)$.

18.20 Consider the excited-state configuration $(1s)(2s)(3s)$ for a lithium atom. Write a table analogous to Table 18.1.

a. Show that quartet states with $S = 3/2$ can occur.

b. Write the term symbols for all terms that occur.

c. Find the zero-order energy eigenvalue for this configuration.

18.7 Atoms with More Than Three Electrons

The treatment of other atoms in zero order is analogous to the helium and lithium treatments. For an atom with atomic number Z (Z protons in the nucleus and Z electrons), the stationary-nucleus Hamiltonian operator is

$$\widehat{H} = -\frac{\hbar^2}{2m}\sum_{i=1}^{Z}\nabla_i^2 - \frac{Ze^2}{4\pi\varepsilon_0}\sum_{i=1}^{Z}\frac{1}{r_1} + \frac{e^2}{4\pi\varepsilon_0}\sum_{i=2}^{Z}\sum_{j=1}^{i-1}\frac{1}{r_{ij}} \tag{18.6-9}$$

where r_i is the distance from the nucleus to the ith electron and r_{ij} is the distance from the ith electron to the jth electron.

The first two sums in Eq. (18.6-9) are a sum of hydrogen-like one-electron Hamiltonian operators. In zero order, we ignore the double sum representing the electron–electron repulsions and obtain the Hamiltonian operator:

$$\widehat{H}^{(0)} = \sum_{i=1}^{Z}\widehat{H}_{\text{HL}}(i) \tag{18.6-10}$$

The time-independent Schrödinger equation corresponding to the zero-order Hamiltonian can be solved by separation of variables, using the trial function

$$\Psi^{(0)} = \psi_1(1)\psi_2(2)\psi_3(3)\psi_4(4)\cdots\psi_Z(Z) = \prod_{i=1}^{Z}\psi_i(i) \tag{18.6-11}$$

where the symbol Π stands for a product of factors, just as the Σ symbol stands for a sum of terms. The factors $\psi_1(1)$, $\psi_2(2)$, $\psi_3(3), \ldots,$ are all hydrogen-like orbitals corresponding to the correct value of Z:

$$\psi_i(i) = \psi_{n_i l_i m_i, m_{si}}(i) \tag{18.6-12}$$

We must antisymmetrize the orbital wave function of Eq. (18.6-11). This can be done by writing a Slater determinant with one row for each spin orbital and one column for each electron:

$$\psi_{(0)} = \frac{1}{\sqrt{Z!}}\begin{vmatrix} \psi_1(1) & \psi_1(2) & \psi_1(3) & \psi_1(4) & \cdots & \psi_1(Z) \\ \psi_2(1) & \psi_2(2) & \psi_2(3) & \psi_2(4) & \cdots & \psi_2(Z) \\ \psi_3(1) & \psi_3(2) & \psi_3(3) & \psi_3(4) & \cdots & \psi_3(Z) \\ \psi_4(1) & \psi_4(2) & \psi_4(3) & \psi_4(4) & \cdots & \psi_4(Z) \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \psi_Z(1) & \psi_Z(2) & \psi_Z(3) & \psi_Z(4) & \cdots & \psi_Z(Z) \end{vmatrix} \tag{18.6-13}$$

where the $1/\sqrt{Z!}$ factor normalizes the wave function if all orbitals are normalized and orthogonal to each other. The Pauli exclusion principle is automatically followed. If two spin orbitals are the same function the determinant vanishes.

The values of M_L, M_S, L, and S can be computed in the same way as with the helium and lithium atoms. The contributions to M_L and M_S for any completely filled subshell cancel. Only partly filled subshells need to be counted. For example, the only term symbol that occurs for the ground state of an inert gas (He, Ne, Ar, and so on) is ${}^1S_0$ and the only term symbol that occurs for an alkali metal in its ground state is ${}^2S_{1/2}$.

The zero-order energy eigenvalue is a sum of hydrogen-like orbital energies with the appropriate value of Z:

$$E^{(0)} = E_{n_1}(\mathrm{HL}) + E_{n_2}(\mathrm{HL}) + \ldots = \sum_{i=1}^{Z} E_{n_i}(\mathrm{HL}) \tag{18.6-14}$$

In the next chapter, we will discuss approximations beyond the zero-order approximation. We will find that the orbitals in different subshells of the same shell do not correspond to the same energy, and will be able to identify ground terms by use of the Aufbau principle.

PROBLEMS

Section 18.7: Atoms with More Than Three Electrons

18.21 Write the possible term symbols for the ground configuration of the boron atom.

18.22 Write the antisymmetrized orbital wave function for one of the states of the carbon atom in its ground configuration $(1s)^2(2s)^2(2p)^2$. Use the Slater determinant notation. How many terms are in the wave function written as a sum of terms without determinant notation?

18.23 Write the antisymmetrized orbital wave function for one of the states of the nitrogen atom in its ground configuration $(1s)^2(2s)^2(2p)^3$. Use the Slater determinant notation. How many terms are in the wave function written as a sum of terms without determinant notation?

18.24 Find the possible term symbols for the lowest-energy configuration of the chlorine atom. Use the fact that a subshell with *n* empty spin orbitals gives the same terms as one with *n* filled spin orbitals.

18.25 Find the possible term symbols for the following atoms in the given configurations:
a. $C(1s)^2(2s)^2(2p)^2$
b. $Se(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^{10}(4p)^4$

18.26 Find the possible term symbols for the following atoms in the given configurations:
a. $Ar(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6$
b. $Mg(1s)^2(2s)^2(2p)^6(3s)^2$

18.27 Find the possible term symbols for each of the following configurations of the Be atom:
a. $(1s)^2(2s)^2$
b. $(1s)^2(2s)(3s)$
c. $(1s)(2s)(3s)(4s)$

18.28 Find the possible term symbols for:
a. $Li(1s)^2(2s)$ configuration
b. $F(1s)^2(2s)^2(2p)^5$ configuration
c. $Mg(1s)^2(2s)^2(2p)^6(3s)^2$ configuration

18.29 Tell how many states correspond to each of the following terms (include all possible values of *J*):
a. ^3D
b. ^4F
c. ^2S

Summary of the Chapter

In the "zero-order" approximation, the repulsions between electrons are neglected. The energy eigenfunctions of a multielectron atom are products of one hydrogen-like spin orbital for each electron, and the energy eigenvalues are the sum of the orbital energies. The wave functions must be antisymmetrized to conform to the physical indistinguishability of the electrons. This leads to the Pauli exclusion principle, which states that no two spin orbitals in any orbital wave function can be the same function. Orbital and spin angular momentum values for various electron configurations can be determined, and Russell–Saunders term symbols can be used to specify the energy levels corresponding to these values.

ADDITIONAL PROBLEMS

18.30 For the beryllium atom, Be:
a. Write the Hamiltonian operator, assuming a stationary nucleus.
b. Write the zero-order Hamiltonian operator (excluding the electron–electron repulsion terms).
c. Write the ground-state wave function in the simple orbital approximation, without antisymmetrization.
d. Write the antisymmetrized ground-state wave function as a Slater determinant.
e. Consider the ground-state configuration $(1s)^2(2s)^2$. Determine the values of S, L, M_L, and M_S that can occur. Write the Russell–Saunders term symbols for all terms that can occur.
f. Consider the subshell configuration $(1s)^2(2s)(2p)$. Determine the values of S, L, M_L, and M_S that can occur. Write the Russell–Saunders term symbols for all terms that can occur.
g. Consider the subshell configuration $(1s)^2(2p)(3p)$. Determine the values of S, L, M_L, and M_S that can occur. Write the Russell–Saunders term symbols for all terms that can occur.

18.31 From the pattern of nodal surfaces observed in the subshells that we have discussed, predict the following:

a. The number of nodal spheres in the 6*s* wave function.

b. The number of nodal spheres in a $6p$ wave function.

c. The number of nodal planes containing the z axis in the real part of the ψ_{6d0} (ψ_{620}) wave function.

d. The number of nodal cones in the real part of the ψ_{6p1} (ψ_{611}) wave function.

18.32 Identify the following statements as either true or false. If a statement is true only under special circumstances, label it as false.

a. Electrons in a multielectron atom move exactly like electrons in a hydrogen-like atom with the appropriate nuclear charge.

b. The correct wave function for a multielectron atom can be written as an antisymmetrized product of orbitals.

c. If a helium atom is not confined in any container, the center of mass of the atom moves exactly like a free particle.

d. The orbital regions for a He^+ ion are approximately the same size as those of a hydrogen atom.

e. The orbital regions of a He^+ ion have one-eighth the volume of the orbital regions of a hydrogen atom.

19

The Electronic States of Atoms. III. Higher-Order Approximations

PRINCIPAL FACTS AND IDEAS

1. The electron–electron repulsions in multielectron atoms are included in several approximation methods:
2. The variation method allows calculation of upper bounds to ground-state energies.
3. The perturbation method allows approximate calculations of energies and wave functions for any states.
4. The self-consistent field method allows generation of the best possible orbital wave function.
5. The density functional method can in principle lead to the correct ground-state energy as a functional of the electron probability density.
6. The energy levels of multielectron atoms can be characterized by orbital and spin angular momentum values in the Russell–Saunders approximation.
7. The ground energy level of an atom can be identified using Hund's rules.
8. The structure of the periodic table of the elements can be understood in terms of higher-order orbital approximations.

19.1 The Variation Method and Its Application to the Helium Atom

The zero-order orbital approximation employed in Chapter 18 completely neglects the electron–electron repulsions in atoms and therefore gives poor energy values. There are several commonly used methods that go beyond this approximation. The *variation method* is based on the variation theorem.

The Variation Theorem

The expectation value of the energy corresponding to a time-independent wave function ψ is given by Eq. (16.4-4):

$$\langle E\rangle = \frac{\int \psi^* \widehat{H}\psi dq}{\int \psi^* \psi dq} \tag{19.1-1}$$

where $\widehat{H}$ is the Hamiltonian operator of the system and where the coordinates of all of the particles of the system are abbreviated by q. The integration is to be done over all values of all coordinates.

The *variation theorem* states: *The expectation value of the energy calculated with any function* φ *obeying the same boundary conditions as the correct system wave functions cannot be lower than* E_{gs}, *the correct ground-state energy eigenvalue of the system:*

$$\frac{\int \varphi^* \widehat{H}\varphi dq}{\int \varphi^* \varphi dq} \geq E_{\mathrm{gs}} \quad \text{(variation theorem)} \tag{19.1-2}$$

The correct Hamiltonian operator must be used. This expectation value is equal to E_{gs} if and only if the function φ is the same function as the correct ground-state energy eigenfunction. The proof of the theorem is assigned in Problem 19.1.

The Variation Method

The variation theorem suggests the variation method for finding an approximate ground-state energy and wave function. The first step of the method is to choose a family of possible approximate wave functions. The second step is to calculate the expectation value of the energy using the different members of the family of functions. This expectation value is called the *variation energy*, and is usually denoted by W. The final step is to find the member of the family that gives a lower (more negative) value of W than any other member of the family. This value of W is a better approximation to the ground-state energy than is obtained from any other member of the family of functions. The theorem does not guarantee that this function is a better approximation to the correct wave function than any other member of the family, but it is likely to be so.

A typical family of functions is represented by a formula containing one or more variable parameters. Such a formula is called a *variation function* or a *variation trial* *function*. The variation energy W is calculated as a function of the parameters, and the minimum value of W is found by the methods of calculus.

EXAMPLE 19.1

Calculate the variational energy of a particle in a hard one-dimensional box of length a, using the variation function $\varphi(x) = Ax(a-x)$.

Solution

To normalize the wave function:

$$1 = A^2 \int_0^a x^2(a-x)^2\,dx = A^2 \int_0^a (a^2x^2 - 2ax^3 + x^4)dx$$

$$= A^2\left(\frac{a^5}{3} - \frac{2a^5}{4} + \frac{a^5}{5}\right) = A^2\frac{a^5}{30}$$

$$A = \left(\frac{30}{a^5}\right)^{1/2}$$

Since there are no variable parameters, the variational energy will not be minimized.

$$W = -A^2\frac{\hbar^2}{2m}\int_0^a x(a-x)\frac{d^2}{dx^2}[x(a-x)]dx = -A^2\frac{\hbar^2}{2m}\int_0^a x(a-x)(-2)dx$$

$$= A^2\frac{\hbar^2}{m}\int_0^a (ax-x^2)dx = A^2\frac{\hbar^2}{m}\left(\frac{a^3}{2}-\frac{a^3}{3}\right)$$

$$= \frac{5\hbar^2}{ma^2} = \frac{5h^2}{4\pi^2 ma^2} = 0.12665\frac{h^2}{ma^2}$$

This variational energy is only 1.32% higher than the correct ground-state energy, in which the factor $1/8 = 0.125$ occurs in place of the factor 0.12665.

Application of the Variation Method to the Helium Atom[1]

Let us first use the zero-order orbital wave function of Eq. (18.3-2) as a variation function. This is a single function, so no energy minimization can be done, but the procedure illustrates some things about the method. The zero-order function is normalized so that the variation energy is

$$W = \frac{1}{2}\int \psi_{100}(1)\psi_{100}(2)[\alpha^*(1)\beta^*(2) - \beta^*(1)\alpha^*(2)]\widehat{H}\psi_{100}(1)\psi_{100}(2)$$
$$\times [\alpha(1)\beta(2) - \beta(1)\alpha(2)]dq_1'dq_2' \tag{19.1-3}$$

where dq_1' and dq_2' indicate integration over space and spin coordinates and where the space orbital ψ_{100} is a hydrogen-like 1s orbital. We omit the symbols for the complex

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[1] Our treatment follows that in J. C. Davis, Jr., *Advanced Physical Chemistry*, The Ronald Press, New York, 1965, p. 221ff.

conjugates because our function is real. We assume that the nucleus is stationary, so the correct Hamiltonian operator is:

$$\widehat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) + \frac{1}{4\pi\varepsilon_0}\left(-\frac{Ze^2}{r_2} - \frac{Ze^2}{r_1} - \frac{e^2}{r_{12}}\right) \tag{19.1-4}$$

where the number of protons in the nucleus is denoted by Z. We will set Z equal to 2 at the end of the calculation.

Since the helium-atom Hamiltonian operator is independent of the spin coordinates, the integral over the spin coordinates can be factored from the space coordinate integration. Because of the normalization and orthogonality of the spin functions, integration over the spin coordinates gives a factor of 2, which cancels the normalizing constant 1/2. We could have omitted the spin factor and the spin integration from the beginning. We now have

$$\begin{aligned} W = \int & \psi_{100}(1)\psi_{100}(2)\left(\widehat{H}_{\text{HL}}(1) + \widehat{H}_{\text{HL}}(2) + \frac{e^2}{4\pi\varepsilon_0 r_{12}}\right) \\ & \psi_{100}(1)\psi_{100}(2)d^3\mathbf{r}_1 d^3\mathbf{r}_2 \end{aligned} \tag{19.1-5}$$

Exercise 19.1

Show that the spin integration in Eq. (19.1-3) leads to a factor equal to 2.

The $\widehat{H}_{\text{HL}}(1)$ and $\widehat{H}_{\text{HL}}(2)$ terms in the Hamiltonian operator give ground-state energy eigenvalues for a hydrogen-like atom after operating and integrating.

Exercise 19.2

Show that the $\widehat{H}_{\text{HL}}(1)$ term in Eq. (19.1-5) yields a contribution to W equal to $E_1(\text{HL})$ and that the $\widehat{H}_{\text{HL}}(2)$ term yields an equal contribution.

We now have

$$W = 2E_1(\text{HL}) + \int \psi_{100}(1)^*\psi_{100}(2)^*\left(\frac{e^2}{4\pi\varepsilon_0 r_{12}}\right)\psi_{100}(1)\psi_{100}(2)dq \tag{19.1-6}$$

Evaluation of the integral in this equation is tedious and we give only the result:[2]

$$W = 2E_1(\text{HL}) + \frac{5Ze^2}{8(4\pi\varepsilon_0 a)} = 2E_1(\text{HL}) - \frac{5Z}{8}\langle\mathscr{V}\rangle_{\text{H}(1s)} \tag{19.1-7}$$

where $\langle\mathscr{V}\rangle_{\text{H}(1s)}$ is the expectation value of the potential energy for the hydrogen atom (not hydrogen-like) in its ground state. From Eq. (17.3-19)

$$W = -2\frac{Z^2e^2}{2(4\pi\varepsilon_0 a)} + \frac{5Ze^2}{8(4\pi\varepsilon_0 a)} = -108.8\,\text{eV} + 34.0\,\text{eV} = -74.8\,\text{eV} \tag{19.1-8}$$

The numerical values in Eq. (19.1-8) are for $Z = 2$. The hydrogen-like orbital energies are proportional to Z^2 while the term due to electron–electron repulsion is

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[2] I. N. Levine, *Quantum Chemistry*, 5th ed., Prentice-Hall, Englewood Cliffs, NJ, 2000, p. 254ff.

proportional to Z. The electron–electron repulsion term in the Hamiltonian does not contain the parameter Z, but the effective radius of the orbital region is inversely proportional to Z, making the average distance between the electrons inversely proportional to Z and making the expectation value of the repulsion energy proportional to Z.

The result in Eq. (19.1-8) is more positive than the correct value of -79.0 eV, as the variation theorem guaranteed. The error of 4 eV is much smaller than the error of -30 eV obtained with the zero-order approximation. Our wave function is still the zero-order wave function obtained by complete neglect of the electron–electron repulsion. The improvement came from using the complete Hamiltonian operator in calculating the variation energy rather than the zero-order Hamiltonian.

We now use a variation trial function that represents a family of functions. We choose a modified 1s space orbital in which the nuclear charge Z is replaced by a variable parameter, Z':

$$\psi'_{100} = \psi'_{100}(Z') = \frac{1}{\sqrt{\pi}}\left(\frac{Z'}{a}\right)^{3/2} e^{-Z'r/a} \tag{19.1-9}$$

where a is the Bohr radius. We label this orbital with a prime ($'$) to remind us that the orbital depends on Z', not on Z. The variation trial function is

$$\varphi = \varphi(Z') = \psi'(1)\psi'(2)\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \tag{19.1-10}$$

where we omit the subscripts on the orbital symbols.

Shielding

There is a physical motivation for choosing this variation function. As an electron moves about in the helium atom, there is some probability that the other electron will be somewhere between the first electron and the nucleus, "shielding" the first electron from the full nuclear charge and causing it to move as though the nucleus had a smaller charge. A value of Z' smaller than 2 should produce a better approximate energy value than the value of -74.8 eV in Eq. (19.1-8).

When the wave function of Eq. (19.1-10) and the correct Hamiltonian are substituted into Eq. (19.1-1) the variation energy is

$$\begin{aligned} W = \int \psi'(1)\psi'(2) \times \Bigg[\widehat{\mathscr{K}}(1) - \frac{Ze^2}{4\pi\varepsilon_0 r_1} + \widehat{\mathscr{K}}(2) - \frac{Ze^2}{4\pi\varepsilon_0 r_2} \\ + \frac{e^2}{4\pi\varepsilon_0 r_{12}}\Bigg]\psi'(1)\psi'(2)dq \end{aligned} \tag{19.1-11}$$

where $\widehat{\mathscr{K}}$ is the kinetic energy operator for one electron. The kinetic energy operator of electron 1 operates only on the coordinates of electron 1, so that

$$\begin{aligned} &\int\int \psi'(1)^*\psi'(2)^*\widehat{\mathscr{K}}(1)\psi'(1)\psi'(2)d^3\mathbf{r}_1 d^3\mathbf{r}_2 \\ &= \int \psi'(1)^*\widehat{\mathscr{K}}(1)\psi'(1)d^3\mathbf{r}_1 \int \psi'(2)^*\psi'(2)d^3\mathbf{r}_2 = \int \psi'(1)^*\widehat{\mathscr{K}}(1)\psi'(1)d^3\mathbf{r}_1 \\ &= Z'^2\langle\mathscr{K}\rangle_{\mathrm{H}(1s)} = -Z'^2 E_1(\mathrm{H}) \end{aligned} \tag{19.1-12}$$

where $\langle\mathscr{K}\rangle_{\mathrm{H}(1s)}$ is the expectation value of the kinetic energy of a hydrogen atom in the 1s state, which is equal to the negative of the total energy, as shown in Section 17.5.

The second term in the Hamiltonian operator in Eq. (19.1-11) gives a contribution analogous to that in Eq. (19.1-6):

$$\text{Contribution to } W = \int \psi'(1)^*\psi'(2)^*\frac{Z\mathscr{e}^2}{4\pi\varepsilon_0 r_1}\psi'(1)\psi'(2)\,dq$$

$$= ZZ'\langle\mathscr{V}\rangle_{\mathrm{H}(1s)} = 2ZZ'E_1(\mathrm{H}) \qquad (19.1\text{-}13)$$

where $\langle\mathscr{V}\rangle_{\mathrm{H}(1s)}$ is the expectation value of the potential energy of a hydrogen (not hydrogen-like) atom in the $1s$ state. We have a factor of Z from the factor Z in the Hamiltonian, and a factor of Z' from use of the $1s$ orbital that corresponds to a nuclear charge of $Z'\mathscr{e}$. The final equality comes from Eq. (17.5-9), which states that the expectation value of the potential energy equals twice the total energy.

The third and fourth terms in the Hamiltonian operator in Eq. (19.1-11) are just like the first two terms except that the roles of particles 1 and 2 are interchanged. After the integrations these two terms give contributions equal to those of the first two terms. The fifth term is the same as in Eq. (19.1-6) except that the orbitals correspond to the nuclear charge of $Z'\mathscr{e}$ instead of $Z\mathscr{e}$, so that its contribution is:

$$\int \psi'(1)^*\psi'(2)^*\left(\frac{\mathscr{e}^2}{4\pi\varepsilon_0 r_{12}}\right)\psi'(1)\psi'(2)dq = -\frac{5}{4}Z'E_1(\mathrm{H}) \qquad (19.1\text{-}14)$$

The final result is

$$W = E_1(\mathrm{H})\left(-2Z'^2 + 4ZZ' - \frac{5}{4}Z'\right) \qquad (19.1\text{-}15)$$

We find the minimum value of W by differentiating with respect to Z' and setting this derivative equal to zero:

$$0 = E_1(\mathrm{H})\left(-4Z' + 4Z - \frac{5}{4}\right)$$

This gives

$$Z' = Z - \frac{5}{16} \qquad (19.1\text{-}16)$$

For $Z = 2$, $Z' = 27/16 = 1.6875$. This corresponds to motion of an electron as though the nucleus had 1.6875 protons instead of 2 protons, or that the second electron has a 31.25% probability of being closer to the nucleus than the first electron. Figure 19.1 shows the hydrogen-like $1s$ orbital with $Z = 2$ and the variation orbital with $Z' = 1.6875$. The variable on the horizontal axis of this figure is the distance from the nucleus divided by the Bohr radius a.

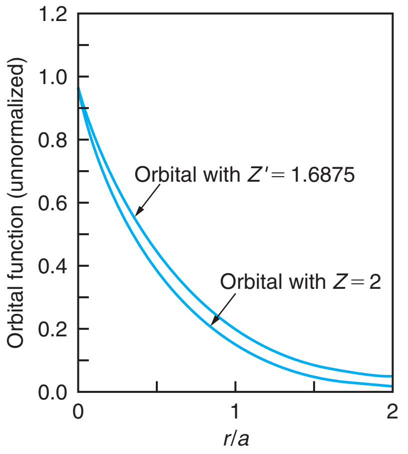

Figure 19.1 Zero-Order and Variationally Obtained Orbitals for the Ground State of the Helium Atom.

For the helium atom ($Z = 2$) the minimum value of W is

$$W = (-13.60\,\mathrm{eV})[-2(1.6875)^2 + 4(2)(1.6875) - \frac{5}{4}(1.6875)] = -77.5\,\mathrm{eV} \qquad (19.1\text{-}17)$$

This value differs from the experimental value of −79.0 eV by 1.5 eV, an error of 2%, an improvement over the error of 4 eV or 5% obtained with the unmodified hydrogen-like orbitals. More nearly accurate values can be obtained by choosing more flexible variation functions. Hylleraas used the variation function[3]

$$\varphi = Ce^{-Z''r_1/a}e^{-Z''r_2/a}(1 + br_{12}) \qquad (19.1\text{-}18)$$

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[3] E. A. Hylleraas, Z. *Physik*, **65**, 209 (1930).

where r_{12} is the distance between the electrons. This function gave a variation energy equal to -78.7 eV with a value of Z'' equal to 1.849 and a value of b equal to 0.364. This energy is in error by 0.3 eV, or about 0.4%. More elaborate variation functions have been used, and have given excellent agreement with experiment.[4]

The presence of the factor $(1 + br_{12})$ corresponds to a larger probability density for larger separations of the electrons than for smaller separations. This explicit dependence on the electron–electron distance represents the tendency of the electrons to repel each other and is called *dynamical electron correlation*. In a one-term orbital wave function the probability density of each electron is independent of the position of the other electrons and there is no electron correlation.

An antisymmetrized orbital wave function can also exhibit electron correlation if it has an antisymmetric space factor like that of Eq. (18.4-2a). Consider the wave function

$$\Psi = C[\psi_1(r_1, \theta_1, \phi_1)\psi_2(r_2, \theta_2, \phi_2) - \psi_2(r_1, \theta_1, \phi_1)\psi_1(r_2, \theta_2, \phi_2)]$$

where ψ_1 and ψ_2 are any two different space orbitals. If $r_1 = r_2, \theta_1 = \theta_2$, and $\phi_1 = \phi_2$ this function vanishes. Since the wave function must be continuous it must have a small magnitude if the two electrons are close to each other. This effect is called *statistical electron correlation*. Statistical correlation does not occur in wave functions with symmetric space factors.

PROBLEMS

Section 19.1: The Variation Method and Its Application to the Helium Atom

19.1 Prove the variation theorem. Assume that all of the energy eigenfunctions and energy eigenvalues are known, and write the variation function as a linear combination of the energy eigenfunctions:

$$\varphi = \sum_{i=1}^{\infty} c_i \psi_i$$

Substitute this expression into the formula for the variation energy and use eigenfunction and orthogonality properties.

19.2 Calculate the variation energy of a particle in a one-dimensional box of length a with the trial function $\varphi(x) = Ax^2(a^2 - x^2)$. Calculate the percent error.

19.3 Calculate the variation energy of a particle in a one-dimensional box of length a with the trial function $t\varphi(x) = Ax^3(a^3 - x^3)$. Calculate the percent error.

19.4 Calculate the variation energy of a harmonic oscillator using the trial function $\varphi(x) = A/(b^2 + x^2)$, where b is a variable parameter. Minimize the energy and find the percent error from the correct ground-state energy.

19.5 Using the variation method, calculate an upper bound to the energy of the ground state of an anharmonic oscillator with potential energy $\mathcal{V} = kx^2/2 + bx$, where k and b are constants. Use the trial function $\varphi = A(\psi_0 + c\psi_1)$, where ψ_0 and ψ_1 are the first energy eigenfunctions of the harmonic oscillator with force constant k. Minimize the energy with respect to c. Assume the numerical values: $k = 576\ \mathrm{J\,m^{-2}}$, $m = 1.672623 \times 10^{-27}$ kg, $a = 9.3075 \times 10^{21}\ \mathrm{m^{-2}}$, and take $b = mg = 1.639 \times 10^{-26}\ \mathrm{J\,m^{-1}}$. These values correspond to a hydrogen molecule held in a vertical position near the surface of the earth with the lower nucleus somehow held fixed. How significant is the effect of gravity?

19.6 Use the variation function $\varphi = Ax^2(x - a)$ to calculate an upper bound to the ground state of a particle in a box of length a. Give the percent error from the correct energy.

19.7 Use the variation function $\varphi = A\sin^2(\pi x/a)$ to calculate an upper bound to the ground-state energy of a particle in a box of length a. Give the percent error from the correct energy.

19.8 Calculate the ground-state energy of a harmonic oscillator using the variation function

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[4] T. Koga, *J. Chem. Phys.*, **94**, 5530 (1991).

$$\varphi(x) = \begin{cases} A\cos(bx) & \text{if } 0 < |x| < \pi/2b \\ 0 & \text{if } |x| > \pi/2b \end{cases}$$

where b is an adjustable parameter.

19.9 An oscillating particle of mass m has the potential energy function

$$\mathcal{V} = cx^4$$

where c is a constant with units J m^{-4}. Find a formula for the variational energy assuming a trial function

$$\varphi = Ae^{-bx^2}$$

where b is a variable parameter.

19.10 An oscillating particle of mass m has the potential energy function

$$\mathcal{V} = cx^4$$

where c is a constant with units J m^{-4}. Use the variation method assuming a trial function

$$\varphi = Ae^{-bx^4}$$

where b is a variable parameter.

19.11 Apply the variation method to the ground state of the hydrogen atom using the trial function

$$\varphi = \begin{cases} A(1 - r/b) & \text{if } 0 < r < b \\ 0 & \text{if } b < r \end{cases}$$

Compare your result with the correct energy, -2.1787×10^{-18} J.

19.12 The ionization potential (energy to remove one electron) of a helium atom in its ground state is 24.58 eV.

a. What effective nuclear charge does this correspond to? Compare with the Z' value from the simple variation calculation.

b. What energy in eV is required to remove both electrons?

19.13. Prove an extended variational theorem, which is that if the trial function φ is orthogonal to ψ_1, the correct ground-state wave function, the variational energy calculated with φ cannot be lower than the correct energy of the first excited state.

19.14. The extended variation theorem states that if a variation trial function is orthogonal to the exact ground-state wave function, it provides an upper limit to the energy of the first excited state. The following trial function is orthogonal to the ground-state wave function of a particle in a box of length a:

$$\varphi = C\left(x^3 - \frac{3}{2}ax^2 + \frac{1}{2}a^2x\right)$$

a. Obtain a formula for the variation energy of the first excited state of this system. Since this is single function, no minimization is possible.

b. Evaluate this energy for an electron in a box of length 10.00 Å. Calculate the percent error.

19.15 The extended variation theorem states that if a variational trial function is orthogonal to the exact ground-state wave function, it provides an upper limit to the energy of the first excited state.

a. Show that the following function is orthogonal to the correct ground-state wave function of a harmonic oscillator:

$$\varphi = \begin{cases} A\sin(bx) & \text{if } -\pi/b < x < \pi/b \\ 0 & \text{if } x > \pi/b \end{cases}$$

b. Calculate an upper bound to the energy of the first excited state of a harmonic oscillator using this variation function and treating b as an adjustable parameter.

19.2 The Self-Consistent Field Method

The *self-consistent field* (SCF) method was introduced in 1928 by Hartree.[5] The goal of this method is similar to that of the variation method in that it seeks to optimize an approximate wave function. It differs from the variation method in two ways: First, it deals only with orbital wave functions; second, the search is not restricted to one family of functions and is capable of finding the best possible orbital approximation. It is a method that proceeds by successive approximations, or iteration.

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[5] D. R. Hartree, *Proc. Camb. Philos. Soc.*, **24**, 89, 111, 426 (1928).

We describe the application of the method to the ground state of the helium atom. If electron 2 were fixed at location $\mathbf{r}_2$ the Schrödinger equation would be

$$-\frac{\hbar^2}{2m}\nabla_1^2\psi(1) - \frac{Ze^2}{4\pi\varepsilon_0 r_1}\psi_1(1) + \frac{e^2}{4\pi\varepsilon_0 r_{12}}\psi_1(1) = E_1\psi_1(1) \tag{19.2-1}$$

where r_{12} is the distance between the fixed position of electron 2 and the variable position of electron 1. We now seek to construct a one-electron equation without assuming that electron 2 is fixed. We assume that electron 2 occupies the normalized orbital $\psi_2(2)$ so that its probability of being found in the volume element $d^3\mathbf{r}_2$ is

$$(\text{Probability of electron 2 being in } d^3\mathbf{r}_2) = \psi_2(2)^*\psi_2(2)d^3\mathbf{r}_2 = |\psi_2(2)|^2 d^3\mathbf{r}_2 \tag{19.2-2}$$

We replace the electron–electron repulsion term in the Hamiltonian of Eq. (19.2-1) by a term containing an average over all positions of electron 2, using the probability density of Eq. (19.2-2):

$$-\frac{\hbar^2}{2m}\nabla_1^2\psi_1(1) - \frac{Ze^2}{4\pi\varepsilon_0 r_1}\psi_1(1) + \left[\int \frac{e^2}{4\pi\varepsilon_0 r_{12}}|\psi_2(2)|^2 d^3\mathbf{r}_2\right]\psi_1(1) = E_1\psi_1(1) \tag{19.2-3}$$

This is an *integrodifferential equation*. It contains both the derivative of an unknown function and an integral containing an unknown function. In the case of the helium atom ground state, both electrons occupy the same space orbital, so ψ_1 and ψ_2 are the same unknown function and there is a single integrodifferential equation. If $\psi_1(1)$ and $\psi_2(2)$ were different orbitals, we would have two simultaneous integrodifferential equations. For an atom with several electrons, there is an integrodifferential equation for each occupied space orbital.

The integrodifferential equation is solved by iteration (successive approximations) as follows: The first approximation is obtained by replacing the orbital under the integral by the zero-order function or some other known function, which we denote by $\psi_{(1s)}^{(0)}(2)$. Equation (19.2-3) for the ground state of the helium atom now becomes

$$\begin{aligned}
-\frac{\hbar^2}{2m}\nabla_1^2\psi_{1s}^{(1)}(1) - \frac{Ze^2}{4\pi\varepsilon_0 r_1}\psi_{1s}^{(1)}(1) + \left[\int \frac{e^2}{4\pi\varepsilon_0 r_{12}}|\psi_{1s}^{(0)}(2)|^2 d^3r_2\right]\psi_{1s}^{(1)} \\
= E_{1s}^{(1)}\psi_{1s}^{(1)}(1)
\end{aligned} \tag{19.2-4}$$

The integral over r_2 contains only known functions. It cannot be integrated mathematically, but can be evaluated numerically for various values of r_1, giving a table of values for different values of r_1. Equation (19.2-4) becomes a differential equation that can be solved numerically, using standard methods of numerical analysis.[6] The solution $\psi_{(1s)}^{(1)}(1)$ is independent of θ_1 and ϕ_1 and is represented by a table of values of $\psi_{1s}^{(1)}(1)$ as a function of r_1.

The next iteration (repetition) is carried out by replacing $\psi_{1s}^{(0)}(2)$ under the integral sign by $\psi_{(1s)}^{(1)}(2)$, obtaining an equation for the next approximation, denoted by $\psi_{1s}^{(2)}(1)$.

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[6] R. L. Burden, J. D. Faires, and A. C. Reynolds, *Numerical Analysis*, 2nd ed., Prindle, Weber, & Schmidt, Boston, 1981, p. 505ff.

This equation is solved numerically and the resulting solution is used under the integral for the next iteration, and so forth. The equation for the jth iteration is:

$$-\frac{\hbar^2}{2m}\nabla_1^2\psi_{1s}^{(j)}(1) - \frac{Ze^2}{4\pi\varepsilon_0 r_1}\psi_{1s}^{(j)}(1) + \left[\int \frac{e^2}{4\pi\varepsilon_0 r_{12}}|\psi_{1s}^{(j-1)}(2)|^2 d^3r_2\right]\psi_{1s}^{(j)}(1)$$
$$= E_{1s}^{(j)}\psi_{1s}^{(j)}(1) \qquad (19.2\text{-}5)$$

When additional iterations produce only negligible changes in the orbital function and the energy, we say that the integral term provides a self-consistent energy of electron 1, or a *self-consistent field*. At this point, the iteration is stopped and we assume that our result resembles the best possible orbital. Hartree carried out this solution prior to the existence of programmable computers.

Douglas Rayner Hartree, 1897–1958, was Professor of Applied Mathematics at the University of Manchester and was later Professor of Mathematical Physics at Cambridge University. He became a computer pioneer, working with ENIAC, one of the early electronic computers. Shortly after World War II he said that computers would have as great an effect on civilization as would nuclear energy.

In the SCF method, the expectation value of the energy is not the sum of the orbital energies, because the electron–electron repulsion has been included in solving Eq. (19.2-3) for each of the electrons. The sum of the two orbital energies therefore includes the electron–electron repulsion energy twice. We correct for this double inclusion by subtracting the expectation value of the electron–electron repulsion energy from the sum of the orbital energies. If n iterations have been carried out, the energy of the helium atom in its ground state is

$$E(\text{atom}) = 2E_{1s}^{(n)} - \int \frac{e^2}{4\pi\varepsilon_0 r_{12}}|\psi_{1s}^{(n)}(1)|^2|\psi_{1s}^{(n)}(2)|^2 d^3\mathbf{r}_1 d^3\mathbf{r}_2$$
$$= 2E_{1s}^{(n)} - J_{1s1s} \qquad (19.2\text{-}6)$$

The integral J_{1s1s} is called a **Coulomb integral** because it represents an approximate expectation value of a Coulomb (electrostatic) repulsion energy between two electrons.

The Hartree–Fock–Roothaan Method

Vladimir Aleksandrovich Fock, 1898–1974, was a Russian physicist who taught at the University of St. Petersburg for over 40 years. He made many contributions to quantum physics and to other fields of physics.

Clemons C. J. Roothaan, 1918–, Dutch-American physicist, first developed his method in his doctoral dissertation in the late 1940s at the University of Chicago, after being imprisoned in a German concentration camp during World War II. He became a professor of physics at the University of Chicago.

The Slater-type orbitals are named after the same John C. Slater after whom the Slater determinant is named.

Fock modified Hartree's SCF method to include antisymmetrization.[7] Roothaan further modified the Hartree–Fock method by representing the orbitals by linear combinations of basis functions similar to Eq. (16.3-34) instead of by tables of numerical values.[8] In Roothaan's method the integrodifferential equations are replaced by simultaneous algebraic equations for the expansion coefficients. There are many integrals in these equations, but the integrands contain only the basis functions, so the integrals can be calculated numerically. The calculations are evaluated numerically. This work is very tedious and it is not practical to do it without a computer.

Various kinds and numbers of basis functions have been used. Hydrogen-like basis functions turn out to consume a lot of computer time. *Slater-type orbitals* (STOs) require less computer time and are a common choice. Each Slater-type orbital is a product of three factors: r raised to some power, an exponential factor, and the correct spherical harmonic function. Using a large basis set of STOs, Clementi and Roetti obtained an approximate energy for the ground state of the helium atom equal to −77.9 eV, compared with the experimental value of −79.0 eV.[9] Basis sets of *Gaussian functions* are also used, in which the radial factor in the orbital is a Gaussian function. Some basis sets include sums of several Gaussian functions that approximate Slater-type orbitals.

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[7] V. Fock, *Zeits. f. Phys.*, **61**, 126 (1930).

[8] C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

[9] E. Clementi and C. Roetti, *At. Data Nucl. Data Tables*, **14**, 177 (1974).

The self-consistent field method can converge to the best orbital wave function, but it does not include any dynamical electron correlation. The difference between the best energy calculated with an orbital wave function and the energy corresponding to the exact solution of the Schrödinger equation is called the *correlation energy* or the *correlation error*. The 1.1 eV error of Clementi and Roetti is presumably an approximation to the correlation error. The *configuration interaction* method eliminates part of the correlation error by constructing a wave function that is a sum of terms, each of which corresponds to a different electron configuration. We discuss this method briefly later in this chapter and in the next chapter.

PROBLEMS

Section 19.2: The Self-Consistent Field Method

19.16 For an electron configuration of a helium atom in which the two electrons occupy different space orbitals, there must be two simultaneous integrodifferential equations in the SCF method. Write the equations for the $(1s)(2s)$ configuration.

19.17 Write the simultaneous SCF integrodifferential equations for the $(1s)^2(2s)$ configuration of the lithium atom. Are three equations needed?

19.3

The Perturbation Method and Its Application to the Ground State of the Helium Atom

We consider a Hamiltonian operator that can be separated into two terms,

$$\widehat{H} = \widehat{H}^{(0)} + \widehat{H}' \tag{19.3-1}$$

such that $\widehat{H}^{(0)}$ gives a Schrödinger equation that can be solved:

$$\widehat{H}^{(0)}\Psi^{(0)} = E^{(0)}\Psi^{(0)} \tag{19.3-2}$$

The wave function $\Psi^{(0)}$ is called the *zero-order wave function* or *unperturbed wave function*. The energy eigenvalue $E^{(0)}$ is called the *zero-order energy eigenvalue* or *unperturbed energy eigenvalue*, and $\widehat{H}^{(0)}$ is called the *zero-order Hamiltonian*. The term $\widehat{H}'$ in the Hamiltonian operator is called the *perturbation*. To apply the method to the helium atom, we take $\widehat{H}^{(0)}$ from Chapter 18 to be the zero-order Hamiltonian and the electron–electron repulsion energy to be $\widehat{H}'$.

We construct a new Hamiltonian operator by multiplying the perturbation term by a fictitious parameter, λ:

$$\widehat{H}(\lambda) = \widehat{H}^{(0)} + \lambda\widehat{H}' \tag{19.3-3}$$

At first, this seems to make an insoluble problem even more complicated, but it will turn out to be useful when we express energies and wave function as power series in λ. The new Schrödinger equation for a particular energy eigenfunction Ψ_n is

$$\widehat{H}(\lambda)\Psi_n(q,\lambda) = E_n(\lambda)\Psi_n(q,\lambda) \tag{19.3-4}$$

where the wave function Ψ_n now depends on λ as well as on the coordinates of the system, which we abbreviate by q in our usual way. The correct wave function would be obtained by letting $\lambda = 1$.

The ground state of the helium atom is nondegenerate. That is, there is only one wave function corresponding to the ground-state energy. We now outline a perturbation scheme to handle the nondegenerate case. The energy eigenvalues and energy eigenfunctions are represented by power series in λ:

$$E_n = E_n^{(0)} + E_n^{(1)}\lambda + E_n^{(2)}\lambda^2 + \cdots \tag{19.3-5}$$

$$\Psi_n = \Psi_n^{(0)} + \Psi_n^{(1)}\lambda + \Psi_n^{(2)}\lambda^2 + \cdots \tag{19.3-6}$$

The idea of the perturbation method is to approximate these series by partial sums of two or three terms. Figure 19.2 shows schematically a typical energy eigenvalue as a function of λ and as represented by the first two partial sums of the series for values of λ between zero and unity. To first order, the energy eigenvalue is given by letting $\lambda = 1$ in the two-term partial sum:

$$E_n \approx E_n^{(0)} + E_n^{(1)} \tag{19.3-7}$$

Appendix G contains a derivation of the formula for the first-order correction to the energy, $E_n^{(1)}$. The result is

$$E_n^{(1)} = \int \Psi_n^{(0)*}\widehat{H}'\Psi_n^{(0)}dq \tag{19.3-8}$$

EXAMPLE 19.2

Apply first-order perturbation theory to the ground state of a system with the potential energy:

$$\mathscr{V}(x) = \begin{cases} \infty & \text{if } x < -a \text{ or } a < x \\ kx^2/2 & \text{if } -a < x < a \end{cases}$$

Solution

We take $\widehat{H}^{(0)}$ to be the particle-in-a-box Hamiltonian with $-a < x < a$, not $0 < x < a$.

$$\widehat{H}' = \frac{kx^2}{2}$$

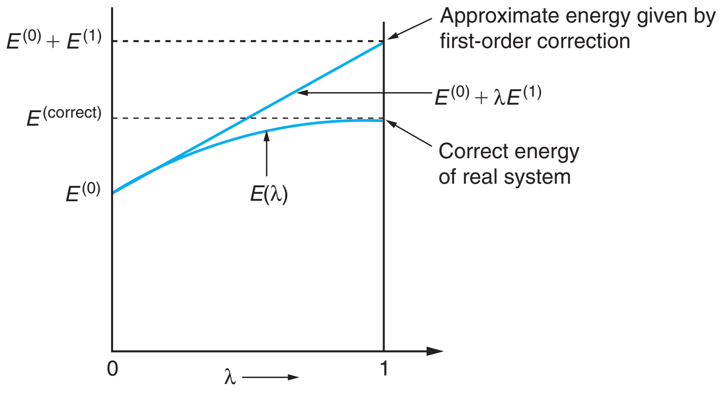

Figure 19.2 An Energy Eigenvalue as a Function of λ for a Hypothetical System.

$$\psi_1^{(0)} = \sqrt{\frac{2}{2a}}\sin\left(\frac{\pi(x+a)}{2a}\right); \quad E_1^{(0)} = \frac{h^2}{8m(2a^2)} = \frac{h^2}{32ma^2}$$

$$E_1^{(1)} = \frac{1}{a}\int_{-a}^{a}\frac{kx^2}{2}\sin^2\left(\frac{\pi(x+a)}{2a}\right)dx$$

From a trigonometric identity,

$$\sin\left(\frac{\pi x}{2a}+\frac{\pi}{2}\right) = \sin(\pi x/2a)\cos(\pi/2) + \cos(\pi x/2a)\sin(\pi/2) = 0 + \cos(\pi x/2a)$$

$$E_1^{(1)} = \frac{k}{2a}\int_{-a}^{a}x^2\cos^2(\pi x/2a)dx = \frac{k}{2a}\left(\frac{2a}{\pi}\right)^3\int_{-\pi/2}^{\pi/2}y^2\cos^2(y)dy, \quad \text{where } y = \frac{\pi x}{2a}$$

$$= \frac{8k}{\pi^3}a^2\int_{0}^{\pi/2}y^2\cos^2(y)dy$$

where we have used the fact that the integral from $-\pi/2$ to $\pi/2$ is twice as large as the integral from 0 to $\pi/2$, since the integrand is an even function of y, having the same value for $-y$ as for y. This integral can be looked up to give

$$E_1^{(1)} = \frac{8k}{\pi^3}a^2\left[\frac{y^3}{6} + \left(\frac{y^2}{4}-\frac{1}{8}\right)\sin(2y) + \frac{y\cos(2y)}{4}\right]_0^{\pi/2} = \frac{8k}{\pi^3}a^2\left(\frac{\pi^3}{48}+0-\frac{\pi}{8}\right)$$

$$= \frac{ka^2}{6} - \frac{ka^2}{\pi^2}$$

$$E = E_1^{(0)} + E_1^{(1)} = \frac{h^2}{32ma^2} + ka^2\left(\frac{1}{6}-\frac{1}{\pi^2}\right) = \frac{h^2}{32ma^2} + (0.06535)ka^2$$

Exercise 19.3

Evaluate $E_1^{(0)}$ and $E_1^{(1)}$ from the previous example in the case that m is the mass of an electron, 9.1094×10^{-31} kg, $a = 10.0$ Å $= 1.00$ nm, and $k = 0.0500\ \mathrm{J\,m^{-2}}$.

We now apply the perturbation method to the ground state of the helium atom. The zero-order Hamiltonian is a sum of two hydrogen-like Hamiltonians:

$$\widehat{H}^{(0)} = \widehat{H}_{\mathrm{HL}}(1) + \widehat{H}_{\mathrm{HL}}(2) \tag{19.3-9}$$

The perturbation term is

$$\widehat{H}' = \frac{e^2}{4\pi\varepsilon_0 r_{12}} \tag{19.3-10}$$

The zero-order ground-state energy $\mathrm{E}_{1s1s}^{(0)}$ is given by Eq. (18.3-13) and $\Psi_{1s1s}^{(0)}$ is given by Eq. (18.3-2). The first order correction to the energy is

$$E_{1s1s}^{(1)} = \int \psi_{100}(1)^{*}\psi_{100}(2)^{*}\left(\frac{e^{2}}{4\pi\varepsilon_{0}r_{12}}\right)\psi_{100}(1)\psi_{100}(2)d^{3}\mathbf{r}_{1}d^{3}\mathbf{r}_{2} \tag{19.3-11}$$

This integral is the same as the integral in Eq. (19.1-6), so that our perturbation method result to first order is

$$E_{1s1s}^{(0)} + E_{1s1s}^{(1)} = -108.8\,\mathrm{eV} + 34.0\,\mathrm{eV} = -74.8\,\mathrm{eV} \tag{19.3-12}$$

This is the same as the result of the variation method using the zero-order wave function.

The first-order correction to the wave function and the second-order correction to the energy eigenvalue are more complicated than the first-order correction to the energy eigenvalue. Appendix F contains the formulas for these quantities. No exact calculation of the second-order correction to the energy of the helium atom has been made, but a calculation made by a combination of the perturbation and variation methods gives an accurate upper bound:[10]

$$E_{1s1s}^{(2)} = -4.3\,\mathrm{eV} \tag{19.3-13}$$

so that the value of the energy through second order is −79.1 eV, within 0.1 eV of the experimental value, −79.0 eV. Since we are not using the variation method, the approximate energy can be lower than the correct energy. Approximate calculations through thirteenth order have been made, and have given values that agree with experiment nearly as well as the best results of the variation method.[11]

PROBLEMS

Section 19.3: The Perturbation Method and Its Application to the Ground State of the Helium Atom

19.18 **a.** Using first-order perturbation, find a formula for the energy of a particle in its ground state in a box of length a with an additional linear potential term:

$$\mathscr{V}(x) = \begin{cases} \infty & \text{if } x < 0 \text{ or } a < x \\ bx & \text{if } 0 < x < a \end{cases}$$

b. An electron in a one-dimensional box of length 10.00 Å is transported to a planet on which the acceleration due to gravity is $6.00 \times 10^{18}\,\mathrm{m\,s^{-2}}$. The box is placed in a vertical position. Find the energy of the electron in first order. Do you think that your answer is a reasonable approximation to the correct energy?

c. Repeat the calculation for the surface of the earth. Do you think that your answer is a reasonable approximation to the correct energy?

19.19 **a.** An electron is confined in a one-dimensional box of length 10.00 Å (1.000×10^{-9} m). The left end of the box corresponds to $x = 0$ and the right end of the box corresponds to $x = 1.00 \times 10^{-9}$ m. An electric field $\mathscr{E}$ is imposed on the electron so that its potential energy is given by

$$\mathscr{V} = -e\mathscr{E}x$$

Assume that $\mathscr{E} = 1.00 \times 10^{9}\,\mathrm{V\,m^{-1}}$ (1.00 volt potential difference between the ends of the box). Using first-order perturbation theory, calculate the ground-state energy of the electron in the box and compare it to the result that you get in the absence of

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[10] C. W. Scherr and R. E. Knight, *Rev. Mod. Phys.*, **35**, 436 (1963).

[11] C. W. Scherr and R. E. Knight, *loc. cit.* (note 10).

the electric field. How important do you think that this electric field is for this particle? Is the first-order perturbation method applicable in this case?

b. Repeat the calculation for $\mathscr{E}_x = 1.00 \times 10^7\ \mathrm{V\,m^{-1}}$. Is the first-order perturbation method applicable in this case?

19.20 Using first-order perturbation, calculate the energy of the ground state of an anharmonic oscillator with potential energy $\mathscr{V} = kx^2/2 + bx$, where k and b are constants. Compare your answer with that of Problem 19.5.

19.21 Using first-order perturbation, calculate the energy of the ground state of an anharmonic oscillator with potential energy function $\mathscr{V} = kz^2/2 + cz^4$, where $k = 576\ \mathrm{J\,m^{-2}}$, $c = 1.00 \times 10^{20}\ \mathrm{J\,m^{-4}}$, and $m = 8.363 \times 10^{-28}$ kg.

19.22 Using first-order perturbation, find a formula for the energy of a hydrogen atom in the $1s$ state that is exposed to an electric field in the z direction, denoted by $\mathscr{E}_z$.

19.23 Consider a system such that one of the zero-order wave functions happens to be an eigenfunction of the perturbation term in the Hamiltonian. Show that first-order perturbation theory gives an exact solution to the Schrödinger equation.

19.4 Excited States of the Helium Atom. Degenerate Perturbation Theory

Excited states are more difficult to treat than ground states. The variation method is usually not used because the variation theorem applies only to ground states. There is an *extended variation theorem*, which states that the calculated variation energy will be no lower than the correct energy of the first excited state if the variation trial function is orthogonal to the correct ground-state energy eigenfunction. It will be no lower than the energy of the second excited state if the variation trial function is orthogonal to both the ground state and the first excited state, and so on.[12] Unfortunately, the correct ground-state energy eigenfunction is not generally known, so that choosing a family of functions exactly orthogonal to it might be impossible. Some calculations have been made in which a family of functions is chosen that is orthogonal to an approximate ground-state variation function. This family of functions might be nearly orthogonal to the correct ground-state function and the minimum variation energy from this family might be a good approximation to the energy of the first excited state. In other cases, even if the correct ground-state wave function is not known, some known property, such as being spherically symmetric, might permit construction of a trial function that is orthogonal to it.

The perturbation method as described in the previous section does not apply if several wave functions correspond to the same zero-order energy (the degenerate case). For example, the zero-order orbital energies of the $2s$ and $2p$ hydrogen-like orbitals are all equal, so that all of the states of the $(1s)(2s)$ and $(1s)(2p)$ helium configurations have the same energy in zero order. A version of the perturbation method has been developed to handle this case. We will describe this method only briefly and present some results for some excited states of the helium atom.[13] There is additional information in Appendix G.

In the degenerate case there is no guarantee that the wave functions that we obtain with the zero-order Schrödinger equation are in one-to-one correspondence with the correct wave functions. If not, the smooth dependence on the parameter λ depicted in Figure 19.2 will not occur. The first task of the degenerate perturbation method is to find the zero-order wave functions that are in one-to-one correspondence with the exact wave functions. We call them the *correct zero-order wave functions*.

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[12] I. N. Levine, *op. cit.*, p. 212ff (note 2).

[13] I. N. Levine, *op. cit.*, p. 259ff (note 2).

The correct zero-order wave functions are expressed as linear combinations of the degenerate "initial" zero-order wave functions:

$$\Psi_{n,\mathrm{cor}}^{(0)} = \sum_{j=1}^{g} c_{nj}\Psi_{j,\mathrm{init}}^{(0)} \tag{19.4-1}$$

where g is the degeneracy (the number of states in the zero-order energy level). The subscript "cor" denotes the correct zero-order functions and the subscript "init" denotes the initial zero-order functions. In order to find the c_{nj} coefficients, one must solve a set of homogeneous linear simultaneous equations that are described in Appendix G. One solution of these equations is that all of the c coefficients vanish. This is called the trivial solution and is not useful to us. A condition that must be satisfied for a nontrivial solution of these equations to exist is called a *secular equation*.[14] Solution of the secular equation gives the first-order corrections to the energies and allows solution of the equations for the c_{nj} coefficients for each correct zero-order function. Additional information can be found in Appendix G. The wave functions of Eq. (18.4-2) are the correct zero-order functions for the $(1s)(2s)$ configuration of the helium atom, and three sets of similar functions are the correct zero-order functions for the $(1s)(2p)$ configuration.

Figure 19.3 shows the results of calculations to first order and to third order for the energies of the four levels that result from the $(1s)(2s)$ and the $(1s)(2p)$

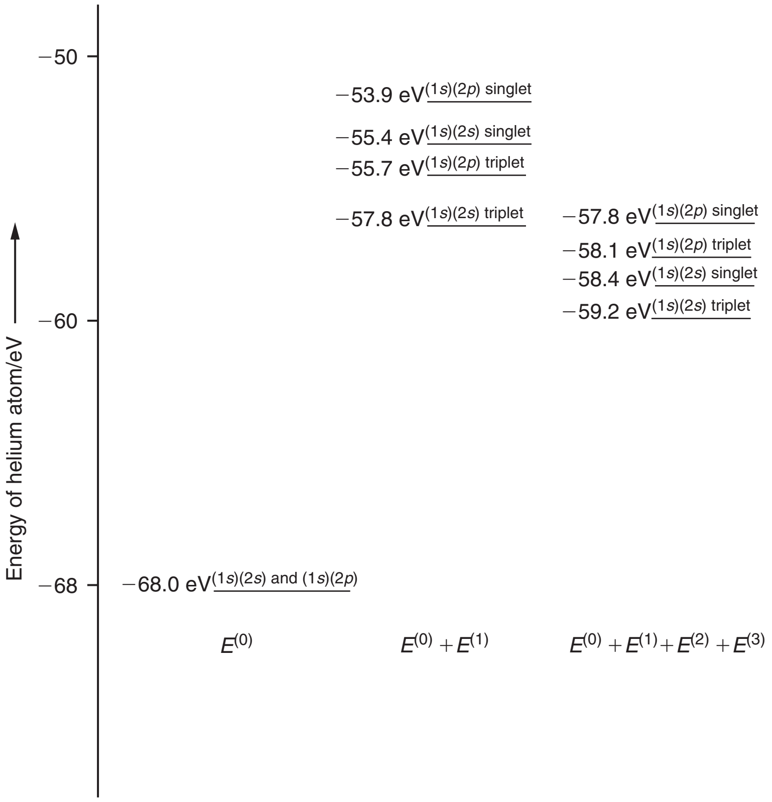

Figure 19.3 Approximate Energies of Helium Excited States.

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[14] Levine, *op. cit.*, p. 262 (note 2).

configurations.[15] We observe the following pattern: (1) Each triplet state has a lower energy than the corresponding singlet state. (2) The orbital energies of the 2*s* subshell are lower than the orbital energies of the $2p$ subshell. The same pattern is generally followed by higher shells and by atoms with more than two electrons. The orbital energies of a *d* subshell lie higher than those of the orbital energies of the *p* subshell in the same shell, the orbital energies of an *f* subshell lie higher than those of the orbital energies of the *d* subshell in the same shell, and so on.

PROBLEMS

Section 19.4: Excited States of the Helium Atom. Degenerate Perturbation Theory

19.24 Write all of the term symbols for the $(1s)(2p)$ excited configuration of He.

19.25 Write all of the term symbols for the $(1s)(3d)$ excited configuration of He.

19.26 Write all of the term symbols for the $(2p)(3p)$ excited configuration of He.

19.5 The Density Functional Method

This method attempts to calculate the molecular energy and other properties from the electron probability density, which was introduced in Section 18.3 for a two-electron system. For a system with N electrons in a state corresponding to the wave function $\Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N)$, the electron probability density is obtained by integrating over the spin coordinates of all particles and over the space coordinates of all of the electrons except one:

$$\rho(\mathbf{r}_1) = N \int \Psi(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N) d\mathbf{r}_2 d\mathbf{r}_3 \ldots d\mathbf{r}_N d^s(1) d^s(2) \ldots d^s(N) \qquad (19.5\text{-}1)$$

Walter Kohn, 1923–, an Austrian-American physicist, shared the 1998 Nobel Prize in chemistry with John A. Pople for his work on density functional theory.

Since the electron probability density depends on only three space coordinates (represented by $\mathbf{r}_1$), it contains much less information than the wave function, which depends on the $3N$ space coordinates of N electrons as well as their spins. However, Hohenberg and Kohn proved a remarkable theorem: For the ground electronic state of a molecule in the Born–Oppenheimer approximation, there is only one wave function and only one energy that correspond to a given electron probability density.[16] This is surprising, since electron correlation involves effects of the mutual repulsion of pairs of electrons. It would seem that a function of the six coordinates of two electrons would be required to describe the energy of the molecule. However, their theorem implies that the effects of electron correlation are uniquely expressed in a function of only three coordinates.

Since the electronic wave function is uniquely determined by the electron probability density and since the energy in the Born–Oppenheimer approximation is determined by the electronic wave function, the ground-state energy is a *functional* of the ground-state electron probability density. A functional is a rule that associates a numerical value of a dependent variable with an independent function in much the same way that an ordinary function associates a numerical value of a dependent variable with a numerical value

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[15] Levine, *op. cit.*, p. 270 (note 2).

[16] P. Hohenberg and W. Kohn, *Phys. Rev.*, **136**, B864 (1964).

of an independent variable. For example, a definite integral is a functional that depends on the integrand function. If we have the definite integral from $x = a$ to $x = b$,

$$I = \int f(x)dx \tag{19.5-2}$$

The definite integral I has a value that depends on the choice of the integrand function f and is a functional of f. The definite integral with different limits would be a different functional, since it would give a different value for the same function. We write the functional relationship symbolically as

$$I = I[f] \tag{19.5-3}$$

The symbol $I[\cdots]$ stands for the functional, which in this case means taking the definite integral from $x = a$ to $x = b$ of the independent function.

According to the Hohenberg–Kohn theorem, the ground-state energy E_{gs} is a functional of the ground-state electron probability density, which we denote by ρ_{gs}:

$$E_{\text{gs}} = E\left[\rho_{\text{gs}}\right] \tag{19.5-4}$$

Two things are needed to provide a useful method: We need a way to determine the electron probability density without first finding the entire wave function, and we need a way to obtain the functional $E[\rho_{\text{gs}}]$. Hohenberg and Kohn proved a variation theorem that provides some information. If the correct functional is available, using it on an incorrect electron probability distribution leads to an energy that cannot be lower than the correct ground-state energy. However, this theorem does not lead to a calculational method as did the quantum-mechanical variation theorem, because it does not specify the functional. Practical approximations must be found for the functional in Eq. (19.5-4). Much work has been done in this area, but discussion of it is beyond the scope of this book.[17] However, some software packages for molecular quantum mechanics can perform density functional calculations, even if the user does not have a detailed understanding of the method. It has been found that the approximation schemes that have been developed work at least as well as Hartree–Fock–Roothaan methods with configuration interaction for most molecular properties, such as bond lengths and energies of molecular ground states.

19.6 Atoms with More Than Two Electrons

The treatment of other atoms is similar to that of helium. In zero order we neglect electron–electron repulsions, and in higher-order calculations these repulsions are treated with the same approximation methods as used with the helium atom. From this point on in the chapter we will discuss only the results of such calculations.

The Lithium Atom

An application of the variation method to the lithium atom ground state uses an orbital wave function containing hydrogen-like orbitals with variable orbital exponents (effective nuclear charges) similar to that used with helium, except that different effective

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[17] I. N. Levine, *op. cit.*, pp. 576–592, and references cited therein.

nuclear charges are used in the 1s and 2s orbitals. The minimum in the variation energy, -201.2 eV, corresponds to effective nuclear charges of 2.686 protons for the 1s orbitals and 1.776 protons for the 2s orbital.[18] The correct value of the ground-state energy is -203.5 eV, so this variation function gives an error of 2.3 eV or 1.1%.

The effective nuclear charge seen by the 1s electrons is nearly the same as would be seen by the 1s electrons in Li^+, because the minimum in the variation energy of a helium-like atom in Eq. (19.1-15) occurs at $Z' = 2.6875$ if $Z = 3$. The 1s electron in a lithium atom apparently sees almost no shielding due to the 2s electron. This is reasonable, since a 2s electron is on the average farther from the nucleus than a 1s electron. The 2s electron sees considerable shielding from the 1s electrons, corresponding to an effective nuclear charge of 1.776 protons, considerably less than the actual nuclear charge of 3 protons. This difference in effective nuclear charge makes the average distance from the nucleus for the 1s and 2s electrons even more different than if they corresponded to the same effective nuclear charge.

EXAMPLE 19.3

Find the value of $\langle r\rangle$ for a hydrogen-like 1s orbital with $Z = 2.686$.

Solution

$$\langle r\rangle_{1s} = 4\pi\left(\frac{Z}{a}\right)^3\left(\frac{1}{\pi}\right)\int_0^\infty r^3 e^{-2Zr/a}dr = 4\left(\frac{Z}{a}\right)^3\left(\frac{a}{2Z}\right)^4\int_0^\infty x^3e^{-x}\,dx = 4\left(\frac{Z}{a}\right)^3\left(\frac{a}{2Z}\right)^4(6)$$

$$= \frac{3a}{2Z} = \frac{3a}{5.732} = 0.5585a = 2.95\times 10^{-11}\ \mathrm{m} = 29.5\ \mathrm{pm}$$

For comparison, the value of $\langle r\rangle$ for a 2s orbital with $Z = 1.776$ is 179 pm, whereas $\langle r\rangle$ for a 2s orbital with $Z = 2.686$ is 118 pm. (See Problem 19.27.)

Many modern calculations employ the self-consistent field (SCF) method. In SCF calculations on any multielectron atom the 2p orbitals are found to be higher in energy than the 2s orbital. A 2p electron is not on the average farther from the nucleus than one in a 2s orbital with the same nuclear charge (see Problem 17.13). Figure 17.11b shows that the radial probability distribution for the 2s orbital has a "hump" close to the nucleus that the 2p orbital does not have. An electron in a 2s orbital therefore has a greater probability of being found close to the nucleus, where the shielding is least effective. The 2p electron is more effectively screened from the nuclear charge than is a 2s electron, so its orbital energy is higher. We say that the 2s orbital is more "penetrating" toward the nucleus than are the 2p orbitals, and the same is true for the s and p subshells in other shells.

The *first ionization potential* is defined as the energy required to remove one electron from an isolated neutral atom. If the orbitals for the other electrons are not significantly changed by the removal of one electron, the ionization potential is nearly equal to the magnitude of the energy of the orbital occupied by the outermost electrons.[19] The ionization potential can therefore be used to obtain an estimate of the effective nuclear charge seen by the outer electrons.

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[18] I. N. Levine, *op. cit.*, p. 298ff (note 2).

[19] I. N. Levine, *op. cit.*, p. 503 (note 2).

EXAMPLE 19.4

Estimate the effective number of protons in the nucleus for the 2*s* electron in a lithium atom from the ionization potential, 124 kcal mol^{-1}. Compare this value with the value of 1.776 obtained with the variation method.

Solution

The ionization potential in electron volts is

$$(\mathrm{IP}) = \frac{(124000\ \mathrm{cal\ mol^{-1}})(4.184\ \mathrm{J\ cal^{-1}})}{96485\ \mathrm{J\ mol^{-1}\ eV^{-1}}} = 5.38\ \mathrm{eV}$$

The energy of the 2*s* hydrogen-like orbital is given by Eq. (17.3-19) as

$$E_2 = -\frac{(13.6\ \mathrm{eV})Z'^2}{2^2}$$

where Z' is the effective number of protons. Setting this energy equal to 5.38 eV gives $Z' = 1.26$, which compares with the value of 1.776 obtained by the variation calculation.

When the perturbation method is applied to the lithium atom, the first-order correction to the ground-state energy is equal to 83.5 eV, resulting in an energy through first order equal to −192.0 eV.[20] This value is considerably less accurate than the value obtained by the variation calculation. The SCF method is the most successful of the three common approximation methods. A careful Hartree–Fock–Roothaan calculation gave a ground-state energy of −202.3 eV, differing from the correct value by 1.2 eV.[21] Assuming that the value of −202.3 eV is a good approximation to the optimum Hartree–Fock energy, 1.2 eV is presumably a good approximation to the correlation error.

One way to include dynamical electron correlation in an orbital wave function is to construct a wave function that is a linear combination of several Slater determinants corresponding to different electron configurations, a method that is known as *configuration interaction* (abbreviated by CI). For example, the ground state of the lithium atom could be represented by

$$\Psi = c_1\Psi_{1s1s2s} + c_2\Psi_{1s2s2s} + c_3\Psi_{1s1s3s} + \ldots \tag{19.6-1}$$

where c_1, c_2, and c_3, and so on, are variable parameters and the Ψs represent wave functions corresponding to the configurations specified in the subscripts. Although it is not obvious from inspection of Eq. (19.6-1) that this wave function includes dynamical correlation, it does depend on electron–electron distances, a fact that we discuss briefly in the next chapter. The configuration interaction process converges slowly, so that many configurations must be used to get good accuracy. Atomic and molecular calculations have been carried out with as many as a million configurations.

Atoms with More Than Three Electrons

Figure 19.4 shows orbital energies in neutral atoms as a function of atomic number, obtained by an approximation scheme called the Thomas–Fermi method.[22] We will not

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[20] I. N. Levine, *op. cit.*, p. 297ff (note 2).

[21] F. L. Pilar, *Elementary Quantum Chemistry*, McGraw-Hill, New York, 1968, p. 336.

[22] H. A. Bethe and R. W. Jackiw, *Intermediate Quantum Chemistry*, 3rd ed., Benjamin-Cummings, 1985, Chapter 5.

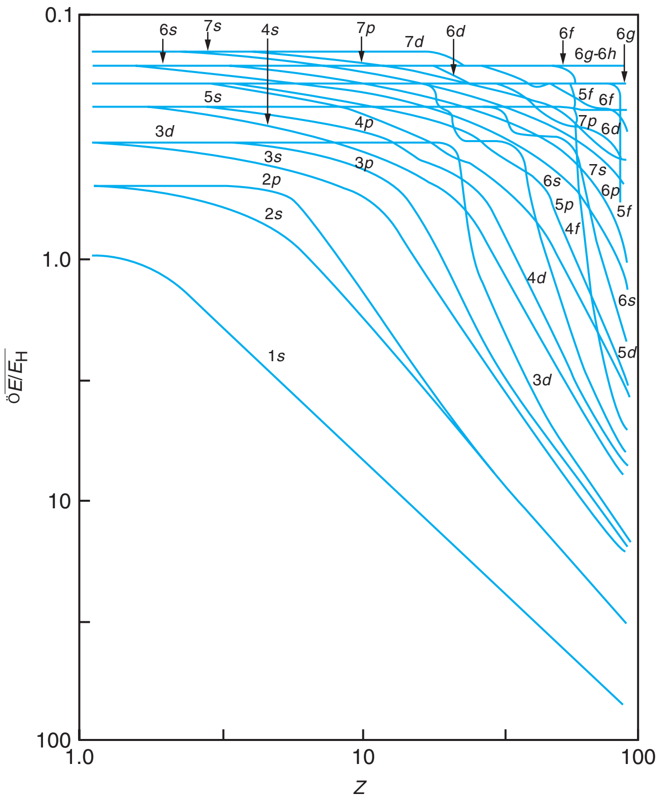

Figure 19.4 Approximate Orbital Energies in Neutral Atoms. Note that the axes in this diagram are logarithmic. From R. Latter, *Phys. Rev.*, **99**, 510 (1955).

discuss the method, but it gives orbital energies that generally agree with those from the Hartree–Fock method. The orbitals in different subshells of the same shell have different energies, with higher values of l generally corresponding to higher energies. These energy differences can be ascribed to shielding. Just as an electron in an s orbital is less effectively shielded than an electron in a p orbital, an electron in a p orbital is less effectively shielded than an electron in a d orbital, and so on. The energies depend strongly on the nuclear charge, with some pairs of curves crossing and recrossing as a function of the nuclear charge.

The Aufbau Principle and Electron Configurations

According to the *Aufbau principle* the ground configuration of an atom is obtained by choosing the lowest-energy set of orbitals compatible with the Pauli exclusion principle. For the first 18 elements, the subshell energies lie in the increasing order $1s, 2s, 2p, 3s, 3p$, so that for example the ground configuration of phosphorus is $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^3$. For atomic numbers 19 through 21, the $3d$ orbital energy is higher than that of the $4s$. Elements 19 (potassium) and 20 (calcium) in their ground states therefore have the $4s$ orbitals occupied in preference to the $3d$ orbitals and element 21 (scandium) has a single $3d$ electron. Beyond atomic number 21, the figure shows the $4s$ energy above the $3d$ energy so that the elements beginning with titanium (element 22) should have no $4s$ electrons. However, it is found experimentally that the elements from titanium through zinc (element 30) have two 4*s* electrons in the ground configuration except for chromium (element 24) and copper (element 29), which have a single 4*s* electron. A similar behavior occurs with the 4*d* and 5*s* orbital energies. Assuming the energies in the figure to be essentially correct, it appears that other factors besides orbital energy are important in determining the ground-level configuration.[23] Two possible factors are the omission of the correlation energy and the fact that the total electronic energy is not equal to the sum of the orbital energies because the sum of the orbital energies includes the potential energy for each pair of electrons twice.

The ground-level configuration for most elements can be obtained from the scheme of Figure 19.5, which shows the "*diagonal mnemonic device*" or the "*diagonal rule*." To determine the order of orbitals for a given element, one follows each diagonal path from upper right to lower left and then moving from the lower end of one diagonal to the upper end of the next lower diagonal. The number of spin orbitals in each subshell is listed at the top of the figure, so that one can tell when enough subshells have been chosen for the electrons of a given atom. The diagonal mnemonic device is equivalent to the "$n + 1$ *rule*," which states that subshells of a given value of $n + 1$ are occupied before those of the next higher value of $n + 1$, and that within a given value of $n + 1$, the subshells are occupied in the order of increasing n. This rule predicts that the 4*s* subshell is always occupied before the 3*d* subshell is occupied.

EXAMPLE 19.5

Give the ground-level configuration of (a) Al, (b) Mn.

Solution

a. Al (13 electrons): $(1s)^2(2s)^2(2p)^6(3s)^2(3p)$

b. Mn (25 electrons): $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(3d)^5(4s)^2$

Configurations are often abbreviated by including an inert gas configuration as part of the configuration. The Mn ground configuration is abbreviated as $[\mathrm{Ar}](3d)^5(4s)^2$ and the Cu ground configuration is abbreviated as $[\mathrm{Ar}](3d)^{10}(4s)$ where [Ar] stands for the ground configuration of argon.

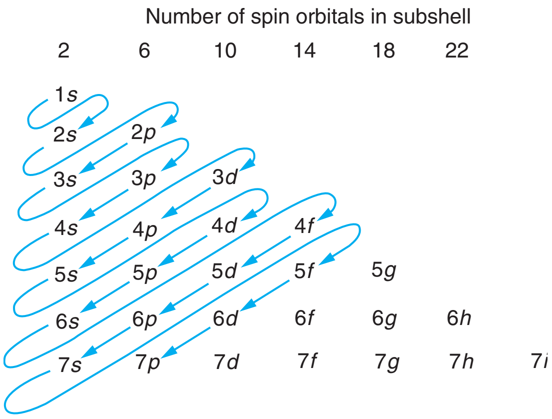

Figure 19.5 The Diagonal Mnemonic Device for Applying the Aufbau Principle to Neutral Atoms. Exceptions to the rules of this device are given in Table 19.1.

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[23] M. P. Melrose and E. R. Scerri, *J. Chem. Educ.*, **73**, 498 (1996).

Exercise 19.4

Give the ground configuration of the elements (a) S, (b) Ta, (c) Hg.

Table 19.1 lists the known exceptions to the diagonal rule through element 103. Some of the prominent exceptions are Cr, Cu, Mo, Ag, and Au. In each of these cases, there is a *d* subshell having 5 or 10 electrons instead of having 4 or 9 electrons. These exceptions to the rule apparently correspond to the idea that a half-filled or filled *p* or *d* subshell is more stable than otherwise expected. If a half-filled subshell has a single electron in each space orbital the electrons can have a fairly low energy of repulsion, because the orbital regions of the *p* and *d* orbitals are well separated from each other in space. However, other factors might be more important.[24] Nickel has sometimes been assigned a configuration with a single 4*s* electron, and most of the elements in the second transition series from element 39 (Y) to element 48 (Cd) have sometimes been assigned configurations with a single 5*s* electron.

There has been some discussion about whether lanthanum and actinium are exceptions to the diagonal mnemonic rule. Lanthanum has sometimes been assigned a 5*d* electron in the ground level, and actinium has been assigned a 6*d* electron. For this reason, these elements are sometimes placed with the transition metals in the periodic table. However, from an analysis of spectroscopic observations, it appears that lanthanum has a 4*f* electron in its ground state and that actinium has a 5*f* electron, as

Table 19.1 Exceptions to the Diagonal Mnemonic Rule

Atomic No.	Symbol	Ground Configuration
24	Cr	$[\mathrm{Ar}](3d)^5(4s)^1$
29	Cu	$[\mathrm{Ar}](3d)^{10}(4s)^1$
41	Nb	$[\mathrm{Kr}](4d)^4(5s)^1$
42	Mo	$[\mathrm{Kr}](4d)^5(5s)^1$
44	Ru	$[\mathrm{Kr}](4d)^7(5s)^1$
45	Rh	$[\mathrm{Kr}](4d)^8(5s)^1$
46	Pd	$[\mathrm{Kr}](4d)^{10}$
47	Ag	$[\mathrm{Kr}](4d)^{10}(5s)^1$
64	Gd	$[\mathrm{Xe}](4f)^7(5d)^1(6s)^2$
65	Tb	$[\mathrm{Xe}](4f)^8(5d)^1(6s)^2$
66	Dy	$[\mathrm{Xe}](4f)^9(5d)^1(6s)^2$
67	Ho	$[\mathrm{Xe}](4f)^{10}(5d)^1(6s)^2$
68	Er	$[\mathrm{Xe}](4f)^{11}(5d)^1(6s)^2$
78	Pt	$[\mathrm{Xe}](4f)^{14}(5d)^9(6s)^1$
79	Au	$[\mathrm{Xe}](4f)^{14}(5d)^{10}(6s)^1$
90	Th	$[\mathrm{Rn}](6d)^2(7s)^1$
91	Pa	$[\mathrm{Rn}](5f)^2(6d)^1(7s)^2$
92	U	$[\mathrm{Rn}](5f)^3(6d)^1(7s)^2$
93	Np	$[\mathrm{Rn}](5f)^4(6d)^1(7s)^2$
94	Cm	$[\mathrm{Rn}](5f)^7(6d)^1(7s)^2$
103	Lr	$[\mathrm{Rn}](5f)^{14}(6d)^1(7s)^2$

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[24] M. P. Melrose and E. R. Scerri, *op. cit.* (note 23).

predicted by the diagonal rule.[25] However, assigning a single configuration to an atom is only an approximation. The correct wave function more nearly resembles a linear combination of various configurations as in Eq. (19.6-1), and in assigning a single configuration we are hoping only to identify the most prominent configuration.

The diagonal mnemonic rule does not necessarily apply to ions, because the shielding is different for ions than for neutral atoms. For example, the iron atom has six 3*d* electrons and two 4*s* electrons, in conformity with the diagonal rule. The Ni^{2+} ion, with the same number of electrons but with two additional protons in the nucleus, has eight 3*d* electrons and no 4*s* electrons. The correct electron configuration for positive ions can usually be obtained by finding the configuration of the neutral atom and then first removing electrons from the outer shell, which is not necessarily the subshell to which the last electrons were assigned by use of the diagonal mnemonic rule.

Hund's Rules

For those elements with partially filled subshells, the values of the quantum numbers L, S, and J of the ground level can be predicted by using three rules due to Hund, which generally agree with experiment and with SCF calculations. *Hund's first rule* is: *For a given configuration, the level with the largest value of* S *has the lowest energy. Hund's second rule* is: *For a given value of* S, *the level with the largest value of* L *has the lowest energy. Hund's third rule* is: *For subshells that are more than half filled, higher values of* J *correspond to lower energies, and for subshells that are less than half filled, lower values of* J *correspond to lower energies.* Hund's second rule is applied only after the first rule has been applied, and the third rule is applied only after the first and second rules have been applied. The second rule can be regarded as a tiebreaker for the first rule, and the third rule can be regarded as a tiebreaker for the second rule.[26] Hund's first rule has been explained by the idea that in the triplet spin state the symmetric spin factor combines with an antisymmetric space factor, corresponding to a lower probability that the electrons will be found close together. This interpretation has been challenged, since calculations have indicated that the electron's proximity to the nucleus or nuclei is the more important property. It is best to regard Hund's rules as empirical rules based on observations. They are quite reliable for ground levels, but less reliable for other levels.[27]

In order to find the possible values of the quantum numbers S, L, and J we determine the possible values of M_S, M_L, and M_J as in Chapter 18. These quantum numbers are algebraic sums:

$$\boxed{M_L = \sum_{i=1}^{Z} m_i} \qquad (19.6\text{-}2)$$

$$\boxed{M_S = \sum_{i=1}^{Z} m_{si}} \qquad (19.6\text{-}3)$$

$$M_J = M_S + M_L \qquad (19.6\text{-}4)$$

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[25] W. B. Jensen, *J. Chem. Educ.*, **59**, 635 (1982).

[26] T. S. Carlton, *J. Chem. Educ.*, **83**, 477 (2006).

[27] I. N. Levine, *op. cit.*, p. 328ff (note 2).

The addition is simplified by the fact that contributions to both M_L and M_S from filled subshells vanish. The possible values of L and S and the Russell–Saunders term symbols can be found as in Chapter 18 from the fact that M_L ranges from $-L$ to $+L$, that M_S ranges from $-S$ to $+S$ and that J ranges from $S + L$ to $|S - L|$. However, the ground-level term can be determined from the ground configuration by using Hund's rules without identifying all of the terms.

EXAMPLE 19.6

Using Hund's rules, find the ground-level term symbol for the nitrogen atom.

Solution

The ground-level configuration is $(1s)^2(2s)^2(2p)^3$. The filled $1s$ and $2s$ subshells make no net contribution to L or S. The three electrons in the $2p$ subshell can have their spins parallel if they occupy different space orbitals, so that the largest value of M_S is $+3/2$ and the largest value of S is $3/2$. The ground level corresponds to $S = 3/2$.

To investigate values of L, we use the complex orbitals that are eigenfunctions of $\widehat{L}_z$. We have assigned one electron to each of the ψ_{2p1}, ψ_{2p0}, and $\psi_{2p,-1}$ space orbitals. The only possibility is $M_L = 1 + 0 - 1 = 0$. The only value of L compatible with the maximum value of S is zero. The only possible value of J is equal to S, so the ground-level term symbol is ${}^4S_{3/2}$ ("quartet S three-halves").

Exercise 19.5

Find the ground-level term symbols for (a) Be, (b) B, (c) C, (d) O, and (e) F.

One possible explanation of Hund's first rule is that the higher values of S correspond to more electrons occupying different space orbitals with parallel spins. Occupying different space orbitals lowers the probability that the electrons will be found close together, thus lowering the potential energy. Statistical correlation can also have an effect. For two electrons, singlet wave functions have symmetric space factors and antisymmetric spin factors. There is no statistical correlation. In the triplet state wave functions the spin factor is symmetric. The space factor is antisymmetric, corresponding to statistical correlation. The electrons have only a small probability of being close together, giving the triplet state a lower electron repulsion energy than the singlet state. However, it is found that the antisymmetric space factor corresponds to lower probability that the electrons will be far apart so that this analysis is oversimplified. There is also a difference in the probability that the electrons will be found close to the nucleus, and this may be an important factor.[28] It is best to regard Hund's rules as empirical rules without theoretical justification.

The Periodic Table of the Elements

Dmitri Mendeleev, 1834–1907, was a Russian chemist who correlated valence with atomic mass. Julius Lothar Meyer, 1830–1895, was a German chemist who correlated atomic volume with atomic mass.

The periodic table was invented independently by Mendeleev and Meyer. Both noticed that if the elements were listed in the order of increasing atomic mass, there was a repetition (periodicity) of chemical and physical properties. For example, lithium, sodium, potassium, rubidium, and cesium all form oxides with the formula M_2O and chlorides

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[28] I. N. Levine, *op. cit.*, p. 328ff (note 2).

with the formula MCl, where M stands for the chemical symbol of the metal. Beryllium, magnesium, calcium, strontium, and barium all form oxides with the formula MO and chlorides with the formula MCl_2. When Mendeleev listed the elements in rows of the appropriate length, lithium, sodium, potassium, rubidium, and cesium all occurred in the first column, beryllium, magnesium, calcium, strontium, and barium occurred in the second column, and so on.

Some elements were unknown at the time of Mendeleev. These elements included all of the inert gases, most of the inner transition elements, and others scattered about the table, such as scandium, gallium, and germanium. Mendeleev had sufficient confidence in the periodicity principle that he left blank spaces in his table for undiscovered elements. These blanks were later filled in with elements having much the same properties as those predicted by Mendeleev.

The modern periodic chart lists the elements in order of atomic number (number of protons in the nucleus), rather than atomic mass. Inside the front cover of this book is such a periodic table. You can see four pairs of stable elements in which the order of atomic number is different from the order of atomic mass (Ar and K, Co and Ni, Te and I, and Th and Pa). Mendeleev was probably unaware of these cases, because argon and protactinium had not been discovered, because he placed cobalt and nickel together in a triple column, and because he did not have accurate atomic masses for tellurium and iodine.

There are several ways of numbering the columns. One scheme is to number the columns IA through VIIIA, and IB through VIIIB as indicated. This system has been commonly used in the United States. Three columns under Fe, Co, and Ni are grouped together as column VIIIB. This numbering corresponds closely to the numbering scheme used by Mendeleev, although the A and B columns were grouped together in his table, which had only eight columns. There is also another numbering scheme in which the A and B designations of columns III through VIII are interchanged. This system has been commonly used in Europe, and is recommended by the International Union of Pure and Applied Chemistry. A new scheme has been devised to overcome the disagreement over the A and B designations. It simply numbers the columns from 1 to 18, and will probably become the standard scheme.

The elements in the columns labeled A are called *representative elements*, and those in the columns labeled B are called *transition elements* or *transition metals*. The column IIB has been assigned to one or the other of these categories, and has sometimes been called a separate category. The two sets of 14 elements at the bottom of the chart are called *inner transition elements* or *inner transition metals*. Figure 19.6 shows a periodic table in which the inner transition elements are listed in the body of the table with all elements through element 109 listed in order of ascending atomic number. Various alternative forms of the periodic table have been proposed, including a version in which columns IA and IIA are placed at the right of the table and other columns are listed as in Figure 19.6.[29]

Uranium (U, element 92) is the heaviest element occurring in the earth's crust in measurable amounts. The elements past U have been synthesized in nuclear reactors. The elements after element 103 (lawrencium, Lr) were given temporary names: Element 104 was unnilquadrium, element 105 was unnilpentium, and so on, based on the Latin version of the atomic numbers. Some of these names have been replaced. The names

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[29] R. L. Rich, *J. Chem. Educ.*, **82**, 1761 (2005).

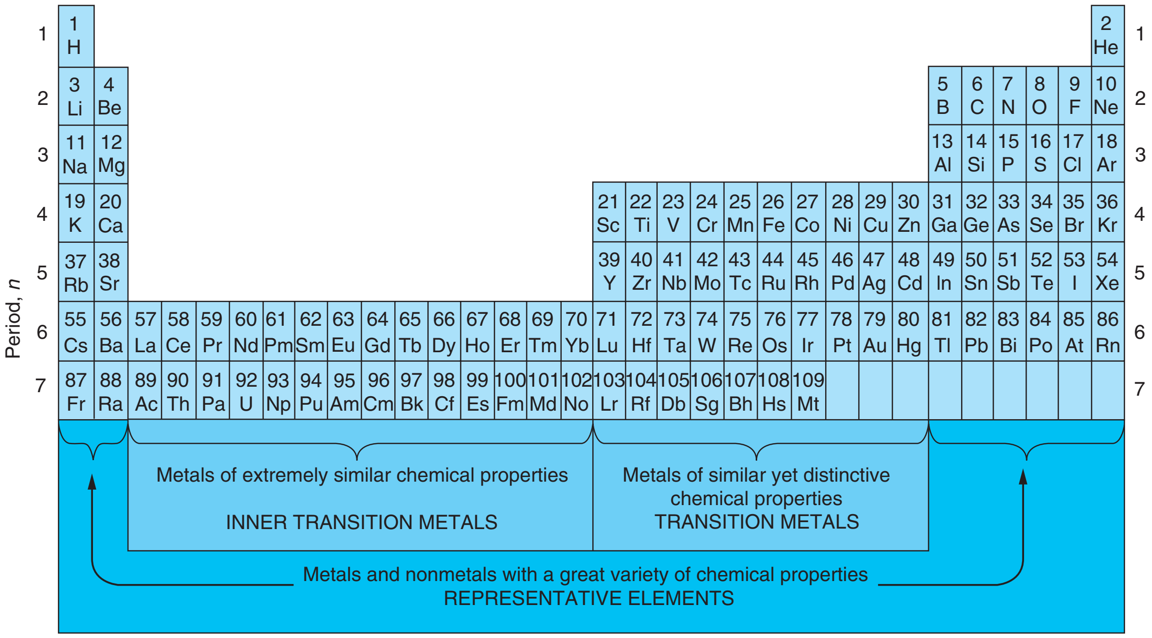

Figure 19.6 A Periodic Table of the Elements with All Elements in the Order of Increasing Atomic Number.

of elements 104–109 that have been accepted by the International Union of Pure and Applied Chemistry are

Atomic Number	Symbol	Name
104	Rf	Rutherfordium
105	Db	Dubnium
106	Sg	Seaborgium
107	Bh	Bohrium
108	Hs	Hassium
109	Mt	Meitnerium

A number of elements beyond element 109 are predicted to lie in an "island of nuclear stability" around elements 112–118. Two atoms of element 112 were recently produced. It had been predicted that element 112 might not have metallic properties and would not belong in column 12 (IIB). However, the researchers found that its chemical properties are similar to those of mercury, since the atoms seemed to form metallic bonds with a gold surface.[30] Small quantities of elements 113 (Uut) and 115 (Uup) have been produced in nuclear reactions between ^{247}Am and ^{48}Ca, apparently forming ^{288}Uup and three neutrons. The ^{288}Uup then decayed to form ^{284}Uut and an alpha particle.[31]

Researchers at the Lawrence Berkeley laboratory claimed to have produced several atoms of element 118. However, the claims were withdrawn after charges were made

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[30] R. Eichler, *et al.*, *Nature*, **447**, 72 (2007).

[31] Yu. Ts. Oganessian, *et al., phys. Rev. C.*, **72**, 34611 (2005).

that the data were faked.[32] Another claim for element 116 has been made.[33] More recently, a plausible claim for production of element 118 has been made. Three atoms of element 118 were produced by bombarding californium 249 with calcium 48. The three nuclei survived for 0.9 ms on the average.[34]

The correlation between position in the periodic table and chemical properties was explained by Niels Bohr, who also introduced the form of the chart with 18 columns. It has also been claimed that C. R. Bury should be given credit as the co-discoverer of this correlation.[35] The similarity of chemical properties of the elements in a given column corresponds to the similarity of their electron configurations in the outermost shell, which is called the *valence shell*. For example, the alkali metals (lithium, sodium, potassium, etc.) easily lose one electron because these elements have only one electron in the valence shell. The halogens (fluorine, chlorine, bromine, iodine, and astatine) have seven electrons in the valence shell, and tend to gain one electron. The eight columns of representative elements occur as two columns on the left and six columns on the right, corresponding to the two spin orbitals of an s subshell and the six spin orbitals of a p subshell. The transition elements occur in ten columns, corresponding to the ten spin orbitals of a d subshell, and the inner transitions elements occur in 14 columns, corresponding to the 14 spin orbitals of an f subshell.

Various properties correlate with position in the periodic table. Figure 19.7 shows the first ionization potential of the elements as a function of atomic number. The ionization potential generally increases from left to right across a row of the periodic table, and decreases from top to bottom in a column. The increase from left to right is attributed to the corresponding increase in the effective nuclear charge. The general decrease from top to bottom is attributed to the fact that as one moves down the column the valence shell is farther from the nucleus, lessening its attraction for the electrons in the valence shell. The corresponding increase in the nuclear charge is compensated for by increased shielding by the inner electrons.

Several elements, including beryllium, nitrogen, magnesium, phosphorus, zinc, and mercury, have higher ionization potentials than both of their immediate neighbors in a

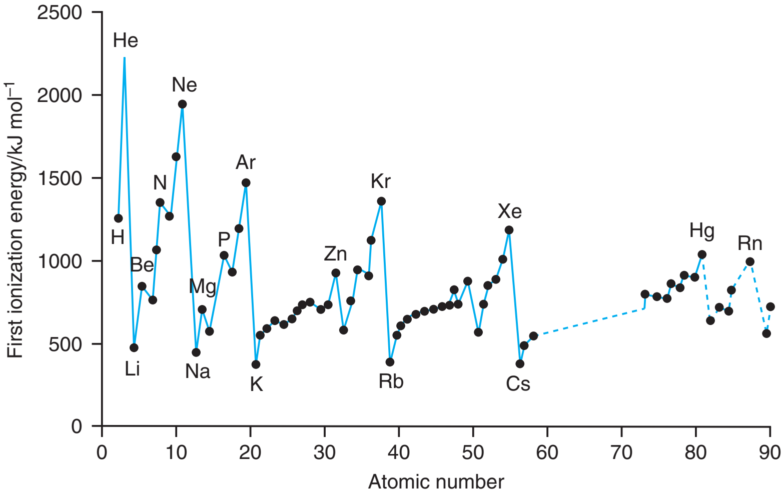

Figure 19.7 First Ionization Potentials of the Elements.

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[32] V. Ninov, *et al.*, *Phys. Rev. Letters*, **83**, 1104 (1999), errata in *Phys. Rev. Letters*, **89**, 39901 (2002).

[33] Yu. Ts. Oganessian, *et al.*, *Phys. Rev. C.*, **63**, 11301 (2002).

[34] Yu. Ts. Oganessian, *et al.*, *Phys. Rev. C.*, **74**, 44602 (2006).

[35] C. Truesdell, *Archives for the History of Exact Sciences*, **41**, 185 (1990).

row of the periodic table. All of these elements have ground-level configurations with only filled subshells (beryllium, magnesium, zinc, and mercury) or with a half-filled valence subshell (nitrogen and phosphorus). As with the ground configurations, this corresponds to the idea that a filled subshell or a half-filled subshell is relatively stable.

The electron affinity is defined as the energy given off in forming a negative ion from a gaseous atom and a free electron. It is also equal to the energy required to remove an electron from a gaseous, singly charged negative ion. It is positive if a gaseous atom spontaneously attracts an electron, and most elements have positive values. A graph of the electron affinity has the same general trend as the graph of the ionization potential, except that the graph is shifted one column to the left, corresponding to the fact that a singly charged negative ion has one more electron than the neutral atom. The elements of column VIIA (the halogens) have the greatest electron affinity, whereas the inert gases have the largest ionization potential. The inert gases have the lowest electron affinity, whereas the metals in column IA (the alkali metals) have the lowest ionization potentials. Accurate values of the electron affinities of beryllium, magnesium, and the inert gases are apparently not available, but these are probably fairly small and negative. Just as the elements in column VA (nitrogen, phosphorus, etc.) have larger ionization potentials than their immediate neighbors, the elements in column IVA (carbon, silicon, etc.) have larger electron affinities than their neighbors. This corresponds to half-filled subshells in the negative ions, just as the ionization potentials correspond to half-filled subshells in the neutral atoms.

Atomic size is also correlated with position in the periodic table, with values generally decreasing from left to right and increasing from top to bottom. Other chemical and physical properties, including melting temperature and electronegativity, can be correlated with electron configuration and thus with position in the periodic table. These correlations are discussed in general chemistry textbooks.

Exercise 19.6

Give explanations for the trends in atomic size.

Unsöld's theorem asserts that the charge distribution in a filled hydrogen-like subshell is spherically symmetric (independent of θ and ϕ).

EXAMPLE 19.7

For hydrogen-like orbitals, show that

$$|\psi_{2p1}|^2 + |\psi_{2p0}|^2 + |\psi_{2p,-1}|^2$$

is independent of θ and ϕ, as asserted by Unsöld's theorem.

Solution

$$\begin{aligned}|\psi_{2p1}|^2 + |\psi_{2p0}|^2 + |\psi_{2p,-1}|^2 &= R_{21}^2\left[\Theta_{11}^2|\Phi_1|^2 + \Theta_{10}^2|\Phi_0|^2 + \Theta_{1,-1}^2|\Phi_{-1}|^2\right]\\ &= \frac{R_{21}^2}{2\pi}\left[\frac{3}{4}\sin^2(\theta) + \frac{6}{4}\cos^2(\theta) + \frac{3}{4}\sin^2(\theta)\right]\\ &= \left(\frac{R_{21}^2}{2\pi}\right)\left(\frac{6}{4}\right)[\sin^2(\theta) + \cos^2(\theta)] = \left(\frac{R_{21}^2}{2\pi}\right)\left(\frac{6}{4}\right)\end{aligned}$$

We have used the identity

$$\sin^2(\theta) + \cos^2(\theta) = 1$$

and the fact that

$$|\Phi_m|^2 = \Phi_m^* \Phi_m = \frac{1}{2\pi} e^{-im\phi} e^{im\phi} = \frac{1}{2\pi}$$

Exercise 19.7

For hydrogen-like orbitals, show that

$$\psi_{2px}^2 + \psi_{2py}^2 + \psi_{2pz}^2$$

is independent of θ and ϕ, as asserted by Unsöld's theorem.

PROBLEMS

Section 19.6: Atoms with More Than Two Electrons

19.27 Find the value of $\langle r \rangle$ for a hydrogen-like 2*s* orbital with $Z = 1.776$. Compare it with the value for $Z = 2.686$.

19.28 Using the values for the orbital exponents (effective number of protons in the nucleus) in Section 19.6, draw graphs of the radial distribution function for each orbital in the ground state of the Li atom. Draw a graph of the total radial distribution function.

19.29 Write the ground-state electron configurations by subshells for the following elements:

a. Fe

b. Rn

c. Tc

d. Rb

19.30 Using Hund's rules, write the ground term symbol for each of the elements in Problem 19.29.

19.31 Using Hund's rules, write the ground term symbol for each of the following elements:

a. N

b. S

c. Cr

d. W

19.32 Write all of the term symbols for the ground configurations of the following elements: (a) P, (b) Ca, (c) Cu, (d) Cl. Omit the values of the quantum number J.

19.33 Without consulting a periodic table give the electron configuration and the term symbol for the lowest-energy term of each of the atoms. The number in parentheses is the atomic number.

a. Fe(26)

b. Kr(36)

c. N(7)

d. Ag(47)

19.34 Without consulting a periodic table give the electron configuration and the term symbol for the lowest-energy term of each of the atoms. The number in parentheses is the atomic number.

a. Cr(24)

b. K(19)

c. S(16)

d. Pd(46)

19.35 Explain why each of the following elements has a ground configuration different from that predicted by the diagonal mnemonic device: (a) Mo, (b) Ag, (c) Pd.

19.36 The ionization potential (energy to remove one electron) of a sodium atom in its ground state is 5.1 eV. Use this to calculate a value for the effective nuclear charge felt by the 3*s* electron in a sodium atom in its ground state. State any assumptions.

19.37 Which of the elements in the first two rows of the periodic table have electronic charge distributions that are spherically symmetric?

19.38 **a.** The Fe^{2+} ion and the Cr atom are isoelectronic (have the same number of electrons). Give the lowest-energy electron configuration for each.

b. Give the lowest-energy term symbols for the Fe^{2+} ion and for the Cr atom.

19.39 **a.** The Fe^{3+} ion and the V atom are isoelectronic (have the same number of electrons). Give the lowest-energy electron configuration for each.

b. Give the lowest-energy term symbols for the Fe^{3+} ion and for the V atom.

19.40 For each of the first 18 elements of the periodic table, give the number of unpaired electrons in the ground state.

Summary of the Chapter

There are several commonly used approximation schemes that can be applied to the electronic states of multielectron atoms. The first approximation scheme was the variation method, in which a variation trial function is chosen to minimize the approximate ground-state energy calculated with it. A simple orbital variation trial function was found to correspond to a reduced nuclear charge in the helium atom. This result was interpreted to mean that each electron in a helium atom shields the other electron from the full charge of the nucleus. A better variation trial function includes electron correlation, a dependence of the wave function on the electron–electron distance.

In the perturbation method the Hamiltonian is written as $\widehat{H}^{(0)} + \widehat{H}'$, where $\widehat{H}^{(0)}$ corresponds to a Schrödinger equation that can be solved. The perturbation term $\widehat{H}'$ is arbitrarily multiplied by a fictitious parameter λ, so that $\lambda = 1$ corresponds to the actual case. The method is based on representations of energy eigenvalues and energy eigenfunctions as power series in λ and approximation of the series by partial sums. The method can be applied to excited states. In the helium atom treatment the electron–electron repulsive potential energy was treated as the perturbation term in the Hamiltonian operator.

The third approximation scheme was the self-consistent field method invented by Hartree and Fock. In this method an optimum orbital wave function is sought without restricting the search to a single family of functions. The original method represented the orbitals numerically, but the method was extended by Roothaan, who introduced linear combination representations of the orbitals. For the helium atom the electron–electron repulsive energy is represented by assuming the probability density for the second electron to be given by an earlier approximate orbital and solving the resulting integrodifferential equation by iteration.

The density functional method is based on a theorem of Hohenberg and Kohn, which states that the ground-state energy of an atom or molecule is a functional of the electron probability density. Schemes exist to obtain a usable approximation to the desired functional and the necessary electron probability density.

Results of various calculations were presented. In the orbital approximation, the energies of the orbitals in multielectron atoms depend on the angular momentum quantum number as well as on the principal quantum number, increasing as l increases. The ground state of a multielectron atom is identified by the Aufbau principle, choosing orbitals that give the lowest sum of the orbital energies consistent with the Pauli exclusion principle.

Hund's first rule is that the largest value of S corresponds to the lowest energy in a configuration. Hund's second rule is that for fixed value of S, the largest value of L, the quantum number for the total orbital angular momentum, corresponds to the lowest energy. The first rule correlates with the fact that the larger values of S correspond to lower probability for small electron–electron distances, lowering the potential energy.

The form of the periodic table is determined by electron configurations. Elements with the same number of electrons in the outer (valence) shell have similar chemical properties. For example, all of the inert gases have eight electrons in the outer shell, corresponding to a stable configuration with fully occupied s and p subshells in the outer shell.

ADDITIONAL PROBLEMS

19.41 **a.** Using first-order perturbation, obtain a formula for the ground-state energy of a particle in a one-dimensional box with an additional potential energy $\widehat{H}' = bx$, where b is a negative constant.

b. Obtain a formula for the ground-state energy of the particle of part a, using the variation method and the zero-order wave function as a trial function. Compare your answer with that of part a.

c. Obtain a formula for the ground-state energy of the particle of part a, using the variation method and the trial function $\varphi = Ax^2(a - x)$. Compare your answer with that of part a.

d. Assume that the particle is an electron in a one-dimensional box of length 1.00 nm and that the ends of the box are charged so that $b = -1.60 \times 10^{-11}$ J m^{-1}. Evaluate the energy according to parts a and c.

19.42 **a.** Obtain a formula for the ground-state energy of the particle of part a, using the variation method and the trial function $\varphi = Ax^n(a - x)$.

b. Evaluate the energy according to part d and find the optimum value of n.

19.43 A particle in a one-dimensional box $(0 < x < a)$ has an additional potential energy imposed on it, given by $\widehat{H}' = -B\sin(\pi x/a)$ where B is a positive constant.

a. Using perturbation theory, obtain a formula for $E^{(0)} + E^{(1)}$ for the ground state $(n = 1)$.

b. If the particle is an electron, if the box length is 10.0 Å, and if $B = 5.00 \times 10^{-21}$ J, find the values of $E^{(0)}$ and $E^{(1)}$. Do you think that $E^{(0)} + E^{(1)}$ would be a usable approximation to the correct energy?

c. How do you think the correct wave function would compare with the unperturbed wave function (that for $B = 0$).

d. Explain why a variation calculation using the zero-order wave function as a trial function leads to the same result as $E^{(0)} + E^{(1)}$ in the perturbation theory.

19.44 If the nucleus of a hydrogen atom is at $z = 0$, and if an electric field $\mathscr{E}$ is applied in the z direction, the energy of the system of the nucleus is equal to zero and the energy of the electron is

$$E_{\mathrm{el}} = -\mathscr{E}\mathscr{e}z = -\mathscr{E}\mathscr{e}r\cos(\theta)$$

where z is the vertical coordinate of the electron and r and θ are polar coordinates of the electron. An electric dipole consists of two charges of equal magnitude, Q, and opposite sign separated by a distance d. The dipole moment is defined to be

$$|\mu| = Qd$$

When a hydrogen atom is placed in an electric field, its electrons are shifted in one direction and its nucleus is shifted in the other direction, creating an induced electric dipole. The polarizability α of the atom is defined by

$$\mu_{\mathrm{induced}} = \alpha\mathscr{E}$$

For a hydrogen atom and for an electric field in the z direction, the Hamiltonian operator is

$$\widehat{H} = \widehat{H}^{(0)} + eEz = \widehat{H}^{(0)} + eEr\cos(\theta)$$

where $\widehat{H}^{(0)}$ is the Hamiltonian in the absence of the field. The magnitude of the dipole moment is

$$\mu = \mathscr{e}\langle z\rangle = \mathscr{e}\langle r\cos(\theta)\rangle$$

a. Use the variation method to find the energy of a hydrogen atom in an electric field in the z direction with magnitude $\mathscr{E}$. Use the $1s$ wave function as the variation trial function. No minimization will be possible. Compare your result with that of the perturbation method in Problem 19.22.

b. Use the variation method to find the energy of a hydrogen atom in an electric field in the z direction with magnitude $\mathscr{E}$. Use the variation trial function

$$\varphi = A(\psi_{1s} + c\psi_{2pz})$$

Minimize the energy with respect to c. Explain any difference between your result and that of part a.

c. Find the polarizability of a hydrogen atom from your answer to part b, using the formula for the energy of an induced dipole

$$E_{\text{dipole}} = -\frac{1}{2}\alpha\mathscr{E}^2$$

19.45 **a.** Each element in the second row of the periodic table has a higher ionization potential than the element to its left, except for nitrogen, which has a higher ionization potential than either carbon or oxygen, and beryllium, which has a higher ionization potential than either boron or lithium. Explain both the general trend and these exceptions to the general trend.

b. The ionization potential is found generally to decrease toward the bottom of a column of the periodic table. Explain this fact in terms of effective nuclear charge and electron shielding.

19.46 Search the World Wide Web and write a brief report on the current status of the controversy about the production of elements 116 and 118.

19.47 Identify each statement as either true or false. If a statement is true only under special circumstances, label it as false.

a. The orbital energy of a $4s$ subshell is always lower than that of a $3d$ subshell in the same atom.

b. The ground state of every inert gas corresponds to a filled valence shell.

c. The inert gases are the only elements with spherically symmetric electron charge distributions.

d. An electron configuration that contains only filled subshells can correspond to only one term symbol.

e. Orbital occupations that do not correspond to Hund's first rule cannot occur.

f. The self-consistent field theory can deliver the best possible orbital wave function for a multielectron atom.

g. A second-order perturbation result is always more nearly correct than a first-order result.

h. An electron configuration with two unpaired electrons cannot correspond to a doublet term symbol.

i. An antisymmetrized orbital wave function contains no electron correlation.

j. An antisymmetrized orbital wave function contains no dynamical correlation.

k. If a variation energy equals the correct ground-state energy, the variation trial function must be equal to the correct ground-state wave function.

19.48 Gaussian orbitals are frequently used in computational chemistry. Use the Gaussian function

$$\varphi = Ae^{-br^2}$$

as a variational function for the ground state of a hydrogen atom. Minimize the energy and compare it with the correct ground-state energy.

19.49 Hoffman has published an article describing an Excel worksheet that carries out the Hartree self-consistent calculation on the ground state of helium.[36] Obtain and use this spreadsheet to carry out the calculation and make an accurate plot of the radial factor of the approximate orbital obtained. Compare it with a plot of the orbital obtained with the simple variational calculation in the chapter.

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[36] G. G. Hoffman, *J. Chem. Educ.*, **82**, 1418 (2005).

20

The Electronic States of Diatomic Molecules

PRINCIPAL FACTS AND IDEAS

1. In the Born–Oppenheimer approximation, the nuclei of a molecule are assumed to be stationary when the electronic states are studied.
2. The Schrödinger equation for the hydrogen molecule ion, H_2^+, can be solved in the Born–Oppenheimer approximation without additional approximations. The solutions are molecular orbitals that represent motion of the electron around both nuclei.
3. Molecular orbitals can be represented approximately as linear combinations of atomic orbitals (LCAOMOs).
4. The electronic wave functions of homonuclear diatomic molecules can be approximated as products of LCAOMOs.
5. The valence-bond method is an alternative to the molecular orbital method.
6. Molecular orbitals of heteronuclear diatomic molecules correspond to unequal sharing of electrons.

20.1

The Born–Oppenheimer Approximation and the Hydrogen Molecule Ion

Max Born, 1882–1970, was a German-British physicist who participated in the early mathematical development of quantum mechanics.

J. Robert Oppenheimer, 1904–1967, was an American physicist who made important contributions to nuclear physics, including work on the Manhattan Project, which developed the first nuclear weapons during World War II.

The Schrödinger equation of a two-particle system such as the hydrogen atom can be solved mathematically by separating the center-of-mass motion from the relative motion. For atoms with more than one electron, we resorted to approximations, including the assumption that the nucleus was stationary when studying the electronic motion. Our study of the electronic motion in molecules is based on a similar assumption, the *Born–Oppenheimer* approximation.[1] This approximation corresponds to assuming that the nuclei are stationary while the electrons move around them. It is a good approximation, because electrons move much more rapidly than the nuclei and adapt quickly to new nuclear positions. For example, as the nuclei of a diatomic molecule carry out one period of vibration, the electrons might orbit the nuclei 500 or 1000 times.

If the electronic Schrödinger equation is solved with stationary nuclei the energy eigenvalue is called the Born–Oppenheimer energy. If it is solved repeatedly with different fixed values of the nuclear positions, a different value of the energy eigenvalue is obtained for each set of nuclear positions. For a diatomic molecule, the Born–Oppenheimer energy depends only on the internuclear distance. A smooth curve can be drawn through a plot representing the Born–Oppenheimer energy as a function of the internuclear distance. Figure 20.1 shows such a curve. The minimum in the curve corresponds to the equilibrium internuclear distance.

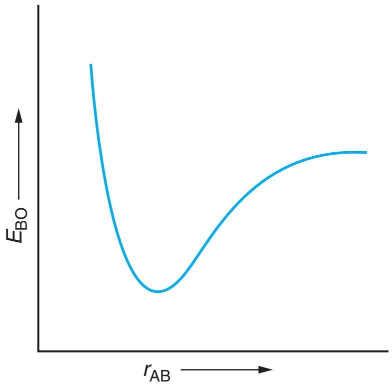

Figure 20.1 Born–Oppenheimer Energy as a Function of Internuclear Distance for a Diatomic Molecule (Schematic).

The Hydrogen Molecule Ion

The hydrogen molecule ion, H_2^+, is the simplest possible molecule. It consists of two nuclei and a single electron, as depicted in Figure 20.2. It is highly reactive, but it is chemically bonded and has been observed spectroscopically in the gas phase. We apply the Born–Oppenheimer approximation and place our coordinate system with the nuclei on the z axis and the origin of coordinates midway between the nuclei. One nucleus is at position A and the other nucleus is at position B. The Born–Oppenheimer Hamiltonian for the hydrogen molecule ion is

$$\widehat{H}_{BO} = -\frac{\hbar^2}{2m}\nabla^2 + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{AB}} - \frac{1}{r_A} - \frac{1}{r_B}\right) \tag{20.1-1}$$

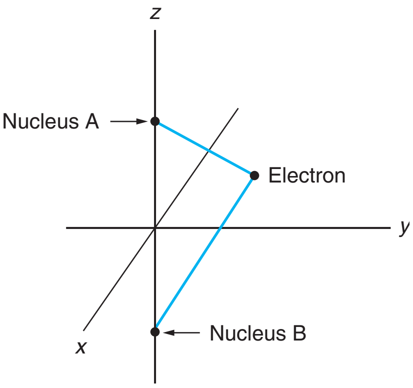

Figure 20.2 The Hydrogen Molecule Ion (H_2^+) System.

where ∇^2 is the Laplacian operator for the electron's coordinates, m is the electron mass, r_{AB} is the internuclear distance, r_A is the distance from the electron to the nucleus at position A, and r_B is the distance from the electron to the nucleus at position B. There are no kinetic energy terms for the nuclei because they are fixed. We denote the potential energy of internuclear repulsion by $\mathscr{V}_{nn}$. It is equal to a constant because the nuclei are fixed:

$$\frac{e^2}{4\pi\varepsilon_0 r_{AB}} = \mathscr{V}_{nn} = \text{constant} \tag{20.1-2}$$

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[1] M. Born and J. R. Oppenheimer, *Ann. Phys.*, **84**, 457 (1927).

We can omit the constant $\mathscr{V}_{\mathrm{nn}}$ from the electronic Hamiltonian and later add that constant to the energy eigenvalues (see Problem 15.6). The Born–Oppenheimer Hamiltonian is now

$$\widehat{H}_{\mathrm{BO}} = \widehat{H}_{\mathrm{el}} + \mathscr{V}_{\mathrm{nn}} \tag{20.1-3}$$

where $\widehat{H}_{\mathrm{el}}$ is the electronic Hamiltonian:

$$\widehat{H}_{\mathrm{el}} = -\frac{\hbar^2}{2m}\nabla^2 + \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{r_{\mathrm{A}}} - \frac{1}{r_{\mathrm{B}}}\right) \tag{20.1-4}$$

The electronic Schrödinger equation is

$$\widehat{H}_{\mathrm{el}}\psi_{\mathrm{el}} = E_{\mathrm{el}}\psi_{\mathrm{el}} \tag{20.1-5}$$

where E_{el} is the electronic energy eigenvalue and ψ_{el} is a one-electron wave function that we call a *molecular orbital*, since it involves motion of the electron around the entire molecule. The Born–Oppenheimer energy is

$$E_{\mathrm{BO}} = E_{\mathrm{el}} + \mathscr{V}_{\mathrm{nn}} \tag{20.1-6}$$

The electronic Schrödinger equation for the H_2^+ ion can be solved by transforming to a coordinate system that is called *confocal polar elliptical coordinates*. One coordinate is $\xi = (r_{\mathrm{A}} + r_{\mathrm{B}})/r_{\mathrm{AB}}$, the second coordinate is $\eta = (r_{\mathrm{A}} - r_{\mathrm{B}})/r_{\mathrm{AB}}$, and the third coordinate is the angle ϕ, the same angle as in spherical polar coordinates. The solutions to the electronic Schrödinger equation are products of three factors:

$$\psi_{\mathrm{el}} = L(\xi)M(\eta)\Phi(\phi) \tag{20.1-7}$$

The factor $\Phi(\phi)$ is the same factor Φ that occurs in hydrogen-like atomic orbitals. As in that case, we can choose either the complex Φ functions Φ_m or the real Φ functions Φ_{mx} and Φ_{my}. The other factors are more complicated and we do not display the formulas representing them.[2] These molecular orbitals are called *exact Born–Oppenheimer molecular orbitals*. They are not exact solutions to the complete Schrödinger equation, but they contain no approximations other than the Born–Oppenheimer approximation.

Figure 20.3 shows the Born–Oppenheimer energy of H_2^+ as a function of r_{AB} for the two states of lowest energy. We denote the molecular orbital for the ground state by ψ_1 since it is customary to number orbitals from the lowest energy to the highest. The ground-state energy has a minimum at $r_{\mathrm{AB}} = 1.06 \times 10^{-10}\,\mathrm{m} = 106\,\mathrm{pm} = 1.06\,\text{Å}$. We denote this equilibrium value of r_{AB} by r_{e}. For large values of r_{AB} the energy approaches a constant value, which we set equal to zero. The difference in energy between this constant value and the value of the energy at $r_{\mathrm{AB}} = r_{\mathrm{e}}$ is denoted by D_{e} and is called the *dissociation energy* of the molecule. The dissociation energy of H_2^+ is equal to 2.8 eV. This dissociation energy is large enough that the molecule is chemically bonded in the ground state. We say that the molecule has a bond order of $1/2$, corresponding to one shared electron. We denote the molecular orbital for the first excited state by ψ_2. This state has an energy that decreases smoothly as r_{AB} increases. If the molecule makes a transition to the first excited state it will then dissociate, forming a hydrogen atom and a H^+ ion (a bare nucleus).

Figure 20.4 shows sketches of the orbital regions for ψ_1 and ψ_2. Both of these orbitals contain the factor Φ_0 and are independent of ϕ. We say that they are *cylindrically*

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[2] D. R. Bates, K. Ledsham, and A. L. Stewart, *Phil. Trans. Roy. Soc.*, **A246**, 215 (1963).

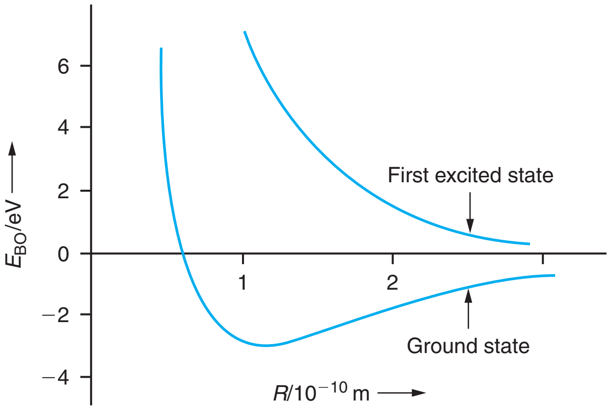

Figure 20.3 The Born–Oppenheimer Energy of the Ground State and First Excited State of the Hydrogen Molecule Ion as a Function of Internuclear Distance.

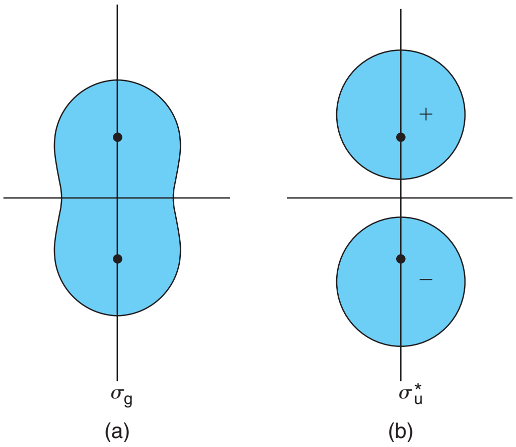

Figure 20.4 The Orbital Regions for the Hydrogen Molecule Ion (Schematic). (a) The ground state. (b) The first excited state.

symmetric about the bond axis. The orbital region of ψ_1 has no nodal surfaces except at $r \to \infty$. The orbital region of ψ_2 has a nodal plane halfway between the nuclei. If the mathematical limit is taken as r_{AB} approaches zero, a hypothetical atom called the *united atom* is obtained. The united atom for H_2^+ is the He^+ ion. In this limit ψ_1 turns into the united-atom $1s$ orbital, and ψ_2 turns into the united-atom $2p_z$ orbital.

A molecular orbital without a nodal surface between the nuclei generally corresponds to an orbital energy with a minimum value as a function of r_{AB} and is called a *bonding molecular orbital*. An orbital with a nodal surface between the nuclei generally corresponds to an orbital energy that decreases as r_{AB} increases and is called an *antibonding molecular orbital*. A bonding orbital corresponds to a significant probability that the electron will be found between the two nuclei, attracting both nuclei and stabilizing the bond. An antibonding orbital corresponds to a small probability that the electron will be found between the nuclei, allowing the nuclei to repel each other more strongly. A bonding orbital also corresponds to a de Broglie wave with a longer wavelength, which means a smaller speed and a smaller kinetic energy than with an antibonding orbital, which has a shorter de Broglie wavelength because of the node between the nuclei.

Angular Momentum Properties of Molecular Orbitals

In Chapter 15 we asserted that a set of commuting operators can have a set of common eigenfunctions. For example, the hydrogen atom spin orbitals can be chosen to be eigenfunctions of $\widehat{H}$, $\widehat{L}^2$, $\widehat{L}_z$, and $\widehat{S}_z$. The $\widehat{L}^2$ operator does not commute with the electronic Hamiltonian of the H_2^+ ion. The physical reason for this is that all directions are not equivalent as they are with atoms, because of the presence of the two fixed nuclei. The operator $\widehat{L}_z$ does commute with the electronic Hamiltonian operator if the internuclear axis is chosen as the z axis. The molecular orbitals can be eigenfunctions of $\widehat{L}_z$:

$$\widehat{L}_z\psi = \hbar m\psi \tag{20.1-8}$$

where m is an integer. There is no quantum number l so that the values of m are not limited to a specific range. We define a non-negative quantum number λ, equal to the magnitude of m:

$$\lambda = |m| \tag{20.1-9}$$

The exact Born–Oppenheimer molecular orbitals ψ_1 and ψ_2 both correspond to $\lambda = 0$. A nonzero value of λ corresponds to two states because m can be positive or negative.

Since l is not a good quantum number, we use the quantum number λ to classify molecular orbitals, using the following Greek-letter designations:

Value of λ	Symbol
0	σ
1	π
2	δ
3	ϕ
etc.	

Note the similarity with the letters s, p, d, and f in the atom case. Both the ground state orbital and the first excited-state orbital of H_2^+ are σ(sigma) orbitals. Sigma orbitals of diatomic molecules contain the factor Φ_0 and have orbital regions that are cylindrically symmetric about the bond axis. The other orbitals can be chosen to include either the real Φ functions or the complex Φ functions, and have nodal planes containing the internuclear axis.

The spin operator $\widehat{S}_z$ commutes with the H_2^+ Hamiltonian operator, so we can have molecular spin orbitals that are eigenfunctions of $\widehat{S}_z$. The spin eigenvalues are equal to $m_s\hbar = \pm(1/2)\hbar$, the same as with the hydrogen atom. We can represent the spin orbitals by a space orbital multiplied by the spin function α or the spin function β, as with atomic orbitals.

Symmetry Properties of the Molecular Orbitals

There is another class of operators that can commute with the electronic Hamiltonian operator of the H_2^+ ion. These operators are *symmetry operators*. Before we can define how these operators operate on functions, we define how they operate on a point in three-dimensional space, moving that point to a new location. As with other operators, we denote a symmetry operator by a letter with a caret ($\widehat{\ }$) over it. For a symmetry operator $\widehat{O}$ we write

$$\widehat{O}P = P' \tag{20.1-10}$$

or

$$\widehat{O}(x, y, z) = (x', y', z') \tag{20.1-11}$$

where P stands for the point at its original location (x, y, z) and P' stands for the point at (x', y', z') to which the operator moves the point.

For each symmetry operator there is a *symmetry element*, which is a point, line, or plane relative to which the motion is carried out. If a point is located at the symmetry element of a particular symmetry operator, that symmetry operator does not move the point. *Point symmetry operators* are symmetry operators that do not move a point if it is at the origin. The symmetry elements of point symmetry operators always include the origin. We will discuss only point symmetry operators.

The *inversion operator* is denoted by $\widehat{i}$. It moves a point on a line through the origin to a location that is at the same distance from the origin as was the original location. The symmetry element for the inversion operator is the origin. If the Cartesian coordinates of the original location are (x, y, z) the inversion operator moves the point to $(-x, -y, -z)$. That is,

$$\widehat{i}(x, y, z) = (x', y', z') = (-x, -y, -z) \tag{20.1-12}$$

Since there is only one origin, there is only one inversion operator among the point symmetry operators.

A *reflection operator* moves a point on a line perpendicular to a specified plane to a location on the other side of the plane at the same distance from the plane as the original location. It is said to reflect the point through the plane, which is the symmetry element. The reflection operator $\widehat{\sigma}_{\mathrm{h}}$ reflects through a horizontal plane:

$$\widehat{\sigma}_{\mathrm{h}}(x, y, z) = (x', y', z') = (x, y, -z) \tag{20.1-13}$$

There is only one horizontal plane through the origin so there is only one $\widehat{\sigma}_{\mathrm{h}}$ operator among the point symmetry operators. A symmetry operator that reflects through a vertical plane is denoted by $\widehat{\sigma}_{\mathrm{v}}$. Since there are infinitely many vertical planes containing the origin, there are infinitely many $\widehat{\sigma}_{\mathrm{v}}$ operators among the point symmetry operators. We can attach subscripts or other labels to distinguish them from each other.

EXAMPLE 20.1

Find the coordinates of the points resulting from the following operations:

a. $\widehat{i}(6, 4, 3)$

b. $\widehat{\sigma}_{\mathrm{h}}(1, 2, -2)$

c. $\widehat{\sigma}_{vxz}(7, -6, 3)$ where $\widehat{\sigma}_{vxz}$ is the reflection operator that reflects through the xz plane

Solution

a. $(-6, -4, -3)$

b. $(1, 2, 2)$

c. $(7, 6, 3)$

Exercise 20.1

Find the coordinates of the points resulting from the operations:

a. $\widehat{i}(1, 2, 3)$

b. $\widehat{\sigma}_{\mathrm{h}}(4, -2, -2)$

c. $\widehat{\sigma}_{vyz}(7, -6, 3)$ where $\widehat{\sigma}_{vyz}$ is the reflection operator that reflects through the yz plane.

Rotation operators move a point as though it were part of a rigid body rotating about a specified axis, which is the symmetry element. By convention rotations are counterclockwise when viewed from the positive end of the rotation axis. There are infinitely many rotation operators among the point symmetry operators since there are infinitely many lines that pass through the origin and infinitely many possible angles of rotation. We consider only rotation operators that produce a full rotation of 360° when applied an integral number of times. A rotation operator that produces one full rotation when applied n times is denoted by $\widehat{C}_n$. The $\widehat{C}_1$ operator rotates by 360° (the same as doing nothing), a $\widehat{C}_2$ operator rotates by 180°, and so on. We can add subscripts to denote the axis. For example, the $\widehat{C}_{4z}$ operator rotates by 90° about the z axis, so that

$$\widehat{C}_{4z}(x, y, z) = (x', y', z') = (-y, x, z) \tag{20.1-14}$$

Figure 20.5 shows the effect of the operators $\widehat{i}$, $\widehat{\sigma}_{\mathrm{h}}$, and $\widehat{C}_{4z}$ on a point in the first octant.

EXAMPLE 20.2

Find the following locations:

a. $\widehat{C}_{2z}(1, 2, 3)$ (the axis of rotation is the z axis).

b. $\widehat{C}_{3z}(1, 0, 1)$ (the axis of rotation is the z axis).

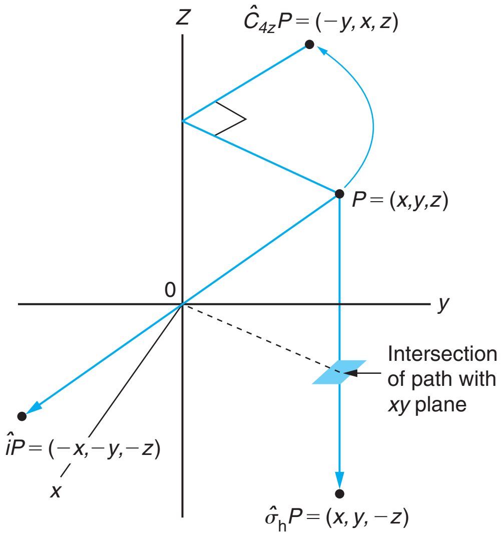

Figure 20.5 The Effect of the Symmetry Operators $\widehat{i}$, $\widehat{\sigma}_{\mathrm{h}}$, and $\widehat{C}_{4z}$.

Solution

a. $(-1, -2, 3)$
b. $(-\frac{1}{2}, \frac{1}{2}\sqrt{3}, 1)$

Exercise 20.2

Find the following locations:
a. $\widehat{C}_{4x}(1, 2, 3)$ (the axis of rotation is the x axis).
b. $\widehat{C}_{3y}(1, 1, 0)$ (the axis of rotation is the y axis).

The *identity operator* does nothing. It is denoted by $\widehat{E}$ for the German word "Einheit," meaning "unity."

$$\widehat{E}(x, y, z) = (x, y, z) \tag{20.1-15}$$

The Operation of Symmetry Operators on Functions

Multiplication operators and derivative operators produce new functions when they operate on mathematical functions. We now define the way in which the symmetry operator $\widehat{O}$ produces a new function $g(x, y, z)$ when it operates on the function $f(x, y, z)$. Let $\widehat{O}$ be a symmetry operator such that

$$\widehat{O}P = P' \tag{20.1-16a}$$

$$\widehat{O}(x, y, z) = (x', y', z') \tag{20.1-16b}$$

We define the new function g that is produced when $\widehat{O}$ operates on $f(x, y, z)$:

$$\widehat{O}\ f(x, y, z) = g(x, y, z) \tag{20.1-17}$$

such that g has the same value at point P' that the function f has at point P:

$$g(x', y', z') = f(x, y, z) \tag{20.1-18}$$

A function can be an eigenfunction of a symmetry operator. The only eigenvalues that occur are $+1$ and -1. If f is an eigenfunction of $\widehat{O}$, there are two possibilities. Either

$$g(x, y, z) = f(x, y, z) \tag{20.1-19}$$

or

$$g(x, y, z) = -f(x, y, z) \tag{20.1-20}$$

EXAMPLE 20.3

Show that the hydrogen-like $1s$ orbital is an eigenfunction of the inversion operator $\widehat{i}$ and find the eigenvalue.

Solution

The function is

$$\psi_{1s} = \sqrt{\frac{1}{\pi}}\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a} = \sqrt{\frac{1}{\pi}}\left(\frac{Z}{a}\right)^{3/2} e^{-Z(x^2+y^2+z^2)^{1/2}/a}$$

When x is replaced by $-x$, y is replaced by $-y$, and z is replaced by $-z$, the value of r is unchanged so that the function is unchanged.

$$\widehat{i}\psi_{1s} = \psi_{1s}$$

The ψ_{1s} function is an eigenfunction of the inversion operator with eigenvalue 1.

EXAMPLE 20.4

Determine the spherical polar coordinates of $\widehat{i}P$ and $\widehat{\sigma}_{\mathrm{h}}P$ if P represents a point whose spherical polar coordinates are (r, θ, ϕ).

Solution

$$\widehat{i}P = \widehat{i}(r, \theta, \phi) = (r, 180^\circ - \theta, 180^\circ + \phi) = (r, \pi - \theta, \pi + \phi)$$
$$\widehat{\sigma}_{\mathrm{h}}P = \widehat{\sigma}_{\mathrm{h}}(r, \theta, \phi) = (r, 180^\circ - \theta, \phi) = (r, \pi - \theta, \phi)$$

Exercise 20.3

Show that the ψ_{2p_z} hydrogen-like orbital is an eigenfunction of the $\widehat{\sigma}_{\mathrm{h}}$ operator with eigenvalue -1.

The electronic energy eigenfunctions of a molecule can be eigenfunctions of the symmetry operators that commute with the electronic Hamiltonian. The symmetry operators that commute with the electronic Hamiltonian are said to "belong" to the molecule. In order for a symmetry operator to commute with the electronic Hamiltonian, it must leave the potential energy unchanged when applied to the electron's coordinates. Otherwise, a different result would occur if the symmetry operator were applied to an electronic wave function after application of the Hamiltonian than if the operators were applied in the other order.

In the Born–Oppenheimer approximation a symmetry operator operates on all of the electron coordinates but does not affect the nuclear coordinates. If a symmetry operator leaves the potential energy unchanged, it must move every electron to a position where it either is at the same distance from each nucleus as in its original position, or is at the same distance from another nucleus of the same kind. We can test whether a symmetry operator belongs to a molecule by applying it to all electrons and seeing if each electron is now at the same distance from each nucleus as it originally was from a nucleus of the same kind.

There is a second test to determine whether a symmetry operator belongs to a molecule in a particular nuclear conformation. We apply it to all of the nuclei of the molecule instead of applying it to the electrons. If a symmetry operator moves every nucleus to a location previously occupied by that nucleus or by a nucleus of the same kind (same isotope of the same element) it belongs to the molecule. For a multielectron molecule, this test is generally easier to apply than the test in which the electrons are moved.

The operation of the inversion operator on the electron of an H_2^+ molecule ion is illustrated in Figure 20.6. This motion brings the electron to the same distance from nucleus A as it originally was from nucleus B and vice versa, and does not change the potential energy. The inversion operator belongs to the H_2^+ molecule ion. We can also apply the inversion operator to the nuclei and see that it simply exchanges the nuclei.

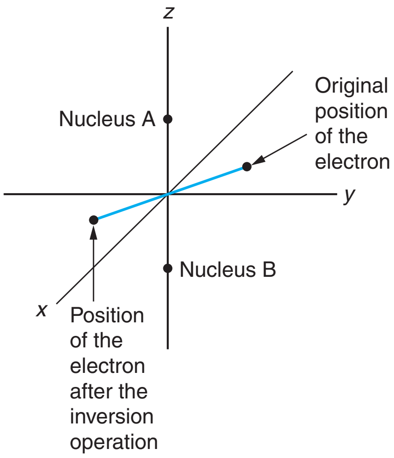

Figure 20.6 The Effect of the Symmetry Operator $\widehat{i}$ on the Electron of the H_2^+ Ion.

Exercise 20.4

a. Show that the symmetry operators $\widehat{\sigma}_h$, $\widehat{C}_{nz}$, and $\widehat{C}_{2a}$ belong to the H_2^+ molecule ion, where n is any positive integer and where a stands for any axis in the xy plane. Show this first by applying the symmetry operators to the electron's position with fixed nuclei. Then apply them to the nuclei with a fixed electron.

b. The $\widehat{C}_{\infty z}$ operator corresponds to an infinitesimal rotation about the z axis, and infinitely many applications of this operator can correspond to rotation by any angle. Show that $\widehat{C}_{\infty z}$ belongs to the H_2^+ ion.

c. There are infinitely many $\widehat{\sigma}_v$ operators. Show that all of them belong to the H_2^+ ion.

The ground-state molecular orbital ψ_1 is an eigenfunction of each of the symmetry operators in Exercise 20.4, and each eigenvalue is equal to +1. The first excited-state orbital ψ_2 is also an eigenfunction of these operators, but the eigenvalues of $\widehat{i}$, $\widehat{\sigma}_h$, and $\widehat{C}_{2a}$ are equal to −1. An eigenfunction having an eigenvalue of $\widehat{i}$ equal to +1 is denoted by a subscript g (from the German *gerade*, meaning "even") and an eigenvalue of $\widehat{i}$ equal to −1 is denoted by a subscript u (from the German *ungerade*, meaning "odd"). An eigenfunction having an eigenvalue of $\widehat{\sigma}_h$ equal to −1 is denoted by an asterisk (*). Orbitals with asterisks are antibonding since they have a nodal plane through the origin perpendicular to the bond axis. No superscript or subscript is used to denote an eigenvalue of $\widehat{\sigma}_h$ equal to +1. We now use the notations $\psi_{1\sigma_g}$ and $\psi_{2\sigma_u^*}$ for our first two H_2^+ molecular orbitals.

PROBLEMS

Section 20.1: The Born–Oppenheimer Approximation and the Hydrogen Molecule Ion

20.1 What is the symmetry operation that is equivalent to the product $\widehat{i}\,\widehat{\sigma}_h$? Is this the same as the product $\widehat{\sigma}_h\,\widehat{i}$?

20.2 What is the symmetry operation that is equivalent to the product $\widehat{C}_{2z}\widehat{i}$? Is it the same as the product $\widehat{i}\,\widehat{C}_{2z}$?

20.3 Write the function that is equal to $\widehat{C}_{4z}\psi_{2p_x}$.

20.4 Write the function that is equal to $\widehat{C}_{2z}\psi_{2p_x}$.

20.5 **a.** Draw a sketch of the orbital region of the $3d_{x^2-y^2}$ hydrogen-like orbital.

b. List the symmetry operators of which this orbital is an eigenfunction. Give the eigenvalue of each operator for the $3d_{x^2-y^2}$ hydrogen-like orbital.

20.6. The symbol (called a column vector) $\begin{bmatrix} a \\ b \\ c \end{bmatrix}$ is used to represent the point given by $x = a$, $y = b$, and $z = c$. The symbol (called a row vector) $[a\ b\ c]$ is equivalent in some ways.

a. Find the resulting point when the product of two operators $C_2(z)C_2(x)$ operates on $\begin{bmatrix} a \\ b \\ c \end{bmatrix}$. Give the single operator equivalent to the product of the two operators.

b. Repeat part a for the operators in the other order.

c. Do the two operators commute?

20.2 LCAOMOs. Approximate Molecular Orbitals That Are Linear Combinations of Atomic Orbitals

The exact Born–Oppenheimer orbitals for H_2^+ are expressed in an unfamiliar coordinate system and we did not explicitly display them. It will be convenient to have some easily expressed approximate molecular orbitals that resemble the correct molecular orbitals. We define *molecular orbitals that are linear combinations of atomic orbitals*, abbreviated LCAOMOs. If $f_1, f_2, f_3, \ldots$ are a set of basis functions, then a *linear combination* of these functions is written as in Eq. (16.3-34):

$$g = c_1 f_1 + c_2 f_2 + c_3 f_3 + \cdots = \sum_{j=1}^{\infty} c_j f_j \tag{20.2-1}$$

where the c coefficients are constants. If the linear combination can be an exact representation of any function that obeys the same boundary conditions as the basis set, the basis set is said to be a *complete set*. A complete basis set ordinarily has infinitely many members. We will not attempt to use a complete set of basis functions, but will begin with a basis set consisting of two atomic orbitals.

We seek approximate LCAOMO representations for the $\psi_{1\sigma_g}$ and $\psi_{2\sigma_u^*}$ molecular orbitals. We denote one nucleus as A and the other as B. We let r_A be the distance from nucleus A to the electron, and let r_B be the distance from nucleus B to the electron. As our first basis set we take a hydrogen-like $1s$ orbital with r_A as its independent variable and a hydrogen-like $1s$ orbital with r_B as its independent variable. We use the abbreviations:

$$\psi_{1sA} = \psi_{1s}(r_A) \tag{20.2-2a}$$

$$\psi_{1sB} = \psi_{1s}(r_B) \tag{20.2-2b}$$

The orbital ψ_{1sA} has its orbital region centered at nucleus A and the orbital ψ_{1sB} has its orbital region centered at nucleus B. We now form molecular orbitals that are linear combinations of these two basis functions:

$$\psi_{MO} = c_A\psi_{1sA} + c_B\psi_{1sB} \tag{20.2-3}$$

We can obtain two independent linear combinations from two independent basis functions, and we seek two that are approximations to the exact Born–Oppenheimer molecular orbitals $\psi_{1\sigma_g}$ and $\psi_{2\sigma_u^*}$.

One way to find the appropriate values of c_A and c_B is to regard ψ_{MO} as a variation trial function and to minimize the energy as a function of c_A and c_B. We do not present this calculation, but the result is that the variation energy is minimized when $c_A = c_B$. An approximation to the first excited state wave function $\psi_{2\sigma_u^*}$ is obtained when the energy has its maximum value, and this corresponds to $c_A = -c_B$.[3] Another procedure is to choose values of c_A and c_B so that the approximate orbital is an eigenfunction of the same symmetry operators as the exact orbitals. The exact Born–Oppenheimer orbital $\psi_{1\sigma_g}$ is an eigenfunction of the inversion operator with eigenvalue $+1$. In order to obtain an LCAOMO with this eigenvalue, we must choose

$$c_A = c_B \tag{20.2-4}$$

In order to obtain a molecular orbital with the same symmetry properties as the exact Born–Oppenheimer orbital $\psi_{2\sigma_u^*}$, we must choose

$$c_A = -c_B \tag{20.2-5}$$

We introduce the symbols for our two LCAOMOs:

$$\psi_{\sigma_g 1s} = c_g(\psi_{1sA} + \psi_{1sB}) \tag{20.2-6}$$

$$\psi_{\sigma_u^* 1s} = c_u(\psi_{1sA} - \psi_{1sB}) \tag{20.2-7}$$

These LCAOMOs are eigenfunctions of all of the symmetry operators that belong to the H_2^+ molecule.

Exercise 20.5

a. Argue that $\psi_{\sigma_g 1s}$ has an eigenvalue of $+1$ for the $\widehat{\sigma}_h$ operator and for the $\widehat{C}_{2a}$ operator, where $\widehat{C}_{2a}$ is a rotation operator whose symmetry element lies anywhere in the xy plane.

b. Argue that $\psi_{\sigma_u^* 1s}$ has an eigenvalue of -1 for the $\widehat{\sigma}_h$ operator and for the $\widehat{C}_{2a}$ operator.

Figure 20.7 schematically shows the orbital regions for the $\sigma_g 1s$ LCAOMO and the $\sigma_u^* 1s$ LCAOMO, as well as the orbital regions for the $1s$ atomic orbitals. The intersection of the two atomic orbital regions is called the *overlap region*. For the $\sigma_g 1s$ orbital the two atomic orbitals combine with the same sign in the overlap region, producing a molecular orbital region with no nodal surface between the nuclei. For the $\sigma_u^* 1s$ orbital the atomic orbitals combine with opposite signs in the overlap region, canceling to produce a nodal surface between the nuclei. The orbital regions of the LCAOMOs have the same general features as the "exact" Born–Oppenheimer orbitals whose orbital regions were depicted in Figure 20.4.

Figure 20.8 shows the electronic energy for each of these LCAOMOs for H_2^+ along with the exact Born–Oppenheimer energies. As we expect from the variational theorem, the approximate energies lie above the exact energies for all values of r. The value of D_e for the $\sigma_g 1s$ orbital is equal to 1.76 eV at $r_e = 132\text{ pm} = 1.32 \times 10^{-10}\text{ m} = 1.32\text{ Å}$.

LCAOMOs can be constructed that are linear combinations of more than two atomic orbitals. For example, to represent $\psi_{1\sigma_g}$ and $\psi_{2\sigma_u^*}$ we could have written a linear combination of six atomic orbitals:

$$\psi = c_{1sA}\psi_{1sA} + c_{1sB}\psi_{1sB} + c_{2sA}\psi_{2sA} + c_{2sB}\psi_{2sB} + c_{2p_zA}\psi_{2p_zA} + c_{2p_zB}\psi_{2p_zB} \tag{20.2-8}$$

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[3] J. C. Davis, Jr., *Advanced Physical Chemistry*, The Ronald Press, New York, 1965, p. 404.

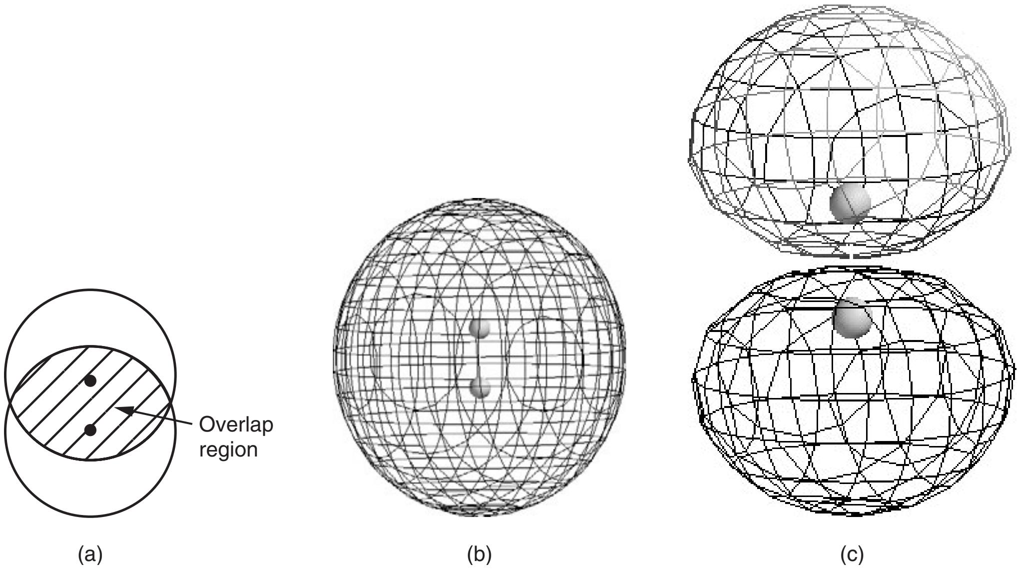

Figure 20.7 The Orbital Region for the $\sigma_g 1s$ and $\sigma_u^* 1s$ LCAO Molecular Orbitals. (a) The overlapping orbital regions of the 1*s*A and 1*s*B atomic orbitals. (b) The orbital region of the $\sigma_g 1s$ LCAOMO. (c) The orbital region of the $\sigma_u^* 1s$ LCAOMO. In parts b and c, positive regions are in black and negative regions are in gray.

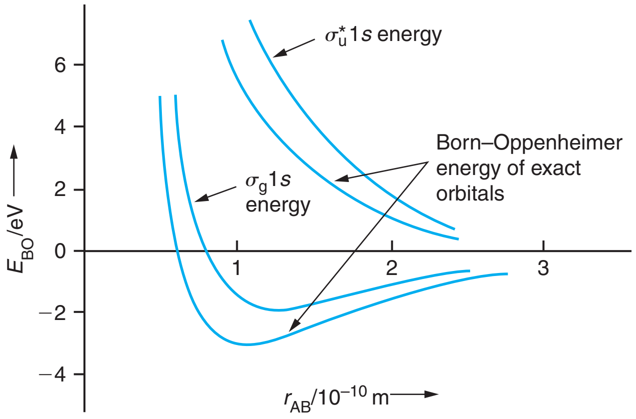

Figure 20.8 The Orbital Energies for the $\sigma_g 1s$ and $\sigma_u^* 1s$ LCAO Molecular Orbitals.

The $2p_x$ and $2p_y$ atomic orbitals are not included in Eq. (20.2-8) because they have different symmetry about the bond axis than does the exact ground-state orbital. If they were included with nonzero coefficients, the LCAOMO would not be an eigenfunction of the same symmetry operators as the exact orbitals. If the variation energy is minimized with respect to the c coefficients, the function of Eq. (20.2-8) would give a better (lower) value than does the $\sigma_g 1s$ orbital.

Exercise 20.6

Argue that the $2p_x$ and $2p_y$ atomic orbitals are eigenfunctions of the $\widehat{C}_{2z}$ operator with eigenvalue -1, while the $2p_z$ orbital is an eigenfunction with eigenvalue $+1$. Argue that a linear combination of all three of these orbitals is not an eigenfunction of the $\widehat{C}_{2z}$ operator.

LCAOMOs for Additional Excited States of H_2^+

The wave functions for additional excited states of H_2^+ are approximated by LCAOMOs using higher-energy hydrogen-like orbitals as basis functions. Two linear combinations of 2*s* orbitals that are eigenfunctions of the appropriate symmetry operators are:

$$\psi_{\sigma_g 2s} = C_g[\psi_{2s}(r_A) + \psi_{2s}(r_B)] = C_g[\psi_{2sA} + \psi_{2sB}] \tag{20.2-9}$$

$$\psi_{\sigma_u^* 2s} = C_u[\psi_{2s}(r_A) - \psi_{2s}(r_B)] = C_u[\psi_{2sA} - \psi_{2sB}] \tag{20.2-10}$$

The $\sigma_g 2s$ orbital is a bonding orbital, and the $\sigma_u^* 2s$ orbital is an antibonding orbital. The $\sigma_g 2s$ orbital energy is higher than that of the $\sigma_u^* 1s$ antibonding orbital since the H_2^+ molecule ion dissociates from the $\sigma_g 2s$ state to a hydrogen nucleus and a hydrogen atom in the 2*s* state, as shown schematically in Figure 20.9. In a later section of this chapter we will obtain still more LCAOMOs, constructed as linear combinations of the $2p$ and higher-energy atomic orbitals.

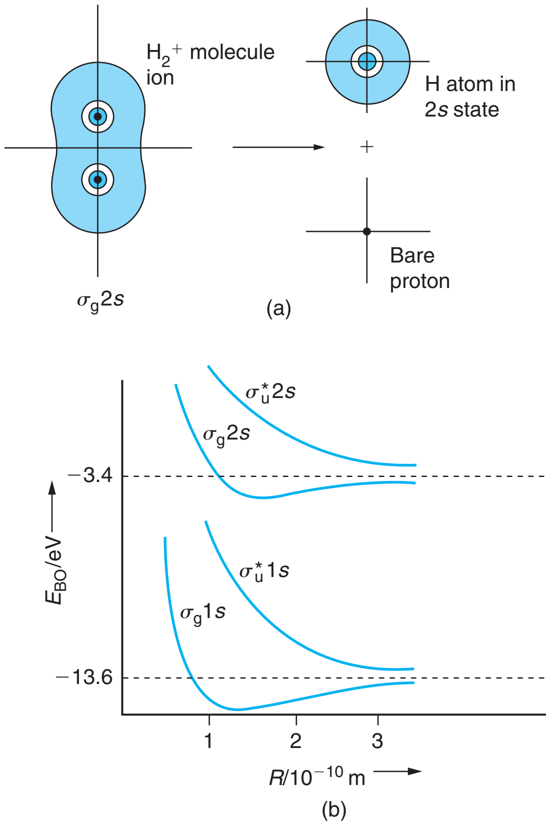

Figure 20.9 (a) The orbital regions before and after dissociation of a hydrogen molecule ion in the $\sigma_g 2s$ state. (b) The energy levels of the LCAO molecular orbitals as a function of internuclear distance.

Exercise 20.7

Draw sketches of the orbital regions for the functions in Eqs. (20.2-9) and (20.2-10). Argue that the designations σ_{g} and σ_{u}^* are correct.

Normalization of the LCAOMOs

Normalization of the $\psi_{1\sigma_{\mathrm{g}}}$ LCAOMO means that

$$1 = |c_{\mathrm{g}}|^2 \int (\psi_{1s\mathrm{A}} + \psi_{1s\mathrm{B}})(\psi_{1s\mathrm{A}} + \psi_{1s\mathrm{B}}) d^3\mathbf{r} \tag{20.2-11}$$

The $1s$ atomic orbitals are real, so we omit the complex conjugate symbols. We choose the normalization constant c_{g} to be real so that

$$1 = c_{\mathrm{g}}^2 \int (\psi_{1s\mathrm{A}^2} + 2\psi_{1s\mathrm{A}}\psi_{1s\mathrm{B}} + \psi_{1s\mathrm{B}^2}) d^3\mathbf{r} \tag{20.2-12}$$

The atomic orbitals $\psi_{1s\mathrm{A}}$ and $\psi_{1s\mathrm{B}}$ are normalized, so that the first term and the last term in the integral will each yield unity when the integration is done. The second term gives an integral that is denoted by S_{1s1s}:

$$\int \psi_{1s\mathrm{A}}\psi_{1s\mathrm{B}}\, d^3\mathbf{r} = S_{1s1s} \tag{20.2-13}$$

The integral S_{1s1s} is called an *overlap integral* because its major contribution comes from the overlap region, inside which both factors are significantly different from zero. Its value depends on r_{AB}, approaching zero if the two nuclei are very far apart and approaching unity when r_{AB} approaches zero, because it then becomes the same as a normalization integral. Similar overlap integrals can be defined for other pairs of atomic orbitals. For any pair of normalized atomic orbitals, the values of overlap integrals must lie between -1 and $+1$, and approach zero as r_{AB} is made large. If we had an overlap integral between a $1s$ and a $2p_z$ orbital or any other pair of different orbitals it would approach zero as r_{AB} approaches zero, because it would then become the same as an orthogonality integral.

We now have

$$1 = c_{\mathrm{g}}^2(1 + 2S + 1) = c_{\mathrm{g}}^2(2 + 2S) \tag{20.2-14}$$

where we omit the subscripts on the overlap integral. The normalized LCAOMO is

$$\psi_{\sigma_{\mathrm{g}}1s} = \frac{1}{\sqrt{2 + 2S}}(\psi_{1s\mathrm{A}} + \psi_{1s\mathrm{B}}) \tag{20.2-15}$$

where we choose the positive square root.

PROBLEMS

Section 20.2: LCAOMOs. Approximate Molecular Orbitals That Are Linear Combinations of Atomic Orbitals

20.7 Sketch the orbital region of the $\sigma_g 3s$ LCAOMO.

20.8 Sketch the orbital regions for the six LCAO molecular orbitals that can be formed from the $3p$ atomic orbitals.

20.9 Sketch the orbital region of the following LCAOMO, with the bond axis on the z axis:

$$\psi = c_A \psi_{1sA} + c_B \psi_{2p_y B}$$

Explain why this orbital is unusable if c_A and c_B are both nonzero.

20.10 Sketch the orbital region of the following LCAOMO:

$$\psi_{\sigma_g 3p} = c(\psi_{3p_z A} + \psi_{3p_z B})$$

20.11 By inspection of the orbital regions, predict which united-atom orbital will result from each of the following LCAOMOs:

a. $\pi_u 2p_x$

b. $\pi_u 2p_y$

20.12 By inspection of the orbital regions, predict which united-atom orbital will result from each of the following LCAOMOs:

a. $\sigma_g 2p_z$

b. $\pi_g^* 2p_y$

20.13 Show that the normalization constant for the $\sigma_u^* 1s$ LCAOMO is

$$c_u = \frac{1}{\sqrt{2-2S}} \tag{20.2-16}$$

20.3 Homonuclear Diatomic Molecules

Homonuclear diatomic molecules have two nuclei of the same element. We base our discussion of these molecules on the LCAO molecular orbitals of the H_2^+ molecule ion in much the same way as we based our discussion of multielectron atoms on the hydrogen-like atomic orbitals.

The Hydrogen Molecule

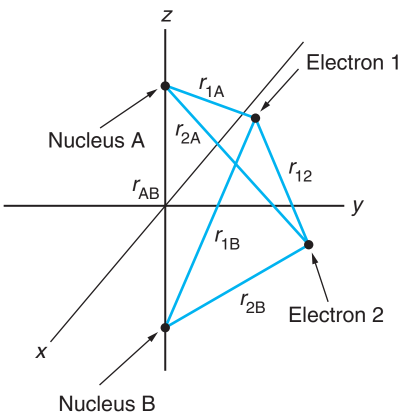

Figure 20.10 The Hydrogen Molecule System.

Figure 20.10 depicts the hydrogen molecule, consisting of two hydrogen nuclei at locations A and B and two electrons at locations 1 and 2. The distances between the particles are labeled in the figure. The Born–Oppenheimer Hamiltonian is

$$\begin{aligned}
\widehat{H}_{BO} &= -\frac{\hbar^2}{2m}\left(\nabla_1^2 + \nabla_2^2\right) + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{AB}} - \frac{1}{r_{1A}} - \frac{1}{r_{1B}} - \frac{1}{r_{2A}} - \frac{1}{r_{2B}} + \frac{1}{r_{12}}\right) \\
&= \widehat{H}_{HMI}(1) + \widehat{H}_{HMI}(2) + \frac{e^2}{4\pi\varepsilon_0 r_{12}} + \frac{e^2}{4\pi\varepsilon_0 r_{AB}} \\
&= \widehat{H}_{el} + \frac{e^2}{4\pi\varepsilon_0 r_{AB}} = \widehat{H}_{el} + \mathcal{V}_{nn}
\end{aligned} \tag{20.3-1}$$

where $\widehat{H}_{HMI}(1)$ and $\widehat{H}_{HMI}(2)$ are the hydrogen-molecule-ion electronic Hamiltonian operators denoted by $\widehat{H}_{el}$ in Eq. (20.1-4). The nucleus–nucleus repulsion term $\mathcal{V}_{nn}$ is a constant in the Born–Oppenheimer approximation, since r_{AB} is fixed. We omit it during the solution of the electronic Schrödinger equation and add it to the resulting electronic energy eigenvalue to obtain the Born–Oppenheimer energy, as in Eq. (20.1-6).

The Zero-Order Approximation

In the zero-order approximation we ignore the electron–electron repulsion, represented by the term proportional to $1/r_{12}$. The zero-order electronic Hamiltonian operator is now a sum of two hydrogen-molecule-ion Hamiltonians:

$$\widehat{H}_{\text{el}}^{(0)} = \widehat{H}_{\text{HMI}}(1) + \widehat{H}_{\text{HMI}}(2) \tag{20.3-2}$$

This zero-order Hamiltonian leads to a separation of variables with a trial function that is a product of two hydrogen-molecule-ion molecular orbitals

$$\Psi^{(0)} = \psi_1(1)\psi_2(2) \tag{20.3-3}$$

The zero-order Born–Oppenheimer energy is a sum of two hydrogen-molecule-ion electronic energies plus $\mathscr{V}_{\text{nn}}$:

$$E_{\text{BO}}^{(0)} = E_{\text{HMI},1} + E_{\text{HMI},2} + \mathscr{V}_{\text{nn}} \tag{20.3-4}$$

Since the electrons can have different spins, the molecular space orbitals in the zero-order ground-state function are the $\psi_{1\sigma_{\text{g}}}$ space orbitals that we discussed in the previous section. The "exact" Born–Oppenheimer orbitals are complicated functions expressed in an unfamiliar coordinate system. We replace them by the $\sigma_{\text{g}}1s$ LCAOMO orbitals. The zero-order orbital approximation is crude enough that this approximate replacement produces no significant further damage. Including spin, the antisymmetrized and normalized zero-order ground-state wave function is:

$$\psi^{(0)} = \frac{1}{\sqrt{2}}\psi_{\sigma_{\text{g}}1s}(1)\psi_{\sigma_{\text{g}}1s}(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \tag{20.3-5}$$

Electron configurations are assigned in much the same way as with atoms. This wave function corresponds to the LCAOMO electron configuration $(\sigma_{\text{g}}1s)^2$. We say that the hydrogen molecule has a *single covalent bond* with one pair of shared electrons occupying a bonding space orbital that extends over both nuclei. This bond is called a σ (sigma) bond because the two shared electrons occupy sigma orbitals. This zero-order wave function gives dissociation energy $D_{\text{e}} = 2.65\,\text{eV}$ and equilibrium internuclear distance $r_{\text{e}} = 84\,\text{pm} = 0.84 \times 10^{-10}\,\text{m} = 0.84\,\text{Å}$, compared with the experimental values of 4.75 eV and 74.1 pm.

Improvements to the Zero-Order Approximation

A variation function with variable orbital exponents in the $1s$ atomic orbitals making up the LCAOMOs of Eq. (20.3-5) gives $D_{\text{e}} = 3.49\,\text{eV}$ and $r_{\text{e}} = 73.2\,\text{pm}$ with an apparent nuclear charge equal to 1.197 protons (a larger charge than the actual nuclear charge). A careful Hartree–Fock–Roothaan calculation gives $D_{\text{e}} = 3.64\,\text{eV}$ and $r_{\text{e}} = 74\,\text{pm}$.[4] If this result approximates the best Hartree–Fock result, the correlation error is approximately 1.11 eV.

Just as with atoms, configuration interaction (CI) can be used to introduce dynamical electron correlation. A CI wave function using the two electron configurations $(\sigma_{\text{g}}1s)^2$ and $(\sigma_{\text{u}}^*1s)^2$ is

$$\Psi_{\text{CI}} = C_{\text{CI}}[\psi_{\sigma_{\text{g}}1s}(1)\psi_{\sigma_{\text{g}}1s}(2) + c_{\text{u}}\psi_{\sigma_{\text{u}}^*1s}(1)\psi_{\sigma_{\text{u}}^*1s}(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)] \tag{20.3-6}$$

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[4] N. Levine, *Quantum Chemistry*, 5th ed., Prentice-Hall, Englewood Cliffs, NJ, 2000, p. 385ff.

where the value of c_{u} is chosen to minimize the variational energy, and the value of c_{CI} is chosen to normalize the function. With the optimum value of the parameter c_{u}, this function gives $D_{\mathrm{e}} = 4.02\,\mathrm{eV}$ and $r_{\mathrm{e}} = 75\,\mathrm{pm}$. The inclusion of a single additional electron configuration in this relatively simple wave function has removed much of the correlation error and has given a better result for the dissociation energy than a sophisticated Hartree–Fock–Roothaan calculation with a single configuration.[5] We will see later how this wave function introduces dynamical electron correlation. Table 20.1 summarizes some results of calculations on the ground state of the hydrogen molecule.

Excited states of the hydrogen molecule correspond to electron configurations other than $(\sigma_{\mathrm{g}}1s)^2$. In the electron configuration $(\sigma_{\mathrm{g}}1s)(\sigma_{\mathrm{u}}^*1s)$ there is one electron in a bonding orbital and one in an antibonding orbital. The antibonding effect of one electron approximately cancels the bonding effect of the other electron, and the molecule will dissociate into two hydrogen atoms if placed in such a state.

The Valence-Bond Method for the Hydrogen Molecule

Orbital wave functions are not the only type of approximate molecular wave functions. In 1927 Heitler and London[6] introduced the *valence-bond function*:

$$\Psi_{\mathrm{VB}} = c_{\mathrm{VB}}[\psi_{1s\mathrm{A}}(1)\psi_{1s\mathrm{B}}(2) + \psi_{1s\mathrm{B}}(1)\psi_{1s\mathrm{A}}(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)] \qquad (20.3\text{-}7)$$

where c_{VB} is a normalizing constant. This wave function expresses the sharing of electrons in a different way from an orbital wave function. It contains one term in which electron 1 occupies an atomic orbital centered on nucleus A while electron 2 occupies an atomic orbital centered on nucleus B and another term in which the locations are switched. This wave function includes dynamical electron correlation,

Table 20.1 Summary of Results of Calculations on the Hydrogen Molecule

	$D_{\mathrm{e}}/\mathrm{eV}$	$r_{\mathrm{e}}/\mathrm{pm}$
Experimental values	4.75	74.1
Molecular Orbital Methods		
Simple LCAOMO	2.65	84
Simple LCAOMO, variable orbital exponent = 1.197	3.49	73.2
CI, two configurations, variable orbital exponent	4.02	75
CI, 33 configurations, elliptical coordinates	4.71	
Valence-Bond Methods		
Simple VB	3.20	80
Simple VB, variable orbital exponent = 1.16	3.78	
VB with ionic terms, $\delta = 0.26$, variable orbital exponent = 1.19	4.02	75
Other Variational Methods		
13 terms, elliptical coordinates	4.72	
100 terms, elliptical coordinate	4.75	
Self-Consistent Field Methods		
Best Hartree–Fock–Roothaan	3.64	74

Data from I. N. Levine, *Quantum Chemistry*, 5th ed., Prentice-Hall, Englewood Cliffs, NJ, 2000.

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[5] I. N. Levine, *op. cit.*, p. 395ff (note 4).

[6] W. Heitler and F. London, *Z. Physik*, **44**, 455 (1927).

since there are no terms with the two electrons assigned to the same atom. When the valence-bond function of Eq. (20.3-7) is used to calculate the variational energy the values $D_e = 3.20$ eV and $r_e = 80$ pm are obtained. These values are in better agreement with experiment than the values obtained from the simple LCAOMO wave function of Eq. (20.3-5), presumably because of the introduction of dynamical electron correlation.

We want to compare the simple LCAOMO wave function with the simple valence-bond wave function. We write the space factor in the LCAOMO function of Eq. (20.3-5) in the form

$$\begin{aligned}\psi_{\sigma_g 1s}(1)\psi_{\sigma_g 1s}(2) &= C_g^2[\psi_{1sA}(1) + \psi_{1sB}(1)][\psi_{1sA}(2) + \psi_{1sB}(2)] \\ &= C_g^2[\psi_{1sA}(1)\psi_{1sA}(2) + \psi_{1sB}(1)\psi_{1sB}(2) \\ &\quad + \psi_{1sA}(1)\psi_{1sB}(2) + \psi_{1sB}(1)\psi_{1sA}(2)] \qquad (20.3\text{-}8)\end{aligned}$$

The last two terms on the right-hand side of Eq. (20.3-8) are the same as the space factor of the simple valence-bond wave function. These terms are called *covalent terms*. The other two terms are called *ionic terms*, because one term has both electrons on nucleus A whereas the other has them on nucleus B.

The simple LCAOMO wave function gives the ionic terms equal weight with the covalent terms while the simple valence-bond function omits them completely. A better result is obtained by including the ionic terms with reduced weight. A modified valence-bond wave function is:

$$\Psi_{MVB} = c_{MVB}[\Psi_{VB} + \delta\Psi_I] \qquad (20.3\text{-}9)$$

where c_{MVB} is a normalizing constant, δ is a variable parameter, and Ψ_I contains the ionic terms:

$$\Psi_I = [\psi_{1sA}(1)\psi_{1sA}(2) + \psi_{1sB}(1)\psi_{1sB}(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)] \qquad (20.3\text{-}10)$$

When the parameter δ is optimized, this wave function is identical to the optimized configuration-interaction function of Eq. (20.3-6). This fact enables us to understand why configuration interaction can introduce dynamical electron correlation. The optimized valence-bond function of Eq. (20.3-9) includes some electron correlation because the optimum value of δ is smaller than unity, making the probability that the electrons are on the same atom smaller than the probability that they are on different atoms. Combining the two configurations in the optimized wave function of Eq. (20.3-6) produces the same wave function as the optimized valence-bond function, reducing the importance of parts of the wave function corresponding to electrons being close together. Although it is not obvious from inspection of a configuration-interaction wave function, addition of more configurations can produce additional dynamical electron correlation through cancellation of parts of the wave function corresponding to small electron–electron distances.

Exercise 20.8

By expressing the function of Eq. (20.3-6) in terms of atomic orbitals, show that it can be made to be the same as the function of Eq. (20.3-9). Express the parameters c_{MVB} and δ in terms of c_{CI} and c_u.

To obtain an additional comparison between the simple LCAOMO method and the valence-bond method for the hydrogen molecule, we obtain the one-electron probability density for the simple LCAOMO wave function of Eq. (20.3-5) by integrating the square of the wave function over the space coordinates of electron 2. We can omit the spin functions and the integration over spin coordinates since this integration would give a factor of unity:

$$\begin{aligned}\rho_{\mathrm{MO}} &= \int \psi_{\sigma_{\mathrm{g}}1s}(1)^2 \psi_{\sigma_{\mathrm{g}}1s}(2)^2 d^3\mathbf{r}_2 = \psi_{\sigma_{\mathrm{g}}1s}(1)^2 \\ &= \frac{1}{2+2S}[\psi_{1s\mathrm{A}}(1)^2 + 2\psi_{1s\mathrm{A}}(1)\psi_{1s\mathrm{B}}(1) + \psi_{1s\mathrm{B}}(1)^2] \qquad (20.3\text{-}11)\end{aligned}$$

We can interpret the three terms in this expressions as follows: The first term is the contribution to the probability from the atomic orbital centered on nucleus A and the last term is the contribution from the atomic orbital centered on nucleus B. The second term represents the contribution of the overlap of the two atomic orbitals.

We now perform the same integration on the square of the simple valence-bond wave function of Eq. (20.3-7):

$$\begin{aligned}\rho_{\mathrm{VB}} &= c_{\mathrm{VB}}^2 \int \Big[\psi_{1s\mathrm{A}}(1)^2\psi_{1s\mathrm{B}}(2)^2 + 2\psi_{1s\mathrm{A}}(1)\psi_{1s\mathrm{B}}(2)\psi_{1s\mathrm{B}}(1)\psi_{1s\mathrm{A}}(2) \\ &\quad + \psi_{1s\mathrm{B}}(1)^2\psi_{1s\mathrm{A}}(2)^2\Big] d^3\mathbf{r}_2 \\ &= c_{\mathrm{VB}}^2[\psi_{1s\mathrm{A}}(1)^2 + 2S\psi_{1s\mathrm{A}}(1)\psi_{1s\mathrm{B}}(1) + \psi_{1s\mathrm{B}}(1)^2] \qquad (20.3\text{-}12)\end{aligned}$$

The difference between this result and the molecular orbital result is the factor S (the overlap integral) in the second term of the valence-bond result. The probability density in the overlap region is smaller than with the LCAOMO function, since the overlap integral S is smaller than unity. However, the electron moves over the entire molecule in much the same way as with the LCAOMO wave function.

The distinction between the valence-bond method and the LCAOMO method for the hydrogen atom disappeared when improvements were made to the simple versions of each method. Further improvements have been made to both methods. A generalized valence-bond method has been developed by Goddard and his collaborators.[7] In this method, the atomic orbitals such as those in Eq. (20.3-7) are replaced by functions that are optimized by minimizing the energy. The two electrons in a chemical bond also do not have to occupy the same space function. Further improvements have been made.[8]

Diatomic Helium

In the Born–Oppenheimer approximation the zero-order electronic Hamiltonian operator for diatomic helium consists of four hydrogen-molecule-ion-like (HMIL) Hamiltonian operators:

$$\widehat{H}^{(0)} = \widehat{H}_{\mathrm{HMIL}}(1) + \widehat{H}_{\mathrm{HMIL}}(2) + \widehat{H}_{\mathrm{HMIL}}(3) + \widehat{H}_{\mathrm{HMIL}}(4) \qquad (20.3\text{-}13)$$

where the HMIL Hamiltonian is

$$\widehat{H}_{\mathrm{HMIL}} = -\frac{\hbar^2}{2m}\nabla^2 + \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{Z}{r_{\mathrm{A}}} - \frac{Z}{r_{\mathrm{B}}}\right) \qquad (20.3\text{-}14)$$

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[7] W. J. Hunt, P. J. Hay, and W. A. Goddard, *J. Chem. Phys.*, **57**, 738 (1972); W. A. Goddard, T. H. Dunning, W. J. Hunt, and P. J. Hay, *Acc. Chem. Res.*, **6**, 368 (1973).

[8] I. N. Levine, *op. cit.*, p. 612ff (note 4).

For the He_2 molecule we let $Z = 2$. Electron–electron repulsion terms are omitted from this zero-order Hamiltonian and the constant nuclear repulsion term $\mathscr{V}_{nn}$ has also been omitted. At the end of the calculation we must add $\mathscr{V}_{nn}$ to the electronic energy to obtain the zero-order Born–Oppenheimer energy.

The zero-order Hamiltonian operator of Eq. (20.3-13) leads to a zero-order electronic wave function that is a product of four hydrogen-molecule-ion-like orbitals and to a zero-order energy that is equal to the sum of four orbital energies. To choose the four orbitals corresponding to the ground state, we apply the Aufbau principle: We choose the set of orbitals with the lowest sum of orbital energies consistent with the Pauli exclusion principle. The zero-order LCAOMO ground-state wave function including spin but without antisymmetrization is

$$\Psi^{(0)} = \psi_{\sigma_g 1s}(1)\alpha(1)\psi_{\sigma_g 1s}(2)\beta(2)\psi_{\sigma_u^* 1s}(3)\alpha(3)\psi_{\sigma_u^* 1s}(4)\beta(4) \tag{20.3-15}$$

Since no two electrons occupy the same spin orbital, this function can be antisymmetrized.

Exercise 20.9

Antisymmetrize the function of Eq. (20.3-15) by writing it as a 4-by-4 Slater determinant. How many terms would there be if you expanded this determinant?

The wave function of Eq. (20.3-15) corresponds to the electron configuration $(\sigma_g 1s)^2(\sigma_u^* 1s)^2$, with two electrons occupying bonding orbitals and two occupying antibonding orbitals. In order to agree with the general chemistry definition, we define the *bond order* as:

$$\text{Bond order} = \text{BO} = \frac{1}{2}(n_{\text{bonding}} - n_{\text{antibonding}}) \tag{20.3-16}$$

where n_{bonding} is the number of electrons occupying bonding orbitals and $n_{\text{antibonding}}$ is the number of electrons occupying antibonding orbitals. The bond order of the diatomic helium molecule in its ground state is 0. The repulsive effect of the antibonding orbitals roughly cancels the attractive effect of the bonding orbitals. The He_2 molecule does not exist in its ground state, but has been observed spectroscopically in excited states.

Molecules with More Than Four Electrons

For homonuclear diatomic molecules with more than four electrons, we require additional molecular orbitals beyond the $\sigma_g 1s$ and $\sigma_u^* 1s$ orbitals. For Li_2 and Be_2 we can use the $\sigma_g 2s$ and the $\sigma_u^* 2s$ orbitals in Eq. (20.2-9) and Eq. (20.2-10). The electron configuration of Li_2 in the ground state is

$$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2$$

and that of Be_2 is

$$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2$$

The bond order for Li_2 equals unity, and the bond order for Be_2 is zero, explaining why Be_2 does not exist in its ground state.

In order to discuss molecules beyond Be_2, we construct additional LCAOMOs, following the same policies that we applied earlier: (1) Each LCAOMO is a combination of two atomic orbitals centered on different nuclei; (2) each LCAOMO is an eigenfunction of the symmetry operators belonging to the molecule. From each pair of atomic orbitals, a bonding orbital and an antibonding orbital can be constructed. We construct six space orbitals from the real atomic orbitals of the 2_p subshells:

$$\psi_{\sigma_g 2p_z} = C(\psi_{2p_z\mathrm{A}} - \psi_{2p_z\mathrm{B}}) \tag{20.3-17a}$$

$$\psi_{\sigma_u^* 2p_z} = C(\psi_{2p_z\mathrm{A}} + \psi_{2p_z\mathrm{B}}) \tag{20.3-17b}$$

$$\psi_{\pi_u 2p_x} = C(\psi_{2p_x\mathrm{A}} + \psi_{2p_x\mathrm{B}}) \tag{20.3-17c}$$

$$\psi_{\pi_g^* 2p_x} = C(\psi_{2p_\mathrm{A}} - \psi_{2p_x\mathrm{B}}) \tag{20.3-17d}$$

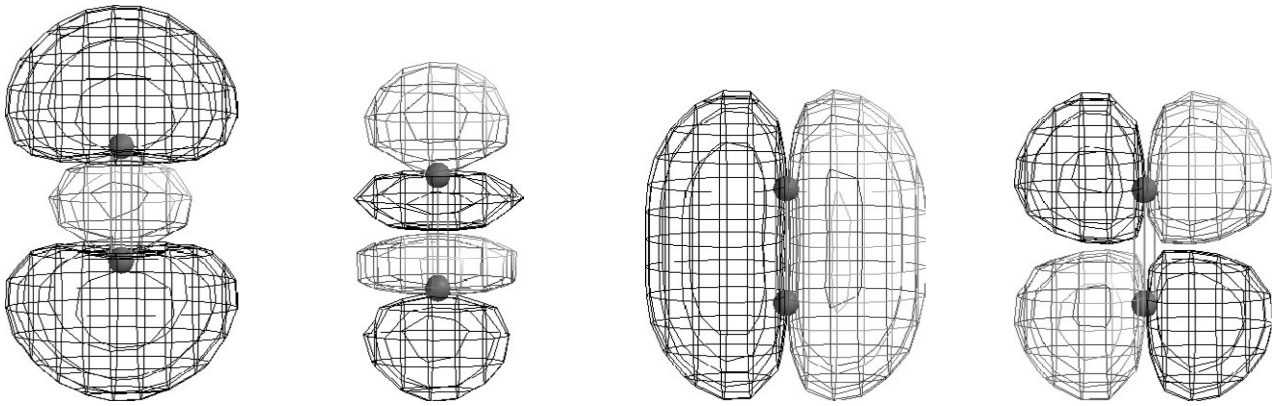
$$\psi_{\pi_u 2p_y} = C(\psi_{2p_y\mathrm{A}} + \psi_{2p_y\mathrm{B}}) \tag{20.3-17e}$$

$$\psi_{\pi_g^* 2p_y} = C(\psi_{2p_y\mathrm{A}} - \psi_{2p_y\mathrm{B}}) \tag{20.3-17f}$$

The normalizing constant c can have a different value in each case. The complex $2p$ atomic orbitals could be used as basis functions instead of the real $2p$ orbitals in order to have a definite value of L_z for each orbital.

Figure 20.11 shows the orbital regions of the real LCAOMOs constructed from $2p$ atomic orbitals. The $2p_z$ atomic orbitals produce sigma molecular orbitals since they correspond to $m = 0$. The $\pi_u 2p_x$ and $\pi_u 2p_y$ orbitals in Eq. (20.3-17) are called pi orbitals since the $2p_x$ and $2p_y$ atomic orbitals are linear combinations of the $2p1$ and $2p, -1$ orbitals. If complex LCAOMOs were constructed from the $2p1$ and $2p, -1$ orbitals, the bonding orbitals would be called $\pi_u 2p1$ and $\pi_u 2p, -1$ and the antibonding orbitals would be called $\pi_g^* 2p1$ and $\pi_g^* 2p, -1$. These orbitals would be eigenfunctions of the $\widehat{L}_z$ operator with $m = 1$ and $m = -1$. The bonding pi orbitals are "u" instead of "g" because the two lobes of the $2p$ atomic orbitals have opposite signs, making the bonding pi orbitals eigenfunctions of the inversion operator with eigenvalue -1.

Figure 20.12 shows a *correlation diagram* in which the energies of the atomic orbitals and the LCAO molecular orbitals are shown schematically with line segments connecting the LCAOMOs and the atomic orbitals from which they were constructed. When using these orbitals for a particular diatomic molecule, the atomic orbitals with



(a) (b) (c) (d)

Figure 20.11 Orbital Regions for LCAO Molecular Orbitals Made from $2p$ Atomic Orbitals. (a) The $\sigma_g 2p_z$ LCAOMO. (b) The $\sigma_u^* 2p_y$ LCAOMO. (c) The $\pi_u 2p_y$ LCAOMO. (d) The $\pi_g^* 2p_y$ LCAOMO. Positive regions are in black and negative regions are in gray.

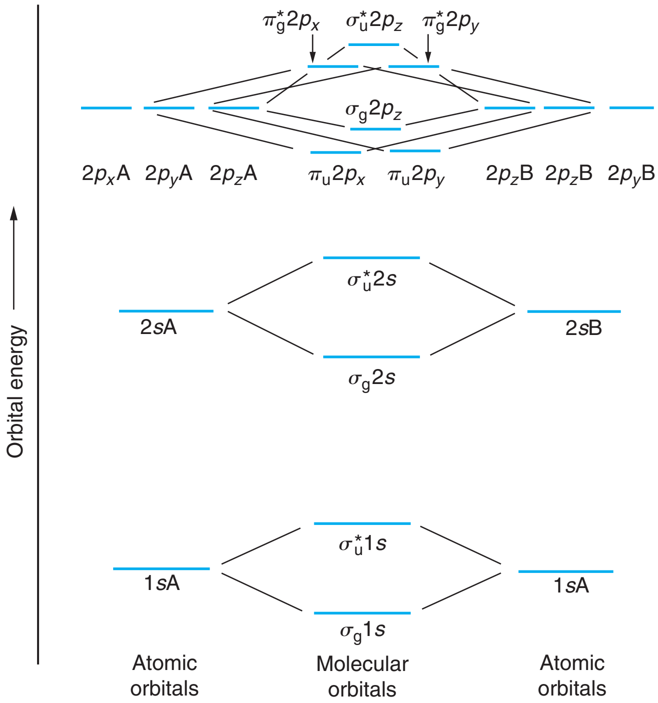


Figure 20.12 Correlation Diagram for Homonuclear Diatomic Molecules.

the appropriate value of Z are used. From Figure 19.4 it is apparent that the atomic orbital energies depend on the nuclear charge, and the LCAOMO energies also depend on nuclear charge as well as on internuclear distance. The order of the LCAOMO energies in the figure is correct for the elements lithium through nitrogen for distances near the equilibrium internuclear distance. For oxygen and fluorine the $\sigma_g 2p_z$ bonding orbital is lower in energy than the $\pi_u 2p_x$ and $\pi_u 2p_y$ bonding orbitals. In a sigma orbital the electron moves in a region more directly between the nuclei and would be more effective in screening the nuclear charges from each other than in a pi orbital. With the larger nuclear charges of the O and F atoms this screening is apparently more important than with the other atoms.

We now have enough orbitals for the ground states of all of the homonuclear diatomic molecules of elements of the first and second rows of the periodic table. The electron configurations are shown in Table 20.2 along with the bond orders. In B_2 and O_2 the final two electrons are assigned to different degenerate space orbitals with parallel spins in accordance with Hund's first rule, which applies to molecules as well as to atoms. Hund's second and third rules do not apply, because L is not a good quantum number for molecules. The electron configurations in Table 20.2 convey all of the information conveyed by writing an orbital wave function.

Two degenerate orbitals are analogous to a subshell and could be lumped together. The ground-state electron configuration of O_2 would then be written

$$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p)^2(\pi_u 2p)^4(\pi_g^* 2p)^2$$

This electron configuration does not explicitly show that the final two antibonding electrons occupy different space orbitals.

Table 20.2 Ground-State Electron Configurations of Homonuclear Diatomic Molecules

	Electron Configuration	Bond Order
H_2:	$(\sigma_g 1s)^2$	1
He_2:	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2$	0
Li_2:	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2$	1
Be_2:	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2$	0
B_2:	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p_x)(\pi_u 2p_y)$	1
C_2:	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2$	2
N_2:	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2(\sigma_g 2p_z)^2$	3
O_2:	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p_z)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2(\pi_g^* 2p_x)(\pi_g^* 2p_y)$	2
F_2:	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p_z)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2(\pi_g^* 2p_x)^2(\pi_g^* 2p_y)^2$	1
Ne_2:	$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\sigma_g 2p_z)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2(\pi_g^* 2p_x)^2(\pi_g^* 2p_y)^2(\sigma_u^* 2p_z)^2$	0

EXAMPLE 20.5

Write an orbital wave function without antisymmetrization or normalization for the diatomic boron molecule in its ground level.

Solution

$$\begin{aligned}\Psi = {} & \psi_{\sigma_g 1_s}(1)\alpha(1)\psi_{\sigma_g 1s}(2)\beta(2)\psi_{\sigma_u^* 1s}(3)\alpha(3)\psi_{\sigma_u^* 1s}(4)\beta(4) \\ & \times\ \psi_{\sigma_g 2s}(5)\alpha(5)\psi_{\sigma_g 2_s}(6)\beta(6)\psi_{\sigma_u^* 2s}(7)\alpha(7)\psi_{\sigma_u^* 2s}(8)\beta(8) \\ & \times\ \psi_{\pi_u 2p_x}(9)\alpha(9)\psi_{\pi_u 2p_y}(10)\alpha(10)\end{aligned}$$

This wave function is one of the three triplet wave functions making up the ground level. Another triplet function contains two β spin functions instead of α factors for electrons 9 and 10 and the third triplet function contains the symmetric spin factor $\sqrt{\frac{1}{2}}[\alpha(9)\beta(10) + \beta(9)\alpha(10)]$. There is also a singlet function containing the antisymmetric spin factor $\sqrt{\frac{1}{2}}[\alpha(9)\beta(10) - \beta(9)\alpha(10)]$.

Exercise 20.10

Write an orbital wave function without antisymmetrization or normalization for

a. Diatomic oxygen in its ground level.

b. Diatomic helium in the excited-state electron configuration $(\sigma_g 1s)^2(\sigma_u^* 1s)(\sigma_g 2s)$. What is the bond order for this molecule? Do you think it could exist?

Term Symbols for Homonuclear Diatomic Molecules

As with atoms, term symbols are used to designate values of angular momentum quantum numbers for homonuclear diatomic molecules. The scheme is slightly different from the Russell–Saunders scheme that is used for atoms, since L is not a good quantum number. The operator $\widehat{L}_z$ does commute with the electronic Hamiltonian and an energy eigenfunction can be an eigenfunction of $\widehat{L}_z$:

$$\widehat{L}_z\Psi = \hbar M_L \Psi \tag{20.3-18}$$

where M_L is the same quantum number as in the atomic case. We define a non-negative quantum number Λ equal to the magnitude of M_L.

$$\Lambda = |M_L| \tag{20.3-19}$$

Since there is no quantum number L, the values of M_L are not limited.

The main part of the molecular term symbol is a capital Greek letter that specifies the value of Λ:

Value of Λ	Symbol
0	Σ
1	Π
2	Δ
3	Φ
etc.	

Notice the similarity with the atomic term symbols with the letters S, P, D, and F.

The spin angular momentum operators commute with the electronic Hamiltonian operator, so the energy eigenfunctions can be eigenfunctions of $\widehat{S}^2$ and $\widehat{S}_z$. The spin quantum numbers S and M_S follow the same pattern as with atoms. A left superscript equal to $2S + 1$ is used on the term symbol as with atoms, and the same terminology is used (singlet, doublet, triplet, quartet, and so on). States with the same values of Λ and S constitute an energy level, which is called a *term*. In the ground state of H_2 both of the electrons occupy σ orbitals with $m = 0$ so that $M_L = 0$ and $\Lambda = 0$. The ground level of the H_2 molecule is nondegenerate and the term symbol is ${}^1\Sigma$ (singlet sigma).

Subscripts and superscripts are added to the term symbol to specify symmetry properties. The energy eigenfunctions of homonuclear diatomic molecules can be chosen to be eigenfunctions of the symmetry operators that belong to the molecule. In an orbital wave function, the symmetry operators must be applied to all of the orbitals. For example, if the wave function contains an even number of orbitals with eigenvalues -1, the eigenvalue of the wave function is $+1$. If the wave function is an eigenfunction of the inversion operator with eigenvalue $+1$, a right subscript g is attached to the term symbol. If it is an eigenfunction of the inversion operator with eigenvalue -1, a right subscript u is attached. With sigma terms, if the wave function is an eigenfunction of a $\widehat{\sigma}_\mathrm{v}$ operator with eigenvalue $+1$ a right superscript $+$ is added, and if it is an eigenfunction of this operator with eigenvalue -1 a right superscript $-$ is added. The complete term symbol for the ground level of a hydrogen molecule is ${}^1\Sigma_\mathrm{g}^+$ ("singlet sigma plus g"). The excited electron configuration $(\sigma_\mathrm{g}1s)(\sigma_\mathrm{u}^*1s)$ of the H_2 molecule can correspond to two different terms, a singlet and a triplet. The eigenvalue of the inversion operator is -1 for both terms, because one orbital is g and the other is u. The term symbols for this configuration are ${}^1\Sigma_\mathrm{u}^+$ and ${}^3\Sigma_\mathrm{u}^+$.

Term symbols can be written for the ground levels of homonuclear diatomic molecules from inspection of their electron configurations and use of Hund's first rule. Consider the ground level of the B_2 molecule, with six electrons. Using the Aufbau principle, we choose the $\sigma_g 1s$ and $\sigma_u^* 1s$ space orbitals for the first four electrons. The electron spins cancel in these orbitals, so they make no contribution to S. These orbitals all correspond to $m = 0$, so they make no contribution to M_L. The two degenerate pi bonding space LCAOMOs are the next available orbitals. By Hund's first rule, the remaining two electrons occupy different space orbitals with unpaired spins so that $S = 1$. To determine the value of Λ, we choose the complex pi orbitals containing the Φ_1 and Φ_{-1} functions instead of the Φ_{1x} and Φ_{1y} functions, so that $m = 1$ for one pi orbital and $m = -1$ for the other. We find that $M_L = 0$ and $\Lambda = 0$, corresponding to a $^3\Sigma$ term.

Both of the real bonding pi orbitals have eigenvalue -1 for the inversion operator, so their product has eigenvalue $+1$. The right subscript is g. The same vertical reflection plane is used for all orbitals to determine whether the term is $+$ or $-$. A vertical mirror plane in the xz plane will give eigenvalue $+1$ for the $\pi_u 2p_x$ orbital and eigenvalue -1 for the $\pi_u 2p_y$ orbital. The eigenvalues would be reversed for a mirror plane in the yz plane, and the product gives an eigenvalue of -1 in either case. The term symbol for the ground state of B_2 is $^3\Sigma_g^-$. The same result could be obtained in a more complicated way by separately considering the real and imaginary parts of the complex pi orbitals.

Exercise 20.11

Argue that the same term symbol occurs for a homonuclear diatomic molecule if the $\pi_u 2, -1$ and $\pi_u 2, +1$ orbitals are considered instead of the $\pi_u 2p_x$ and $\pi_u 2p_y$ orbitals.

An Alternative Set of Configurations

The attractive effect of an electron in a bonding orbital and the repulsive effect of an electron in an antibonding orbital approximately cancel, so the variational energy will be almost unchanged if we replace one bonding LCAOMO and one antibonding LCAOMO by the two atomic orbitals from which these LCAOMOs were constructed. If this is done, electrons occupying atomic orbitals are counted as nonbonding and are omitted from bond order calculations.

EXAMPLE 20.6

Give the electron configuration for the ground state of C_2 using nonbonding orbitals as much as possible.

Solution

There are 12 electrons. The electron configuration is

$$(1s\mathrm{A})^2(1s\mathrm{B})^2(2s\mathrm{A})^2(2s\mathrm{B})^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2$$

The bond order is equal to 2, with four bonding electrons, no antibonding electrons, and eight nonbonding electrons.

Exercise 20.12

a. Using as many nonbonding orbitals as possible give the ground-state electron configuration of B_2. Write the corresponding orbital wave function without antisymmetrization.

b. Using as many nonbonding orbitals as possible give the ground-state electron configuration of O_2. Write the corresponding orbital wave function without antisymmetrization.

Homonuclear Diatomic Molecules in the Valence-Bond Approximation

For the ground states of some homonuclear diatomic molecules satisfactory simple valence-bond wave functions can be constructed. In this approximation each pair of bonding electrons occupies a bonding factor constructed from two atomic orbitals on different nuclei as in Eq. (20.3-7). All other electrons occupy nonbonding orbitals since the valence-bond theory has nothing analogous to antibonding orbitals. The resulting wave function is very similar to LCAOMO wave functions that employ nonbonding orbitals as in Example 20.6. We make no attempt to describe the ground states of diatomic boron and diatomic oxygen since the bonding factors do not accommodate unpaired electrons.

EXAMPLE 20.7

Write a simple valence bond wave function for C_2 in its ground state.

Solution

$$\begin{aligned}\Psi = {}& \psi_{1s\mathrm{A}}(1)\alpha(1)\psi_{1s\mathrm{A}}(2)\beta(2)\psi_{1s\mathrm{B}}(3)\alpha(3)\psi_{1s\mathrm{B}}(4)\beta(4)\\ &\times \psi_{2s\mathrm{A}}(5)\alpha(5)\psi_{2s\mathrm{A}}(6)\beta(6)\psi_{2s\mathrm{B}}(7)\alpha(7)\psi_{2s\mathrm{B}}(8)\beta(8)\\ &\times \sqrt{\frac{1}{2}}[\psi_{2p_x\mathrm{A}}(9)\psi_{2p_x\mathrm{B}}(10) + \psi_{2p_x\mathrm{B}}(9)\psi_{2p_x\mathrm{A}}(10)]\\ &\times [\alpha(9)\beta(10) - \beta(9)\alpha(10)]\\ &\times \sqrt{\frac{1}{2}}[\psi_{2p_y\mathrm{A}}(11)\psi_{2p_y\mathrm{B}}(12) + \psi_{2p_y\mathrm{B}}(11)\psi_{2p_y\mathrm{A}}(12)]\\ &\times [\alpha(11)\beta(12) - \beta(11)\alpha(12)] \qquad (20.3\text{-}20)\end{aligned}$$

Exercise 20.13

Write the wave function corresponding to the configuration of C_2 in Example 20.6 without antisymmetrization and compare it with the wave function in Eq. (20.3-20).

A bonding factor corresponds to a single covalent bond, so the bond order for the C^2 wave function in Example 20.7 is equal to 2, as in the LCAOMO description of Example 20.6. This wave function does not include ionic terms, but ionic terms can be added to each bonding factor in the wave function to make an improved valence-bond function.

Exercise 20.14

a. Write a simple valence-bond wave function for the ground state of diatomic fluorine. Construct the bonding factor from $2p_z$ orbitals and place the "lone pairs" in the nonbonding $2s$, $2p_x$, and $2p_y$ orbitals.

b. Write a modified valence-bond wave function for the ground state of diatomic fluorine, including ionic terms.

Excited States of Homonuclear Diatomic Molecules

Excited states are represented in the LCAOMO approximation by electron configurations other than that of the ground state. Term symbols can be written for an excited electron configuration.

EXAMPLE 20.8

a. Write the term symbols that can occur for the excited Be_2 electron configuration

$$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)(\sigma_u 2p1)$$

b. Which term will have the lowest energy?

c. What is the bond order for this electron configuration?

d. Do you think the Be_2 molecule could exist in the excited state corresponding to this electron configuration?

Solution

a. $M_L = 1$ and there are two u orbitals, so that the term symbols are ${}^3\Pi_g$ and ${}^1\Pi_g$.

b. The lowest energy term symbol will have the maximum value of S, according to Hund's rule: ${}^3\Pi_g$

c. Bond order $= (1/2)(5 - 3) = 1$

d. Since the bond order is nonzero, the molecule should exist in this configuration.

PROBLEMS

Section 20.3: Homonuclear Diatomic Molecules

20.14 Give the term symbol or symbols for each of the excited electron configurations of the hydrogen molecule:

a. $(\sigma_g 1s)(\pi_u 2p1)$

b. $(\pi_u 2p1)(\sigma_g^* 2p, -1)$

20.15 Give the term symbol or symbols for each of the excited electron configurations of the hydrogen molecule:

a. $(\sigma_g 2p0)^2$

b. $(\sigma_g 1s)(\sigma_g 2p0)$

20.16 Give the term symbol for the ground-state electron configuration of each of the second-row homonuclear diatomic molecules (Li_2 through F_2).

20.17 Excited states of diatomic neon exist, although the ground state has bond order zero. Give the electron configuration and term symbol for two different excited states that might exist.

20.18 For each of the following ions or molecules, give the bond order and the number of unpaired electrons in the ground state:

a. C_2^+

b. B_2^+

c. Be_2^+

20.19 For each of the following ions or molecules, give the bond order and the number of unpaired electrons in the ground state of:

a. O_2^-

b. N_2^+

c. F_2^+

20.20 Give the electron configuration, bond order, and term symbol for the ground state of:

a. O_2

b. O_2^-

c. O_2^+

Which will have the shortest bond? Which will have the largest vibrational frequency? Explain your answers.

20.21 The ionization potential is defined as the energy required to remove an electron from a gaseous atom or molecule. Sketch a rough graph of your predictions of the ionization potentials of the homonuclear molecules Li_2 through F_2 as a function of atomic number. Explain.

20.22 The electron affinity is defined in Chapter 19, and applies to molecules as well as to atoms. It is energy given off when a gaseous atom or molecule gains an electron. Decide which of the homonuclear diatomic molecules from Li_2 through F_2 would likely have a positive electron affinity (spontaneously attract an electron) and give your reasoning.

20.23 If a hydrogen molecule is somehow excited into the state with configuration $(\sigma_g 2s)^2$ will the molecule dissociate? Explain.

20.24 An important excited state of O_2 is a singlet state. It is highly toxic and biological organisms have defenses against it. Write the electron configuration and the term symbol for the lowest-energy singlet state of O_2.

20.4 Heteronuclear Diatomic Molecules

Heteronuclear diatomic molecules are not as symmetrical as homonuclear molecules, and we cannot evaluate coefficients in LCAO molecular orbitals by requiring that the orbitals have the proper symmetry. Variational, SCF, or density functional calculations must be used to evaluate the coefficients.

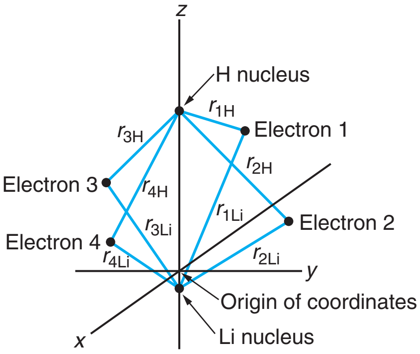


Figure 20.13 The LiH Molecule System.

Lithium Hydride

The simplest stable heteronuclear molecule is lithium hydride, LiH. Like He_2, LiH has two nuclei and four electrons. We say that these two molecules are *isoelectronic* (have the same number of electrons). However, LiH is a stable molecule in the ground state while He_2 is not. Figure 20.13 shows the LiH system. We apply the Born–Oppenheimer approximation and place the nuclei on the z axis and place the origin of coordinates at the center of mass of the nuclei. The zero-order electronic Hamiltonian operator for the LiH molecule is (omitting the constant internuclear repulsion term $\mathcal{V}_{\mathrm{nn}}$)

$$\widehat{H}_{\mathrm{el}}^{(0)} = \widehat{H}_1(1) + \widehat{H}_1(2) + \widehat{H}_1(3) + \widehat{H}_1(4) \tag{20.4-1}$$

where $\widehat{H}_1(i)$ is a one-electron Hamiltonian operator for electron number i:

$$\widehat{H}_1(i) = -\frac{\hbar^2}{2m}\nabla_i^2 + \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{r_{i\mathrm{H}}} + \frac{3}{r_{i\mathrm{Li}}}\right) \qquad (i = 1, 2, 3, 4) \tag{20.4-2}$$

We denote the distance from the hydrogen nucleus to electron number i by $r_{i\mathrm{H}}$ and the distance from the lithium nucleus to electron number i by $r_{i\mathrm{Li}}$.

The zero-order Hamiltonian operator of Eq. (20.4-1) gives a time-independent Schrödinger equation in which the variables can be separated by assuming a product wave function:

$$\Psi^{(0)} = \psi_1(1)\psi_2(2)\psi_3(3)\psi_4(4) \tag{20.4-3}$$

where each factor is a molecular orbital. We construct LCAOMOs to represent these molecular orbitals, but must now abandon our policy of including only two atomic orbitals in our basis set. We take a basis set consisting of four atomic orbitals: the lithium $1s$ orbital, the lithium $2s$ orbital, the lithium $2p_z$ orbital, and the hydrogen $1s$ orbital. This is called a *minimal basis set*. All of these basis orbitals correspond to $m = 0$. The symmetry operators belonging to the molecule are the identity operator, all of the rotation operators about the z axis, and all of the $\widehat{\sigma}_{\mathrm{v}}$ operators. The $2p_x$ and $2p_y$ orbitals are not included since they have different eigenvalues for these symmetry operators. Each of the basis functions is an eigenfunction of these operators with eigenvalues equal to 1. Any linear combination of the basis functions will be a sigma orbital and will be an eigenfunction of these symmetry operators with eigenvalue equal to 1.

Four independent LCAOMOs can be made from our basis set of four atomic orbitals. We denote them by

$$\psi_{j\sigma} = c_{1s\mathrm{Li}}^{(j)}\psi_{1s\mathrm{Li}} + c_{2s\mathrm{Li}}^{(j)}\psi_{2s\mathrm{Li}} + c_{2p_z\mathrm{Li}}^{(j)}\psi_{2p_z\mathrm{Li}} + c_{1s\mathrm{H}}^{(j)}\psi_{1s\mathrm{H}} \tag{20.4-4}$$

where the label j can equal 1, 2, 3, or 4. We have added a σ subscript to indicate that all of these LCAOMOs are sigma orbitals. Values of the coefficients in the LCAOMOs can be obtained by the variation method or the Hartree–Fock–Roothaan method.[9] Table 20.3 shows the results of a Hartree–Fock–Roothaan calculation and Figure 20.14 is a correlation diagram showing schematically the atomic and molecular orbital energies. By the Aufbau principle, the ground-state wave function is (without antisymmetrization)

$$\Psi_{\mathrm{g}\sigma} = \psi_{1\sigma}(1)\alpha(1)\psi_{1\sigma}(2)\beta(2)\psi_{2\sigma}(3)\alpha(3)\psi_{2\sigma}(4)\beta(4) \tag{20.4-5}$$

where the orbitals are numbered from the lowest energy to the highest energy. The 1σ molecular orbital is nearly the same as the lithium $1s$ orbital and is essentially nonbonding. The 2σ molecular orbital is a bonding orbital. The molecule has two

Table 20.3 Results of a Hartree–Fock–Roothaan Calculation for the LiH Ground State at an Internuclear Distance of 159 pm

MO	$c_{1s\mathrm{Li}}$	$c_{2s\mathrm{Li}}$	$c_{2p_z\mathrm{Li}}$	$c_{1s\mathrm{H}}$
1	0.9996	−0.0000	−0.0027	0.0035
2	0.0751	0.3288	−0.2048	−0.7022
3	−0.0115	0.7432	0.6601	0.1236
4	−0.1256	0.8769	−1.0107	1.2005

From A. M. Karo, *J. Chem. Phys.*, **30**, 1241 (1959).

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[9] C. C. J. Roothaan, *Rev. Modern Phys.*, **23**, 69 (1951).

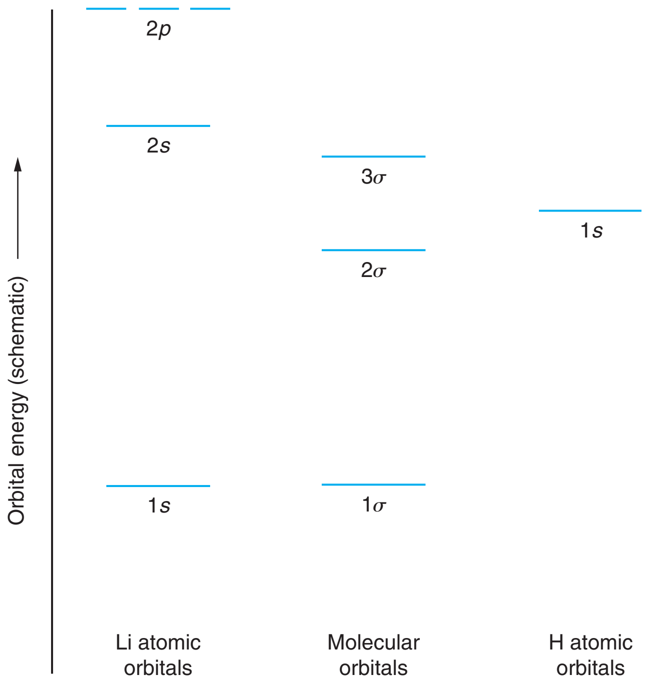


Figure 20.14 Correlation Diagram for the Lithium Hydride Molecule.

nonbonding electrons and two bonding electrons for a single bond, in contrast with the He_2 molecule, which has two bonding and two antibonding electrons, for a bond order of zero.

Hybrid Orbitals

We would like to have a simple method of predicting roughly what an optimized orbital wave function for a given molecule should be without doing any calculations. The SCF results for LiH suggest a pattern that we can use for such predictions. We want to construct a wave function that is approximately the same as that of Eq. (20.4-5) but contains linear combinations of no more than two atomic orbitals.

The 1σ LCAOMO is nearly the same as the $1s$ lithium orbital, so we replace this LCAOMO by the $1s$ lithium orbital, a nonbonding orbital. The 2σ orbital contains three atomic orbitals with coefficients that are appreciably nonzero. The coefficients of the $2s$ lithium and $2p_z$ lithium orbitals in the 2σ LCAOMO are roughly the same magnitude with opposite signs. To a usable approximation, we will replace these two atomic orbitals by a *hybrid atomic orbital*:

$$\psi_{2sp(1)} = c_1(-\psi_{2s} + \psi_{2p_z}) \tag{20.4-6}$$

where c_1 is a normalizing constant that can be shown to be equal to $\sqrt{1/2}$. The designation $2sp$ means that the new atomic orbital is a linear combination of the $2s$ and a $2p$ orbital, and the 1 subscript indicates that this is the first orbital of this type. Since we can define two independent linear combinations from two functions, there is another $2sp$ hybrid orbital:

$$\psi_{2sp(2)} = c_2(-\psi_{2s} - \psi_{2p_z}) \tag{20.4-7}$$

This orbital is orthogonal to $\psi_{2sp(1)}$.

EXAMPLE 20.9

Using the fact that the $2s$ and $2p_z$ orbitals are normalized and orthogonal to each other, show that c_1 and c_2 both equal $\sqrt{1/2}$ to normalize the hybrid orbitals.

Solution

$$\int \psi^*_{2sp(1)}\psi_{2sp(1)}dq = 1$$

$$c_1^2\int[-\psi_{2s} + \psi_{2pz}][-\psi_{2s} + \psi_{2pz}]dq = 1$$

$$c_1^2\int \psi_{2s}^2 dq - 2c_1^2\int \psi_{2s}\psi_{2pz}dq + c_1^2\int \psi_{2pz}^2 dq = c_1^2(1 - 2\times 0 + 1) = 2c_1^2 = 1$$

$$c_1 = \frac{1}{\sqrt{2}}$$

$$\int \psi^*_{2sp(2)}\psi_{2sp(2)}dq = 1$$

$$c_2^2\int[-\psi_{2s} - \psi_{2pz}]^2 dq = 1$$

$$c_2^2\int \psi_{2s}^2 dq + 2c_2^2\int \psi_{2pz}\psi_{2s}dq + c_2^2\int \psi_{2pz}^2 dq = c_2^2(1 + 0 + 1) = 2c_2^2 = 1$$

$$c_2 = \frac{1}{\sqrt{2}}$$

Exercise 20.15

Show that the $2sp(1)$ and $2sp(2)$ hybrid orbitals are orthogonal to each other.

Figure 20.15 shows cross sections of the orbital regions of the $2s$ and $2p_z$ orbitals and of the $2sp(1)$ and $2sp(2)$ hybrid orbitals. In the $2sp(1)$ hybrid orbital the $2s$ and the $2p_z$ orbitals add in the direction of the positive z axis and partially cancel in the direction of the negative z axis. We say that this hybrid orbital is "directional," with its orbital region extending in the positive z direction. The orbital region of the $2sp(2)$ hybrid orbital extends in the opposite direction from that of the $2sp(1)$ orbital.

Using these hybrid orbitals as part of the basis set, we can approximate the two occupied LCAOMOs as linear combinations of no more than two atomic orbitals:

$$\psi_{1\sigma} = \psi_{1sLi} \tag{20.4-8a}$$

$$\psi_{2\sigma} = c_{2sp(1)\mathrm{Li}}\psi_{2sp(1)\mathrm{Li}} + c_{1s\mathrm{H}}\psi_{1s\mathrm{H}} = -0.47\psi_{2sp(1)\mathrm{Li}} - 0.88\psi_{1s\mathrm{H}} \tag{20.4-8b}$$

In the second expression for the 2σ orbital the values of the coefficients were chosen to maintain approximately the same relative weights of the atomic orbitals as in the Hartree–Fock–Roothaan orbital. Figure 20.16 shows the orbital region of the 2σ LCAOMO and shows that it is a bonding orbital with overlap between the nuclei. It

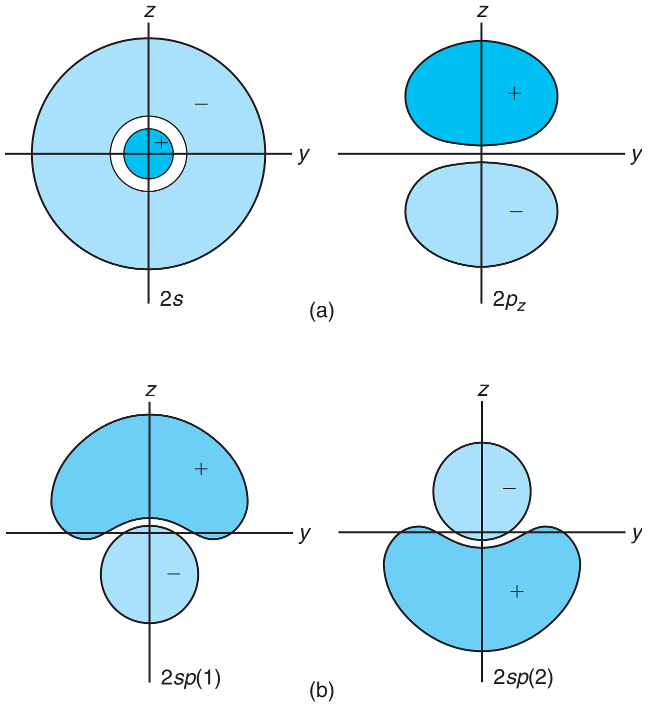


Figure 20.15 Orbital Regions for Nonhybridized and Hybridized Atomic Orbitals. (a) The nonhybridized orbital regions. (b) The hybridized orbital regions.

has cylindrical symmetry around the bond axis, as is always the case with a sigma orbital.

The 3σ molecular orbital has roughly equal coefficients for the $2s$ and $2p$ atomic orbitals with a nearly negligible contribution from the hydrogen $1s$ orbital. We approximate it by the $2sp(2)$Li hybrid orbital. The 4σ orbital can be approximated as a linear combination of the $2sp(1)$Li hybrid orbital and the hydrogen $1s$ orbital. Our new orbitals only roughly approximate the Hartree–Fock–Roothaan orbitals but can be used for a qualitative description of the electronic states of the LiH molecule. With two electrons in the nonbonding $1s$Li orbital and two in the bonding 2σ orbital, we have a single bond.

Exercise 20.16

a. Is the 3σ molecular orbital a bonding, an antibonding, or a nonbonding orbital?

b. Estimate the coefficients to represent the 4σ molecular orbital as a linear combination of the $2sp(1)$Li hybrid orbital and the $1s$H orbital. Is this a bonding, an antibonding, or a nonbonding orbital?

Dipole Moments

In the approximate 2σ bonding orbital the coefficient of the $1s$H orbital is roughly twice as large as the coefficient of the $2sp(1)$Li orbital. There is thus a larger probability of finding an electron in the vicinity of the hydrogen nucleus than in the vicinity of the

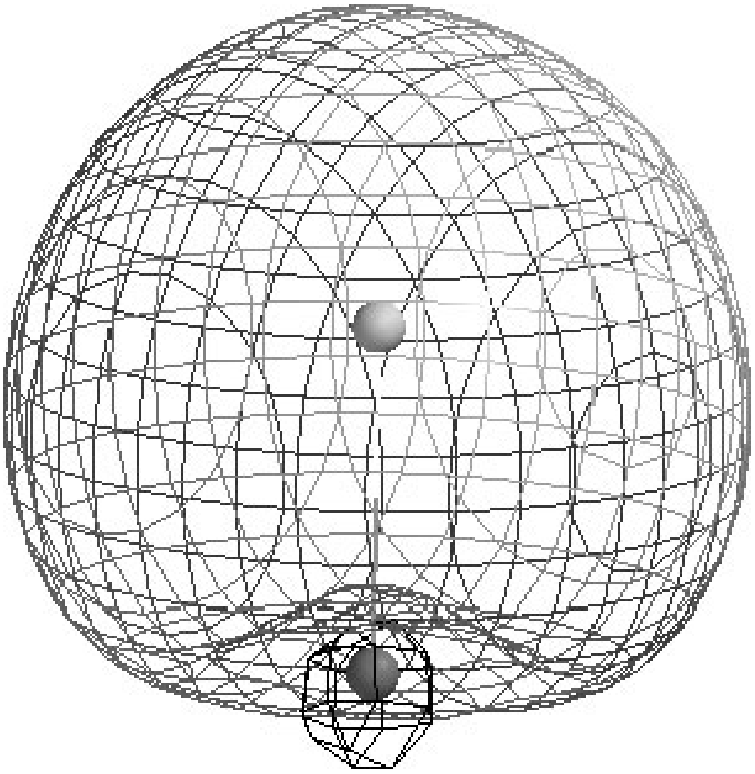


Figure 20.16 The Orbital Region of the Bonding LiH Orbital. Positive regions are in black and negative regions are in gray.

lithium nucleus if it occupies this space orbital. We call a chemical bond responding to this situation a *polar covalent bond*. The ends of the molecule possess net charges, giving the molecule a *dipole moment*.

If a collection of n electrical charges has a net charge of zero, its dipole moment is a vector defined by

$$\mu = \sum_{i=1}^{n} Q_i \mathbf{r}_i \tag{20.4-9}$$

where Q_i is the value of charge number i and $\mathbf{r}_i$ is its position vector. If there are only two electric charges $+Q$ and $-Q$ separated by a distance r, the magnitude of its dipole moment is

$$|\mu| = \mu = Qr \tag{20.4-10}$$

The dipole moment vector points from the negative charge to the positive charge. A larger dipole moment corresponds to a larger distance between the charges and/or larger charges.

EXAMPLE 20.10

For two charges of equal magnitude and opposite signs at arbitrary locations, show that the magnitude of the vector in Eq. (20.4-9) is the same as that given by Eq. (20.4-10).

Solution

Place a charge Q at $\mathbf{r}_2$ and a charge of $-Q$ at $\mathbf{r}_1$. The x component of μ is

$$\mu_x = Qx_2 + (-Q)_{x_1} = Q(x_2 - x_1)$$

The y and z components are similar.

$$\begin{aligned}|\mu| = \mu &= \left(\mu_x^2 + \mu_y^2 + \mu_z^2\right)^{1/2} \\ &= \left(Q^2(x_2 - x_1)^2 + Q^2(y_2 - y_1)^2 + Q^2(z_2 - z_1)^2\right)^{1/2} = Q|\mathbf{r}_2 - \mathbf{r}_1|\end{aligned}$$

Exercise 20.17

A quadrupole is the next level beyond a dipole for describing a charge distribution. A particular simple quadrupole consists of a charge $+Q$ at the origin, a charge $-Q$ at the point $(1,0)$, a charge $+Q$ at $(1,1)$, and a charge $-Q$ at $(0,1)$. Show that if there are no other charges, the dipole moment of this collection of charges vanishes.

The classical expression for the dipole moment in Eq. (20.4-9) contains no momentum components, so its quantum mechanical operator is the operator for multiplication by this expression. The expectation value of the electric dipole of a molecule in a state Ψ is

$$\langle\mu\rangle = \int \Psi^* \mu \Psi \, dq = \int \mu |\Psi|^2 dq \qquad (20.4\text{-}11)$$

where q is an abbreviation for the coordinates of all particles in the molecule. The factor $|\Psi|^2$ is the probability density for finding the charged particles in the system. The operator contains no spin dependence so spin functions and spin integrations can be omitted.

In the Born–Oppenheimer approximation the nuclei are fixed and we can sum their contributions without integrating. The nuclear contribution is given by

$$\mu_{\text{nuc}} = \sum_{A=1}^{n_{\text{n}}} \mathcal{e} Z_A \mathbf{r}_A \qquad (20.4\text{-}12)$$

where n_{n} is the number of nuclei and $\mathbf{r}_A$ is the position vector of nucleus number A, which contains Z_A protons. With a one-term orbital wave function in which the orbitals are orthogonal to each other, each orbital makes its contribution to the probability density independently, as in Eq. (18.3-8), which also holds for molecular orbitals. In an antisymmetrized orbital wave function the total electron probability density is the same as in the one-term function, as shown in Eq. (18.4-5). The expectation value of the dipole moment is given by

$$\langle\mu\rangle = \mu_{\text{nuc}} - \mathcal{e} \sum_{i=1}^{n_{\mathcal{e}}} \int \psi_i(i)^* \mathbf{r}_i \psi_i(i) d^3\mathbf{r}_i = \mu_{\text{nuc}} - \mathcal{e} \sum_{i=1}^{n_{\mathcal{e}}} \int \mathbf{r}_i |\psi_i(i)|^2 d^3\mathbf{r}_i \qquad (20.4\text{-}13)$$

where ψ_i is the ith occupied space orbital and where $n_{\mathcal{e}}$ is the number of electrons.

The formula shown in Eq. (20.4-13) is the same as if the ith electron were a "smeared-out" charge with a density distribution equal to $|\psi_i|^2$. It is a theorem of electrostatics that a spherically symmetrical distribution of charge has an effect outside of the charge distribution as though the charge were concentrated at the center of symmetry. An electron moving in an undistorted and unhybridized atomic orbital contributes to the charge density just as though it were at the nucleus. Electrons moving in LCAOMOs that have unequal coefficients make a larger contribution to the negative charge at the end of the molecule with the coefficient of larger magnitude, so that the LiH molecule has a sizable dipole moment, with the hydrogen end negative.

The SI unit in which dipole moments are measured is the coulomb-meter (C m). The experimental bond length of the LiH molecule is 1.596×10^{-10} m, so that if the bond were purely ionic with an undistorted Li^+ ion and an undistorted H^- ion,

$$\mu_{\text{ionic}} = (1.6022 \times 10^{-19}\ \mathrm{C})(1.595 \times 10^{-10}\ \mathrm{m}) = 2.56 \times 10^{-29}\ \mathrm{C\,m}$$

The Debye unit is named for Peter J. W. Debye, 1884–1966, a Dutch-American chemist who became famous for the Debye–Hückel theory of ionic solutions, but whose 1936 Nobel Prize in chemistry was for his work on dipole moments.

There is a common non-SI unit named the *Debye*, which is defined by

$$\boxed{1\ \text{Debye} = 3.335641 \times 10^{-30}\ \mathrm{C\,m}} \tag{20.4-14}$$

The Debye unit was originally defined in terms of the c.g.s. unit of charge, the electrostatic unit (esu), such that 1 Debye equals 10^{-18} esu cm (10^{-10} esu Å). The charge on a proton equals 4.80×10^{-10} esu, so that molecular dipole moments generally range from 0 to 10 Debye.

EXAMPLE 20.11

Estimate the dipole moment of the LiH molecule from the orbitals of Eq. (20.4-8).

Solution

The lithium nucleus has charge $3e$. The two nonbonding electrons in the 1σ orbital contribute as though they were at the lithium nucleus. The probability density of an electron in the 2σ orbital is

$$|\psi_{2\sigma}|^2 = (0.47)^2\psi_{2sp(1)\mathrm{Li}}^2 + (0.47)(0.88)\psi_{2sp(1)\mathrm{Li}}\psi_{1s\mathrm{H}} + (0.88)^2\psi_{1s\mathrm{H}}^2$$

We neglect the second term in this expression because it is appreciably nonzero only in the overlap region. The third term will make its contribution to the integral in Eq. (20.4-13) as though the electron were centered at the hydrogen nucleus. The $2sp(1)$ hybrid orbital does not have its center of charge exactly at the lithium nucleus, but we approximate the contribution of the first term as though it did. The net charge at the lithium nucleus is

$$Q_{\mathrm{Li}} = 3e - 2e - 2(0.47)^2 e = 0.56e = 8.9 \times 10^{-20}\ \mathrm{C}$$

The net charge at the hydrogen nucleus is

$$Q_{\mathrm{H}} = e - 2(0.88)^2 e = -0.56e = -8.9 \times 10^{-20}\ \mathrm{C}$$

with a bond length of 1.595×10^{-10} m,

$$\mu \approx (8.9 \times 10^{-20}\ \mathrm{C})(1.595 \times 10^{-10}\ \mathrm{m}) = 1.42 \times 10^{-29}\ \mathrm{C\,m} = 4.3\ \text{Debye}$$

This estimate of the dipole moment is about 60% as large as the value for a purely ionic bond, indicating a bond that is roughly 60% ionic in character. It agrees only roughly with the experimental value, 5.88 Debye.

Qualitative Description of Bonding in Molecules

The results of the Hartree–Fock–Roothaan treatment of lithium hydride conform to a general pattern that enables us to make qualitative predictions about other molecules. We will assume the following factors in making these predictions:

1. *Two atomic orbitals on different nuclei must have roughly equal orbital energies to form a good bonding LCAOMO.* If LCAOMOs are made from two atomic orbitals of moderately different energies, a bonding LCAOMO and an antibonding LCAOMO will result. The bonding LCAOMO will have a coefficient of larger magnitude for the atomic orbital of lower energy, and the antibonding LCAOMO will have a coefficient of larger magnitude for the higher-energy atomic orbital. If the atomic orbitals have equal energies, the coefficients of the two atomic orbitals will have equal magnitudes in both LCAOMOs. If the energies are greatly different, the lower-energy LCAOMO will be almost the same as the lower-energy atomic orbital, making it nearly a nonbonding orbital, like the $1s$ lithium orbital in LiH.
2. *Two atomic orbitals on different nuclei must have a fairly large overlap region to form a good bonding LCAOMO.* This rule is related to the fact that effective bonding electrons must have a fairly large probability of being found between the nuclei in order to attract both nuclei and stabilize the bond.
3. *Two atomic orbitals on different nuclei must have the same symmetry around the bond axis to form a good bonding LCAOMO.* In a diatomic molecule, two orbitals with different symmetry cannot form an eigenfunction of the appropriate symmetry operators. We will assume the same behavior in a polyatomic molecule.

We can relate the results of the lithium hydride calculation to this pattern. The $1s$ lithium orbital does not form a good bonding LCAOMO with the hydrogen $1s$ orbital because the difference in energies is large and because the overlap region of these two orbitals is small. The lithium $1s$ orbital therefore acts as a nonbonding orbital. The $2sp(1)$ hybrid has a large overlap region with the hydrogen $1s$ orbital and forms a good bonding orbital with it. The $2sp(2)$ orbital does not have a large overlap region with the hydrogen $1s$ orbital and constitutes a nonbonding orbital that is vacant in the ground state.

EXAMPLE 20.12

Describe the bonding in HF. Include a statement about the polarity of the molecule.

Solution

The fluorine $1s$ orbital acts as a nonbonding orbital. The fluorine $2p_x$ and $2p_y$ atomic orbitals do not have the same symmetry around the z axis (the bond axis), as does the hydrogen $1s$ orbital, and are not included in the bonding molecular orbital. They will act as nonbonding "lone-pair" orbitals. We make two hybrid orbitals with the fluorine $2s$ and $2p_z$ orbitals, denoted by $2sp(1)$ and $2sp(2)$. The $2sp(1)$ orbital forms a bonding orbital called the 1σ orbital with the hydrogen $1s$ orbital. There is also an antibonding orbital, which we denote by $2\sigma^*$ but which remains vacant in the ground state. The $2sp(2)$ orbital acts as a nonbonding lone-pair orbital. The energy of the fluorine $2sp(1)$ hybrid is lower than that of the hydrogen $1s$ orbital so the fluorine $2sp(1)$ atomic orbital will have a coefficient of larger magnitude in the bonding molecular orbital than will the hydrogen $1s$ orbital. The corresponding antibonding orbital (which remains vacant in the ground state) will have a coefficient of larger magnitude for the hydrogen $2s$ orbital. The molecule will be polar with the fluorine end negative.

The energies of the LCAOMOs and hybrid orbitals are shown schematically in the correlation diagram of Figure 20.17. The line segment for the bonding orbital is drawn closer to the fluorine side to indicate that this orbital has a greater contribution from the fluorine atomic orbital. The ground-state electron configuration is

$$(1s\mathrm{F})^2(2sp(2)\mathrm{F})^2(2p_x\mathrm{F})^2(2p_y\mathrm{F})^2(1\sigma)^2$$

Exercise 20.18

Describe the bonding in LiF. How much ionic character do you think there will be in the bond?

A qualitative description of the chemical bonding in carbon monoxide (CO) is obtained by constructing LCAOMOs similar to those of N_2, except that the coefficients for the C orbital and the O orbital will not have equal magnitudes. We use all of the atomic orbitals in the first two shells of both atoms as our basis set, but construct LCAOMOs with no more than two atomic orbitals in each linear combination. The $2p_x$ and $2p_y$ orbitals will combine to form pi molecular orbitals, while the $2p_z$ orbitals will combine to make a sigma molecular orbital. Oxygen's effective nuclear charge is greater than that of carbon so its orbital energies will lie somewhat lower than those of carbon, and the bonding LCAOMOs will have somewhat larger coefficients for the oxygen orbitals than for the carbon orbitals. The electron configuration of the molecule is the same as that of the N_2 molecule, although the orbitals are different:

$$(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^2$$

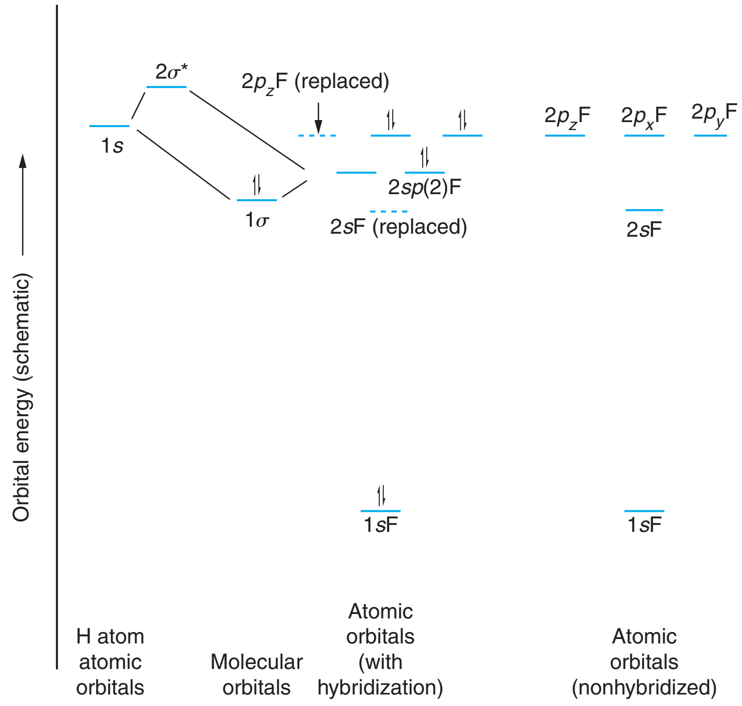


Figure 20.17 Correlation Diagram for Hydrogen Fluoride.

The designations g and u are not used because the orbitals are not eigenfunctions of the inversion operator, but we use the * symbol to designate an antibonding orbital. The bond order is 3, the same as in N_2. The bonding and antibonding effects in the lowest-energy four orbitals approximately cancel, so we can use the alternative electron configuration

$$(1s\mathrm{C})^2(1s\mathrm{O})^2(2s\mathrm{C})^2(2s\mathrm{O})^2(\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^2$$

The coefficients of the oxygen orbitals are greater in the bonding orbitals, so the bonding electrons contribute a net negative charge at the oxygen end of the molecule. The oxygen nucleus has two more protons than the carbon nucleus, and this contributes a net positive charge at the oxygen end, which slightly more than cancels the charge due to the electrons. The dipole moment of the CO molecule is rather small, about 0.1 Debye. The carbon end is negative, and it is this end that coordinates to transition metal atoms in various complexes, including the iron atom in hemoglobin in cases of CO poisoning.

EXAMPLE 20.13

Assuming the alternate electron configuration with eight electrons occupying nonbonding $1s$ and $2s$ orbitals and making zero net contribution to the dipole moment and assuming that the coefficients of the atomic orbitals in all three of the bonding molecular orbitals are the same, estimate the values of the coefficients corresponding to the experimental value of the dipole moment of the CO molecule.

Solution

The experimental bond length is 1.128 Å $= 1.128 \times 10^{-10}$ m.

$$\mu_{\mathrm{exp}} = 0.1\ D = 3.336 \times 10^{-31}\ \mathrm{C\,m}$$

The dipole moment is equal to the net charge at one end of the dipole times the bond length. The charge at the carbon end of the molecule is $(6e - 4e - 6x^2e)$ if C_{C} is the coefficient of the carbon orbital in the bonding LCAOMOs.

$$\text{Carbon: } (6e - 4e - 6C_{\mathrm{C}}^2e)(1.128 \times 10^{-10}\ \mathrm{m}) = 3.336 \times 10^{-31}\ \mathrm{C\,m}$$

$$C_{\mathrm{C}} = 0.575$$

Neglecting the overlap integrals, if C_{O} is the oxygen coefficient

$$C_{\mathrm{C}}^2 + C_{\mathrm{O}}^2 = 1$$
$$C_{\mathrm{O}}^2 = 1 - C_{\mathrm{C}}^2 = 1 - 0.330 = 0.670$$
$$C_{\mathrm{O}} = 0.818$$

This corresponds to the greater electronegativity of oxygen.

Exercise 20.19

a. Calculate the dipole moment that would occur for CO if the electrons were equally shared.

b. Write an improved electron configuration using $2sp$ hybrid orbitals to make the sigma bond and for the unshared valence electrons.

Electronegativity

Relative energies of atomic orbitals on different atoms are not always immediately available when we want to construct an approximate description of a molecule with unequal sharing of electrons. The *electronegativity* is an empirical parameter that can be used to estimate the degree of inequality of electron sharing in a bond between atoms of two elements. It was introduced by Pauling, who observed that polar covalent bonds generally have larger bond dissociation energies than nonpolar covalent bonds. If the electronegativity of element A is denoted by X_A and that of element B is denoted by X_B, Pauling defined

$$|X_A - X_B| = (0.102\,\text{mol}^{1/2}\,\text{kJ}^{-1/2})(\Delta E_{AB})^{1/2} \tag{20.4-15}$$

where ΔE_{AB} is the difference between the average bond energy of an A–B bond and the mean of the average bond energies of A–A and B–B bonds:

$$\Delta E_{AB} = E_{AB} - \frac{1}{2}[E_{AA} + E_{BB}] \tag{20.4-16}$$

Linus Pauling, 1901–1994, was a prominent American chemist who won the 1954 Nobel Prize in chemistry for his work on molecular structure and the 1963 Nobel Peace Prize for his work on nuclear disarmament.

Because Eq. (20.4-15) defines only electronegativity differences, Pauling arbitrarily chose the value of 4.0 for fluorine, which makes the electronegativities range in value from 0.7 to 4.0. Table A.21 in Appendix A contains electronegativity values for several elements. Fluorine is the most electronegative element, followed by oxygen, nitrogen, and chlorine. The alkali metals are the least electronegative.

In any row of the periodic table the electronegativity increases from left to right, and in any column it decreases from top to bottom. We can understand these trends on the basis of effective nuclear charges. As one moves from left to right across a row of the periodic table, the effective nuclear charge increases, corresponding to lower orbital energies and to the observed increase in the electronegativity. As one moves from top to bottom in a column of the periodic chart, there are opposing tendencies. The nuclear charge increases, which would seem to increase the electronegativity. However, each row corresponds to a larger value of the principal quantum number than the shell above it, so that the average distance of the electron from the nucleus is larger and there is an additional shell of electrons to shield the electron from the nuclear charge. This tendency dominates, corresponding to a less negative orbital energy for electrons in the valence shell and a decrease in the electronegativity.

EXAMPLE 20.14

Using average bond energies from Table A.9 of the appendix, calculate the difference in electronegativity between H and F.

Solution

We omit the units on the factors:

$$|X_H - X_{Li}| = (0.102)[568 - (1/2)(436 + 158)]^{1/2} = 1.7 \quad \text{(Table value = 1.9)}$$

Exercise 20.20

Using average bond energies from Table A.9 of the appendix, calculate the differences in electronegativity between (a) C and O, and (b) C and Cl. Compare your results with the values in Table A.21 of the appendix.

Table 20.4 Selected Values of Average Bond Energies

Bond	Bond Energy (kJ mol^{-1})
C–C	343
C=C	615
C–Cl	326
C–F	490
C–H	416
C–N	290
C–O	351
Cl–Cl	244
F–F	158
H–Cl	432
H–H	436
H–F	568
H–N	391
N–N	160
N–O	176
O–O	144
O–H	464

From F. T. Wall, *Chemical Thermodynamics*, 3rd ed., W. H. Freeman, San Francisco, 1974, p. 63.

A rule of thumb is that if the difference between the electronegativities of two elements is greater than 1.7, a bond between those elements will be primarily ionic. A difference of less than 1.7 corresponds to a polar covalent bond, and a nonpolar covalent bond requires a difference of zero.

Exercise 20.21

Classify the bonds between the following pairs of elements as purely covalent, polar covalent, and primarily ionic: (a) Li and H, (b) C and O, (c) N and Cl, (d) H and F, (e) Li and F, and (f) F and F.

The Valence-Bond Method for Heteronuclear Diatomic Molecules

A valence-bond wave function like that of Eq. (20.3-7) or Eq. (20.3-20) corresponds to equally shared electrons. Inclusion of both of the two ionic terms in Eq. (20.3-10) does not correspond to ionic bonding, because one ionic term corresponds to bond polarity in one direction and the other to bond polarity in the opposite direction. For a polar molecule such as LiH a modified valence-bond wave function can be constructed by including only one ionic term:

$$\Psi_{\mathrm{MVB}} = c_{\mathrm{VB}}\Psi_{\mathrm{VB}} + c_{\mathrm{I}}\Psi_{\mathrm{I}} \tag{20.4-17}$$

where Ψ_{VB} contains the covalent terms:

$$\begin{aligned}\Psi_{\mathrm{VB}} = {} & \psi_{1s\mathrm{Li}}(1)\alpha(1)\psi_{1s\mathrm{Li}}(2)\beta(2)[\psi_{2sp(1)\mathrm{Li}}(3)\psi_{1s\mathrm{H}}(4) + \psi_{1s\mathrm{H}}(3)\psi_{2sp(1)\mathrm{Li}}(4)] \\ & \times [\alpha(3)\beta(4) - \beta(3)\alpha(4)]\end{aligned} \tag{20.4-18}$$

and Ψ_{I} contains a single ionic term:

$$\Psi_{\mathrm{I}} = \psi_{1s\mathrm{Li}}(1)\alpha(1)\psi_{1s\mathrm{Li}}(2)\beta(2)\psi_{1s\mathrm{H}}(3)\psi_{1s\mathrm{H}}(4)[\alpha(3)\beta(4) - \beta(3)\alpha(4)] \qquad (20.4\text{-}19)$$

The coefficients c_{VB} and c_{I} could be optimized by the variation method. If $|c_{\mathrm{VB}}|$ is larger than $|c_{\mathrm{I}}|$ this corresponds to a bond that is primarily covalent and if $|c_{\mathrm{VB}}|$ is smaller than $|c_{\mathrm{I}}|$ this corresponds to a bond that is primarily ionic.

EXAMPLE 20.15

Calculate the values of c_{VB} and c_{I} that make the wave function Ψ_{MVB} equivalent to the LCAOMO wave function for LiH in Eq. (20.4-5) if the orbitals of Eq. (20.4-8) are used. Find the percent ionic character, defined as $[c_{\mathrm{I}}^2/(c_{\mathrm{VB}}^2 + c_{\mathrm{I}}^2)] \times 100\%$.

Solution

The molecular orbitals of Eq. (18.4-8) are

$$\psi_{1\sigma} = \psi_{1s\mathrm{Li}}$$

$$\psi_{2\sigma} = c_{2sp(1)\mathrm{Li}}\psi_{2sp(1)\mathrm{Li}} + c_{1s\mathrm{H}}\psi_{1s\mathrm{H}} \approx -0.47\psi_{2sp(1)\mathrm{Li}} - 0.88\psi_{1s\mathrm{H}}$$

The modified valence-bond function for LiH in Eqs. (13.4-15) and (13.4-16) is

$$\Psi_{\mathrm{MVB}} = c_{\mathrm{VB}}\Psi_{\mathrm{VB}} + c_{\mathrm{I}}\Psi_{\mathrm{I}}$$

where

$$\begin{aligned}\Psi_{\mathrm{VB}} &= \psi_{1s\mathrm{Li}}(1)\alpha(1)\psi_{1s\mathrm{Li}}(2)\beta(2)[\psi_{2sp(1)\mathrm{Li}}(3)\psi_{1s\mathrm{H}}(4) + \psi_{1s\mathrm{H}}(3)\psi_{2sp(1)\mathrm{Li}}(4)]\\ &\quad \times [\alpha(3)\beta(4) - \beta(3)\alpha(4)]\\ \Psi_{\mathrm{I}} &= \psi_{1s\mathrm{Li}}(1)\alpha(1)\psi_{1s\mathrm{Li}}(2)\beta(2)\psi_{1s\mathrm{H}}(3)\psi_{1s\mathrm{H}}(4)[\alpha(3)\beta(4) - \beta(3)\alpha(4)]\end{aligned}$$

The molecular-orbital wave function can be written, omitting the spin factors

$$\begin{aligned}\Psi_{\mathrm{MO}} &= \psi_{1s\mathrm{Li}}(1)\psi_{1s\mathrm{Li}}(2)[-0.47\psi_{2sp1\mathrm{Li}}(3) - 0.88\psi_{1s\mathrm{H}}(3)]\\ &\quad \times \left[-0.47\psi_{2sp(1)\mathrm{Li}}(4) - 0.88\psi_{1s\mathrm{H}}(4)\right]\\ &= \psi_{1s\mathrm{Li}}(1)\psi_{1s\mathrm{Li}}(2)\big[0.22\psi_{2sp(1)\mathrm{Li}}(3)\psi_{2sp(1)\mathrm{Li}}(4) + 0.41\big[\psi_{2sp(1)\mathrm{Li}}(3)\psi_{1s\mathrm{H}}(4)\\ &\quad + \psi_{1s\mathrm{H}}(3)\psi_{2sp(1)\mathrm{Li}}(4)\big] + 0.77\psi_{1s\mathrm{H}}(3)\psi_{1s\mathrm{H}}(4)\big]\end{aligned}$$

Exact equivalence cannot be achieved, because the term $\psi_{2sp(1)\mathrm{Li}}(3)\psi_{2sp(1)\mathrm{Li}}(4)$ does not appear in Ψ_{MVB}. This term corresponds to ionic bonding with both electrons on the lithium atom, and is best omitted. By comparison, we have

$$c_{\mathrm{VB}} = 0.41$$

$$c_{\mathrm{I}} = 0.77$$

$$\%\ \text{ionic} = \frac{(0.77)^2}{(0.77)^2 + (0.41)^2}(100\%) = 78\%$$

PROBLEMS

Section 20.4: Heteronuclear Diatomic Molecules

20.25 Describe the bonding in the possible molecule LiB. Do you think the molecule could exist?

20.26 For a heteronuclear diatomic molecule, sketch the orbital region for the LCAOMO

$$\psi = c_1\psi_{2s\mathrm{A}} + c_2\psi_{2p_z\mathrm{A}} + c_1\psi_{2s\mathrm{B}} - c_2\psi_{2p_z\mathrm{B}}$$

where c_1 is slightly larger than c_2 and both are positive. Take the z axis as the bond axis. Determine whether this orbital is an eigenfunction of $\widehat{i}$ and of $\widehat{\sigma}_\mathrm{h}$. Give the eigenvalues if it is an eigenfunction.

20.27 Using the modified valence-bond method, describe the bonding of the gaseous NaCl molecule. Predict whether the coefficient of the covalent term or the ionic term will be larger. Look up the electronegativity of sodium if necessary.

20.28 By analogy with the 2*sp* hybrid orbitals, sketch the orbital region of the two 3*sp* hybrid orbitals.

20.29 Using the molecular orbital method, describe the bonding of an NaCl molecule in the gas phase. Predict what the bonding molecular orbitals will look like if optimized.

20.30 Describe the bonding in the carbon monoxide molecule using the valence-bond method. Include ionic terms.

20.31 Give a qualitative description of the bonding of the BN molecule using molecular orbitals. Compare it with diatomic carbon.

20.32 The dipole moment of the HCl molecule in its ground state equals 1.1085 Debye and the internuclear distance equals 127.455 pm. Estimate the percent ionic character and the values of the coefficients of the covalent and ionic terms in the modified valence-bond wave function.

20.33 The dipole moment of the HF molecule in its ground state equals 1.82 Debye and the internuclear distance equals 91.68 pm. Estimate the percent ionic character and the values of the coefficients of the covalent and ionic terms in the modified valence-bond wave function.

20.34 Using average bond energies from Table 20.4 calculate the electronegativity differences for H and C and for H and N. Compare with the values in Table A.21 of the appendix.

20.35 Using average bond energies from Table 20.4, calculate the electronegativity differences for C and N and for C and F. Compare with the values in Table A.21 in the appendix.

20.36 Using average bond energies from Table 20.4, calculate the electronegativity differences for O and N and for O and Cl. By subtraction find the electronegativity difference for N and Cl. Compare with the values in Table A.21 in the appendix.

20.37 Using average bond energies from Table 20.4, calculate the electronegativity differences for H and N and for H and F. Compare with the values in Table A.21 in the appendix.

Summary of the Chapter

In this chapter, we have discussed the quantum mechanics of electrons in diatomic molecules using the Born–Oppenheimer approximation, which is the assumption that the nuclei are stationary as the electrons move. With this approximation the time-independent Schrödinger equation for the hydrogen molecule ion, H_2^+, can be solved without further approximation to give energy eigenvalues and orbitals that depend on the internuclear distance.

Linear combinations of atomic orbitals, called LCAOMOs, provide approximate representations of molecular orbitals for H_2^+. The ground-state LCAOMO, called the $\sigma_\mathrm{g}1s$ function, is a sum of the $1s$ atomic orbitals for each nucleus, and is called a bonding orbital. The first excited-state LCAOMO, called the σ_u^*1s function, is an antibonding orbital.

An approximate wave function for a diatomic molecule is a product of LCAOMOs similar to those of H_2^+. The ground state of the H_2 molecule corresponds to the electron configuration $(\sigma_\mathrm{g}1s)^2$. A wave function with a single configuration can be improved by adding terms corresponding to different electron configurations. This procedure is called using configuration interaction (CI), and can introduce dynamical electron correlation. Most of the information about a one-term LCAOMO wave function is contained in the specification of the electron configuration, which is constructed for the ground state by the Aufbau principle, much as with atoms. Molecular term symbols can be assigned much as with atoms.

In the valence-bond method, bonding factors are included in the wave function instead of molecular orbitals. A bonding factor represents electron sharing between nuclei by containing two "covalent" terms, with each electron occupying an orbital on one nucleus in one term and on the other nucleus in the other term. Ionic terms, with both electrons on the same nucleus, can also be included.

An approximate molecular orbital wave function for the LiH molecule was constructed using hybrid orbitals called *sp* hybrids, which are a linear combination of *s* and *p* atomic orbitals on the same nucleus. A bonding molecular orbital made from a 2*sp* hybrid on the Li nucleus and a 1*s* orbital on the H nucleus provides an adequate description of the bonding in LiH.

Criteria for a good bonding LCAOMO were presented, based on results of Hartree–Fock calculations: A good bonding LCAOMO is formed from a pair of atomic orbitals with roughly equal energies, considerable overlap, and the same symmetry about the bond axis. The use of hybrid orbitals in forming such LCAOMOs was discussed.

The use of electronegativity, an empirical parameter, to estimate bond polarity was discussed. The use of the valence-bond method for heteronuclear diatomic molecules was discussed, including the addition of a single ionic term to give bond polarity.

ADDITIONAL PROBLEMS

20.38 Predict what will be formed if a hydrogen molecule ion in the state corresponding to the $\pi_u 2p_y$ LCAOMO dissociates.

20.39 Describe the bonding in the possible molecule BeC using the molecular orbital method. Do you think the molecule could exist in the ground state? If not, is there an excited configuration that could correspond to a bound molecule? Why do you think that the simple valence-bond method would not be appropriate for this molecule?

20.40 Describe the bonding in the boron nitride (BN) molecule using both the molecular orbital method and the valence-bond method. Compare the BN molecule with diatomic carbon.

20.41 Identify each statement as either true or false. If a statement is true only under special circumstances, label it as false.

a. Use of the Born–Oppenheimer approximation prevents one from studying the motion of the nuclei in a molecule.

b. The total electronic angular momentum of a diatomic molecule is a good quantum number.

c. The orbital angular momentum of the electrons of a diatomic molecule is a good quantum number.

d. The component on the bond axis of the orbital angular momentum of an electron in a diatomic molecule is a good quantum number.

e. Hybrid orbitals are used to allow reasonable approximate molecule orbitals to be written as linear combinations of only two atomic orbitals.

f. Every orbital must be an eigenfunction of every operator that belongs to the molecule.

g. The simple valence-bond method does not include any dynamical electron correlation.

h. Molecular orbital methods without configuration interaction can include dynamical electron correlation.

i. Configuration interaction can introduce dynamical electron correlation.

j. The use of bond energy data is the only means of evaluating electronegativity differences.

21

The Electronic Structure of Polyatomic Molecules

PRINCIPAL FACTS AND IDEAS

1. The electronic structure of polyatomic molecules can be described approximately with LCAOMOs that involve only two atomic orbitals if appropriate hybrid orbitals are used.
2. Qualitative descriptions of the electronic states of molecules can be obtained by using general criteria for forming good bonding LCAOMOs.
3. Group theory can be used to obtain useful information about molecular orbitals of polyatomic molecules.
4. Various semiempirical and ab initio techniques exist for carrying out molecular quantum mechanical calculations, and software packages are available to carry out these techniques.

21.1 The BeH_2 Molecule and the *sp* Hybrid Orbitals

Beryllium hydride, BeH_2, is the simplest triatomic molecule. This substance has apparently not been shown experimentally to exist, but calculations indicate that it should be a bound linear molecule with two equal Be–H bond distances. We assume this equilibrium conformation and apply the Born–Oppenheimer approximation. We place the molecule in a Cartesian coordinate system with the Be atom at the origin and with the H atoms on the z axis, as shown in Figure 21.1. We denote one of the H atoms by H_a and the other by H_b. The molecule possesses the same symmetry operations as H_2^+: E, i, σ_h, $C_{\infty z}$, and infinitely many σ_v and C_2 operations perpendicular to the bond axis.

We seek a wave function that is a product of LCAOMOs. Table 21.1 shows the first three optimized LCAOMOs from a Hartree–Fock–Roothaan calculation using a minimal basis set of Slater-type orbitals: $1s$, $2s$, and $2p_z$ on the Be atom and the two $1s$ orbitals on the hydrogens. The six basis functions give six independent LCAOMOs, but

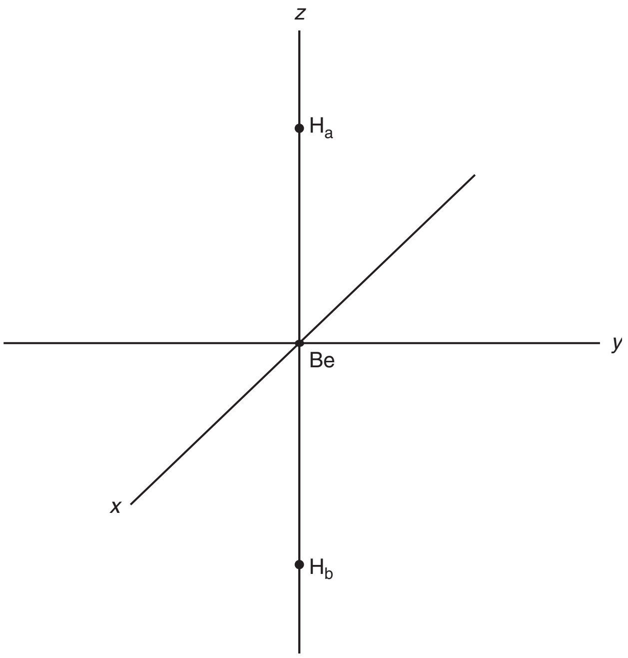
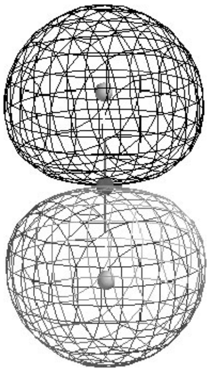


Figure 21.1 The BeH_2 molecule.

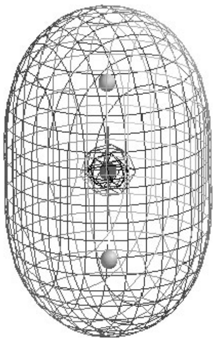
Table 21.1 Results of a Hartree–Fock–Roothaan Calculation for the BeH_2 Ground-State at a Be–H Bond Distance of 134 pm

MO	$c_{1s\text{Be}}$	$c_{2s\text{Be}}$	$c_{2pz\text{Be}}$	$c_{1s\text{H}_a}$	$c_{1s\text{H}_b}$
$1\sigma_g$	0.99718	0.01597	0.00000	−0.00163	−0.00163
$2\sigma_g$	0.17095	−0.40852	0.00000	0.45033	0.45033
$3\sigma_u$	0.00000	0.00000	0.44253	0.44126	−0.44126

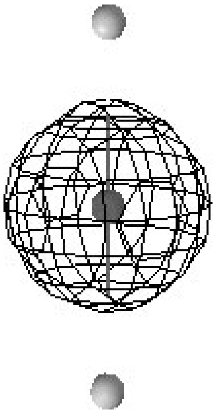
From R. G. A. R. Maclagan and G. W. Schnuelle, *J. Chem. Phys.*, **55**, 5431 (1971).



The orbital region of the $3\sigma_u$ orbital



The orbital region of the $2\sigma_g$ orbital



The orbital region of the $1\sigma_g$ orbital.

Figure 21.2 The Orbital Regions of Two Bonding Orbitals of the BeH$_2$ Molecule. Positive regions are in black and negative regions are in gray.

we do not discuss the higher-energy orbitals. The LCAOMOs are all sigma orbitals, since all of the atomic orbitals in the basis set correspond to $m = 0$. The molecular orbitals are numbered from the lowest to the highest energy, and are labeled g or u depending on the eigenvalue of the inversion operator. Since there are six electrons in the molecule, all three of these LCAOMOs are occupied in the ground-state.

The $1\sigma_g$ orbital is nearly the same as the $1s$Be atomic orbital. This orbital is an eigenfunction of all of the symmetry operators that belong to the molecule with all eigenvalues equal to $+1$. The $2\sigma_g$ LCAOMO is a completely bonding orbital and is also an eigenfunction of all of the relevant symmetry operators with eigenvalues $+1$. The $3\sigma_u$ orbital has a nodal surface through the Be atom, but also counts as a bonding orbital, because it has no nodal surfaces between the atoms. It is also an eigenfunction of the relevant symmetry operators, but some of the eigenvalues are equal to -1. Each bonding orbital corresponds to a one-half order bond between the beryllium atom and each of the hydrogen atoms, because the pair of bonding electrons moves over both bonds. We have two single bonds. Figure 21.2 depicts the orbital regions of the $2\sigma_g$ and $3\sigma_g$ molecular orbitals.

Exercise 21.1

Determine the eigenvalues of all of the relevant symmetry operators for the $3\sigma_u$ LCAOMO.

The orbitals that result from a Hartree–Fock–Roothaan calculation are called *canonical orbitals*. There is only one possible set of such orbitals for a given molecule and a given basis set, except that different linear combinations of degenerate orbitals can occur. Two of the canonical orbitals of BeH$_2$ extend over the entire molecule and do not conform to the elementary chemical notion that bonding electrons are shared between two nuclei. We can transform these orbitals to another set of orbitals that nearly conform to this notion.

The wave function of the molecule must be antisymmetrized, which is done by constructing a 6×6 Slater determinant in which the three space LCAOMOs are used to form six spin orbitals. The first three rows of this determinant are:

$$\begin{vmatrix} \psi_{1\sigma_g}(1)\alpha(1) & \psi_{1\sigma_g}(1)\beta(1) & \psi_{2\sigma_g}(1)\alpha(1) & \psi_{2\sigma_g}(1)\beta(1) & \psi_{3\sigma_u}(1)\alpha(1) & \psi_{3\sigma_u}(1)\beta(1) \\ \psi_{1\sigma_g}(1)\alpha(1) & \psi_{1\sigma_g}(2)\beta(2) & \psi_{2\sigma_g}(2)\alpha(2) & \psi_{2\sigma_g}(2)\beta(2) & \psi_{3\sigma_u}(2)\alpha(2) & \psi_{3\sigma_u}(2)\beta(2) \\ \psi_{1\sigma_g}(3)\alpha(3) & \psi_{1\sigma_g}(3)\beta(3) & \psi_{2\sigma_g}(3)\alpha(3) & \psi_{2\sigma_g}(3)\beta(3) & \psi_{3\sigma_u}(3)\alpha(3) & \psi_{3\sigma_u}(3)\beta(3) \\ & & & \text{etc.} & & \end{vmatrix}$$

The other three rows contain the same spin orbitals as the first three rows, but with electron labels 4, 5, and 6. Each column of the determinant contains one spin orbital.

A useful property of determinants is stated as property (5) of determinants in Eq. (B-100) of Appendix B: If each element of a column is replaced by that element plus the same constant times the corresponding element of one of the other columns, the value of the determinant is unchanged.

Exercise 21.2

Using expansion by minors, show that the equality in Eq. (B-100) is valid.

We replace $\psi_{2\sigma_g}$ with $c_1(\psi_{2\sigma_g} + \psi_{3\sigma_u})$ and $\psi_{3\sigma_u}$ with $c_2(\psi_{2\sigma_g} - \psi_{3\sigma_u})$ in every row of the determinant, where c_1 and c_2 are constants. According to property (5) and property

(3) of determinants in Appendix B, the value of the Slater determinant is unchanged except for being multiplied by a constant, so that the antisymmetrized wave function is not changed. These new orbitals are

$$\begin{aligned}\psi_{\sigma 2'} = c_1(&0.17095\psi_{1s\mathrm{Be}} - 0.40852\psi_{2s\mathrm{Be}} + 0.44243\psi_{2p_z\mathrm{Be}} \\ &- 0.00907\psi_{1s\mathrm{H_a}} - 0.89159\psi_{1s\mathrm{H_b}})\end{aligned} \tag{21.1-1}$$

and

$$\begin{aligned}\psi_{\sigma 3'} = c_2(&0.17095\psi_{1s\mathrm{Be}} - 0.40852\psi_{2s\mathrm{Be}} - 0.44243\psi_{2p_z\mathrm{Be}} \\ &- 0.89159\psi_{1s\mathrm{H_a}} - 0.00907\psi_{1s\mathrm{H_b}})\end{aligned} \tag{21.1-2}$$

The first of these orbitals contains almost no contribution from hydrogen a and the second contains almost no contribution from hydrogen b. They correspond very nearly to chemical bonds that consist of pairs of electrons shared by two nuclei. These orbitals give the same wave function as the canonical orbitals after antisymmetrization.

The coefficients of the $2s$Be and the $2p_z$Be atomic orbitals in our new LCAOMOs $\psi_{\sigma 2'}$ and $\psi_{\sigma 3'}$ are roughly equal in magnitude and the coefficients of the $1s$Be orbital are quite small. This is similar to the situation in the LiH molecule that we discussed earlier, and we can to an adequate approximation introduce the $2sp$ hybrid orbitals. Since Maclagan and Schnuelle used Slater-type $2s$ orbitals, which are positive everywhere, the expressions for the hybrid orbitals in Eqs. (20.4-6) and (20.4-7) are replaced by

$$\psi_{2sp(1)} = \sqrt{1/2}(\psi_{2s} + \psi_{2p_z}) \tag{21.1-3}$$

and

$$\psi_{2sp(2)} = \sqrt{1/2}(\psi_{2s} - \psi_{2p_z}) \tag{21.1-4}$$

We now write the approximate LCAOMOs

$$\begin{aligned}\psi_{2'} &\approx c_1(-0.40852\psi_{2s\mathrm{Be}} + 0.44243\psi_{2pz\mathrm{Be}} - 0.89159\psi_{1s\mathrm{H_b}}) \\ &\approx c_1(-0.42\sqrt{2}\,\psi_{2sp(2)\mathrm{Be}} - 0.90\psi_{1s\mathrm{H_b}}) \\ &\approx c_1(-0.59\psi_{2sp(2)\mathrm{Be}} - 0.90\psi_{1s\mathrm{H_b}})\end{aligned} \tag{21.1-5}$$

and

$$\begin{aligned}\psi_{3'} &\approx c_2(-0.40852\psi_{2s\mathrm{Be}} - 0.44243\psi_{2pz\mathrm{Be}} - 0.89159\psi_{1s\mathrm{H_a}}) \\ &\approx c_2(-0.42\sqrt{2}\,\psi_{2sp(1)\mathrm{Be}} - 0.89\psi_{1s\mathrm{H_a}}) \\ &\approx c_2(-0.59\psi_{2sp(1)\mathrm{Be}} - 0.89\psi_{1s\mathrm{H_a}})\end{aligned} \tag{21.1-6}$$

We now have two localized bonding orbitals, each one of which is made with a $2sp$ hybrid orbital on the Be atom and a $1s$ hydrogen orbital, and is roughly the same as one of the orbitals in Eqs. (21.1-1) and (21.1-2). Each of these space orbitals is occupied by two electrons, making two single bonds between the Be atom and the two H atoms.

The LCAOMOs conform to the same pattern that we observed with LiH: The $1s$Be orbital corresponds to a much lower energy than the other atomic orbitals, and is a nonbonding orbital. The two bonding LCAOMOs correspond to significant overlap between a hybrid orbital and a hydrogen $1s$ orbital. The hybrid orbital and the hydrogen 1*s* orbital have the same symmetry around the bond axis. The LCAOMOs have coefficients of larger magnitude for the hydrogen atoms than for the beryllium atom, corresponding to the greater electronegativity of the hydrogen atoms.

There is also a procedure in which linear combinations of the canonical orbitals are formed such that the energy of repulsion between electrons in different orbitals is minimized. The resulting orbitals are called *energy-localized* orbitals.[1] For the BeH_2 molecule, the energy-localized orbitals are very similar to the localized orbitals in Eqs. (21.1-1) and (21.1-2).

From our experience with LiH and BeH_2, we now assert that to some usable approximation we can construct localized LCAOMOs for various molecules using hybrid orbitals where appropriate and including only two atomic orbitals in our LCAOMOs. We use the same rules that we applied to LiH and BeH_2: Each bonding LCAOMO will be constructed of two atomic orbitals centered on different atoms such that the orbitals (1) have orbital energies that are fairly close together in value, (2) overlap significantly, and (3) have the same symmetry about the bond axis.

PROBLEMS

Section 21.1: The BeH_2 Molecule and the *sp* Hybrid Orbitals

21.1 Construct an accurate graph of the beryllium $\psi_{2sp(1)}$ hybrid orbital along the z axis, using z/a as the independent variable. Use a value of Z_{eff} equal to 2.776 (1.00 greater than the value of Z_{eff} for Li in Section 19.4).

21.2 **a.** The ionization potential of a sodium atom is 5.139 eV. Find the effective number of protons seen by the 3*s* electron in a sodium atom as was done in Example 19.4.

b. Construct an accurate graph of the sodium $\psi_{3sp(1)}$ hybrid orbital along the z axis, using z/a as the independent variable. Since the 3*s* orbital is positive in the bonding region while the sp_z orbital is negative in the bonding region, we take

$$\psi_{3sp(1)} = \sqrt{1/2}(\psi_{3s} - \psi_{3p_z})$$

instead of using the signs that were used for ψ_{2s} in $\psi_{2ps(1)}$. Use the value of Z_{eff} from part a.

c. Sketch the orbital region of the $\psi_{3sp(1)}$ hybrid orbital.

21.3 Describe the bonding in the B_2 molecule using LCAOMOs made from 2*sp* hybrid orbitals. What is the bond order? Compare your description with that of Table 20.2. Which seems more reasonable according to the VSEPR theory?

21.4 Assume that BH_2 has a linear equilibrium conformation. Compare its bonding with that of BeH_2. What orbital does the unpaired electron occupy?

21.2 The BH_3 Molecule and the sp^2 Hybrid Orbitals

The BH_3 molecule is known from experiment to have an equilibrium nuclear conformation that is trigonal planar (planar with three 120° bond angles). We assume the Born–Oppenheimer approximation and use this conformation. We place the B atom

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[1] P.-O. Löwdin, ed., *Quantum Theory of Atoms, Molecules, and the Solid State*, Academic Press, San Diego, 1966, pp. 263–280.

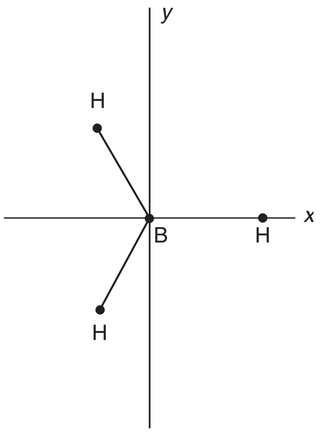

Figure 21.3 The BH_3 Molecule.

at the origin, one of the H atoms on the x axis, and the other H atoms in the xy plane with bond angles of 120° as shown in Figure 21.3. In order to make LCAOMOs that contain only two atomic orbitals, we require hybrid orbitals that have orbital regions pointing in the directions of the H atoms. These hybrid orbitals are called the $2sp^2$ *hybrid orbitals* and are constructed from the $2s$, $2p_x$, and $2p_y$ orbitals:

$$\psi_{2sp^2(1)} = -\sqrt{\frac{1}{3}}\psi_{2s} + \sqrt{\frac{2}{3}}\psi_{2p_x} \tag{21.2-1a}$$

$$\psi_{2sp^2(2)} = -\sqrt{\frac{1}{3}}\psi_{2s} - \sqrt{\frac{1}{6}}\psi_{2p_x} + \sqrt{\frac{1}{2}}\psi_{2p_y} \tag{21.2-1b}$$

$$\psi_{2sp^2(3)} = -\sqrt{\frac{1}{3}}\psi_{2s} - \sqrt{\frac{1}{6}}\psi_{2p_x} - \sqrt{\frac{1}{2}}\psi_{2p_y} \tag{21.2-1c}$$

The directions of maximum extension of these hybrid orbitals lie in the xy plane, 120° apart. They overlap with the $1s$ orbitals of the hydrogen atoms, as shown in Figure 21.4a. Figure 21.4b shows a cross section of the orbital region of one of them. The orbital region resembles those of the $2sp$ hybrid orbitals.

EXAMPLE 21.1

Predict the electronic structure of the BH_3 molecule that would likely agree roughly with a Hartree–Fock–Roothaan calculation.

Solution

The $1s$B orbital is much lower in energy than the other orbitals, so it is used as a nonbonding orbital and occupied by a pair of electrons. Each of the $2sp^2$ hybrid orbitals is combined with a $1s$ orbital on a hydrogen atom to form a bonding LCAOMO and an antibonding LCAOMO. These orbitals should resemble the orbitals obtained by energy localization of the canonical orbitals from the Hartree–Fock–Roothaan procedure. The bonding orbitals are occupied by pairs of electrons and the antibonding orbitals remain unoccupied. The electronegativity of boron is 2.0 and that of hydrogen is 2.1, so these bonding orbitals should exhibit only a small polarity, with the coefficient for the hydrogen $1s$ orbitals slightly larger in magnitude than that for the $2sp^2$ orbital.

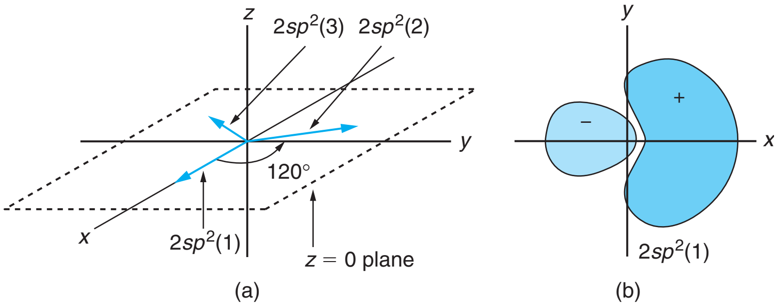

Figure 21.4 The *sp*^{2} Hybrid Orbitals. (a) Directions of the symmetry axes of the orbital regions of the 2*sp*^{2} hybrid orbitals. (b) A cross section of an orbital region.

PROBLEMS

Section 21.2: The BH_3 Molecule and the sp^2 Hybrid Orbitals

21.5 **a.** Using EXCEL® or some other graphing program, construct an accurate graph of the value of the boron $\psi_{2sp^2(1)}$ hybrid orbital along the x axis, using x/a as the independent variable. Use a value of Z_{eff} equal to 3.776.

b. Sketch the orbital region of the $\psi_{3sp^2(1)}$ hybrid orbital.

21.6 **a.** Construct an accurate graph of the value of the boron $\psi_{3sp^2(1)}$ hybrid orbital along the x axis, using x/a as the independent variable. Use a value of Z_{eff} equal to 3.776.

b. Sketch the orbital region of the $\psi_{3sp^2(1)}$ hybrid orbital.

21.7 Show that the $2sp^2$ hybrid orbitals of Eq. (21.2-1) are normalized and orthogonal to each other.

21.8 In Chapter 20, the double bond in the C_2 molecule was described as two pi bonds using the $\pi_u 2p_x$ and $\pi_u 2p_y$ bonding orbitals. Describe the bonding using a sigma and pi bond. What hybrid orbitals are used for the sigma bond? What orbitals are occupied by the lone pairs? Is the Lewis octet rule satisfied? Do you think that the molecule would have any unpaired electrons?

21.9 Attempt a description of the O_2 molecule using a sigma bond and a pi bond for the double bond instead of the bonding described in Table 20.2. Does your description include the two unpaired electrons?

21.10 Using LCAOMOs containing no more than two atomic orbitals, describe the bonding in the CO_2 molecule. How do the two pi bonding LCAOMOs differ from each other in their orientation?

21.3 The CH_4, NH_3, and H_2O Molecules and the sp^3 Hybrid Orbitals

The Methane Molecule

Methane, CH_4, has an equilibrium nuclear conformation with four bonds oriented symmetrically, with all bond angles equal to 109.5°. In order to create LCAOMOs that contain only two atomic orbitals and point in these directions, we create a third set of hybrid orbitals, the **$2sp^3$** *hybrid orbitals*:

$$\psi_{2sp^3(1)} = \frac{1}{2}[-\psi_{2s} + \psi_{2p_x} + \psi_{2p_y} + \psi_{2p_z}] \tag{21.3-1a}$$

$$\psi_{2sp^3(2)} = \frac{1}{2}[-\psi_{2s} + \psi_{2p_x} - \psi_{2p_y} - \psi_{2p_z}] \tag{21.3-1b}$$

$$\psi_{2sp^3(3)} = \frac{1}{2}[-\psi_{2s} - \psi_{2p_x} + \psi_{2p_y} - \psi_{2p_z}] \tag{21.3-1c}$$

$$\psi_{2sp^3(4)} = \frac{1}{2}[-\psi_{2s} - \psi_{2p_x} - \psi_{2p_y} + \psi_{2p_z}] \tag{21.3-1d}$$

Exercise 21.3

Using the fact that the $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals are normalized and are orthogonal to each other, choose one of the hybrid orbitals in Eq. (21.3-1) and show that it is normalized. Choose a pair of orbitals in Eq. (21.3-1) and show that they are orthogonal to each other.

Figure 21.5a shows a cube centered at the nucleus with faces perpendicular to the coordinate axes. The $2p_z$, $2p_x$, and $2p_y$ orbitals have the largest positive values along the respective positive axes. The three $2p$ orbitals contribute to the $2sp^3(1)$ hybrid orbital such that its largest positive value lies between the positive axes, toward the upper right front corner of the cube, as shown in the figure with an arrow. This direction is an axis of cylindrical symmetry of this hybrid orbital. The symmetry axes of the other three hybrid orbitals are shown in the figure, pointing toward alternate corners of the cube.

Exercise 21.4

Pick one of the $2sp^3$ hybrid orbitals other than $2sp^3(1)$ and argue that its orbital region is directed as shown in Figure 21.5a.

Since connecting the four alternate corners of a cube with line segments constructs a regular tetrahedron, the angle between any two of the axes shown in Figure 21.5a is called the *tetrahedral angle* and is equal to 109 degrees, 28 minutes, 16.39 . . . seconds (≈ 109.5°).

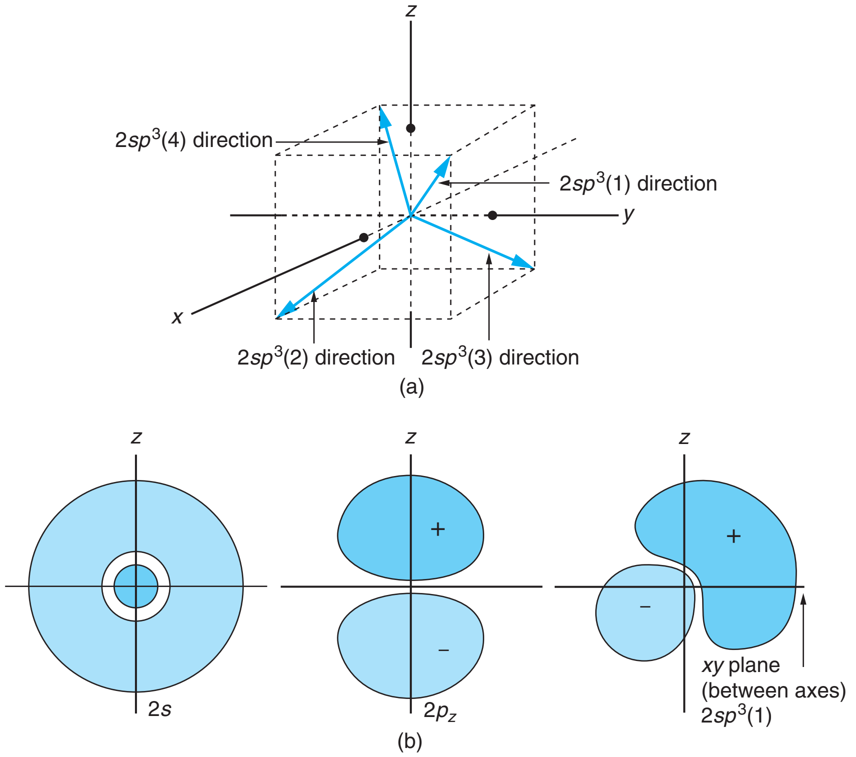

Figure 21.5 The sp^3 Hybrid Orbitals. (a) The addition of *s* and *p* atomic orbitals to form sp^3 hybrid orbitals (represented by vectors in the directions of positive contributions). (b) The orbital regions of 2*s*, 2*p*, and $2sp^3$ orbitals.

EXAMPLE 21.2

Show that the angle between alternate diagonals of a cube is 109 degrees, 28 minutes, 16.39 . . . seconds.

Solution

The diagonal of a face of a cube with sides equal to unity is $\sqrt{2}$ by the Pythagorean theorem. The diagonal through opposite corners is then equal to

$$(1^2 + (\sqrt{2})^2)^{1/2} = \sqrt{3}$$

by the Pythagorean theorem. A line drawn from the center of the cube to the center of a face of the cube bisects the angle between two corner-to-corner diagonals. Denote the angle between this line and one diagonal by α:

$$\alpha = \arcsin\left(\frac{(0.5)(\sqrt{2})}{(0.5)(\sqrt{3})}\right) = \arcsin\left(\sqrt{\frac{2}{3}}\right) = 54.735610 \text{ degrees}$$

Twice this angle gives the angle between alternate diagonals, 109.471221 degrees = 109 degrees, 28 minutes, 16.39428 . . . seconds.

A cross section of the orbital region of a $2sp^3$ orbital in a plane containing its axis of symmetry is shown in Figure 21.5b. For comparison, cross sections of the orbital regions for the $2s$ and $2p_z$ unhybridized orbitals are also shown. The orbital region of the hybrid orbital extends farther in the direction of its symmetry axis than that of either the $2s$ or $2p$ orbital, making it possible to form a larger overlap region with an orbital on another atom by using a $2sp^3$ hybrid orbital instead of a $2s$ or a $2p$ orbital, as well as making a bond in the desired direction possible.

To describe the bonding in the methane molecule, we place the hydrogen atoms at alternate corners of the cube shown in Figure 21.5b. We form four bonding molecular orbitals, each of which is a linear combination of a $2sp^3$ carbon hybrid orbital and a $1s$ hydrogen orbital. The bonds point in the tetrahedral directions, toward the hydrogen atoms. The molecule has 10 electrons. We assign one pair of electrons to the $1s$ carbon nonbonding orbital and the other four pairs to the bonding LCAOMOs. The molecule has four sigma bonds.

The Ammonia Molecule

For the NH_3 molecule, we place the hydrogen atoms on three of the symmetry axes of the $2sp^3$ hybrid orbitals. We form three sigma bonding orbitals with these hybrid orbitals and $1s$ orbitals on the hydrogen atoms. There are 10 electrons. We place two electrons in the $1s$ orbital of the N atom (a nonbonding orbital), two in each of the bonding orbitals, and a lone (nonbonding) pair in the fourth hybrid orbital. This gives bond angles of 109.5°, in rough agreement with the experimental bond angles of 107°.

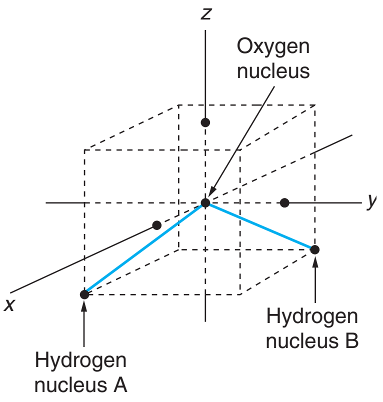

Figure 21.6 The Positions of the Nuclei in the Description of the Water Molecule Using sp^3 Hybrid Orbitals.

The Water Molecule

Figure 21.6 shows the placement of the two hydrogen atoms of the H_2O molecule to obtain maximum overlap with two of the $2sp^3$ hybrid orbitals. This corresponds to an equilibrium bond angle of 109.5° instead of the experimental bond angle of 104.5°. The 1*s* orbital of each of the hydrogen atoms forms a bonding molecular orbital with one of the $2sp^3$ hybrid orbitals:

$$\psi_{\sigma A} = c_O\psi_{2sp^3(2)} + c_H\psi_{1sA} \tag{21.3-2a}$$

$$\psi_{\sigma B} = c_O\psi_{2sp^3(3)} + c_H\psi_{1sB} \tag{21.3-2b}$$

where the H atoms are denoted by A and B. From the fact that oxygen is more electronegative than hydrogen we can assume that

$$|c_O| > |c_H| \tag{21.3-3}$$

This also corresponds to the fact that the oxygen $2sp^3$ hybrid orbitals are lower in energy than the hydrogen 1*s* orbitals.

A *correlation diagram* for the H_2O molecule is shown in Figure 21.7. In this diagram the energies of the unhybridized atomic orbitals are shown with broken lines, because they have been used to construct the hybrid orbitals and are no longer available for use in LCAOMOs. The energies of the $2sp^3$ hybrids are shown with solid lines. In addition to the bonding orbitals σA and σB, the correlation diagram shows the energies of the corresponding antibonding orbitals σ^*A and σ^*B, which have larger coefficients on the hydrogen end, and which remain vacant in the ground-state.

The 1*s* orbital of the O atom is occupied by a nonbonding pair of electrons and each of the bonding molecular orbitals is occupied by two electrons. Two $2sp^3$ hybrids are

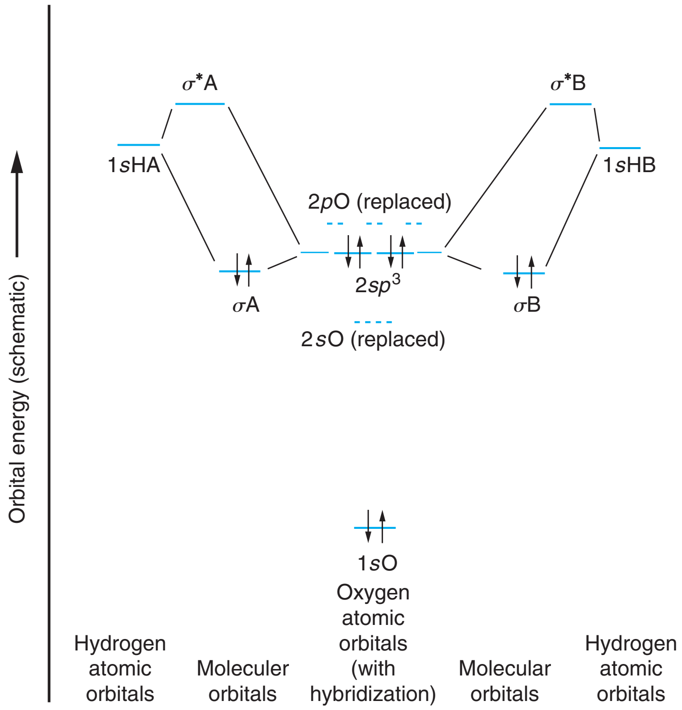

Figure 21.7 Correlation Diagram for the Water Molecule Using $2sp^3$ Hybrid Orbitals.

occupied by lone pairs of electrons. The electron configuration of the ground-state is $(1sO)^2(2sp^3(1))^2(2sp^3(4))^2(\sigma A)^2(\sigma B)^2$. The electron configuration is also denoted in Figure 21.7 by arrows pointing up and down to represent electrons occupying a space orbital with spin up and spin down.

Our simple descriptions of the NH_3 and H_2O molecules do not exactly correspond to the experimental bond angles. Better descriptions can be constructed by carrying out calculations using LCAOMOs that are linear combinations of all atomic orbitals in the basis set. Hybrid orbitals are then not needed and the canonical molecular orbitals can extend over the entire molecule prior to energy localization.[2] Improvements can also be obtained by using a larger basis set.

Gilbert Newton Lewis, 1875–1946, was a long-time professor at the University of California at Berkeley. He made contributions both to chemical thermodynamics and to chemical bonding, and was among the first to propose that a covalent bond involved the sharing of an electron pair.

We can now understand the *octet rule* of G. N. Lewis. According to this elementary rule, atoms in molecules tend to have eight electrons in their valence shells, counting both bonding and nonbonding electrons. This rule was proposed by Lewis prior to the discovery of quantum mechanical shells and subshells and is remarkably effective in predicting the electronic structure of many molecules. For the water molecule and other molecules made from elements of the second row of the periodic table (Li through Ne) the valence shell is the second shell, in which eight spin orbitals (four space orbitals) occur. From an atomic orbital, one bonding LCAOMO and one antibonding LCAOMO can be made with an atomic orbital on another atom. If the antibonding orbitals remain vacant and nonbonding and bonding orbitals are occupied the total number of occupied spin orbitals around a given nucleus of a second-row element equals eight, corresponding to the octet rule.

There are exceptions to the octet rule. Some stable molecules, such as BeH_2 and BH_3, do not have enough valence electrons to form an octet. Other molecules containing elements beyond the second row of the periodic table involve d orbitals in the bonding and can have "expanded octets" with more than eight electrons in bonding and nonbonding orbitals around a given atom.

The *valence-shell electron pair repulsion* (VSEPR) theory is an elementary theory that is surprisingly effective in predicting the equilibrium nuclear conformation of covalently bonded molecules. The basic idea is that electron pairs (or sets of pairs in a double or triple bond), either in nonbonding or bonding orbitals, repel each other and are located as far away from each other as possible. Four pairs of electrons maximize their distances when located on alternate corners of a cube, which is called the tetrahedral *electron geometry*. The theory thus predicts that CH_4 has a tetrahedral electron geometry. The H_2O and NH_3 molecules also have a tetrahedral electron geometry. The molecular shape involving only bonds and not lone pairs is called the *molecular geometry*. We say that the H_2O molecule has angular molecular geometry and that the NH_3 molecule has trigonal pyramidal molecular geometry. The VSEPR theory is usually elaborated by assuming that lone pairs occupy a slightly larger volume than bonded pairs, since they have no nucleus to attract them. For example, assigning a larger volume to the lone pairs in the H_2O molecule requires that the bond angle is slightly smaller than the tetrahedral angle of 109.5°, giving an explanation for the fact that the experimental angle is 104.5°. The VSEPR theory also includes conformations for expanded octets with five electron pairs (trigonal bipyramidal electron geometry) and six electron pairs (octahedral electron geometry).

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[2] I. N. Levine, *Quantum Chemistry*, 5th ed., Prentice-Hall, Englewood Cliffs, NJ, 2000, p. 498ff.

EXAMPLE 21.3

Are the bonds in the CH_4 molecule polar or nonpolar? Does the CH_4 molecule have a nonzero dipole moment?

Solution

The four single bonds are slightly polar, since the electronegativity of carbon on the Pauling scale is 2.5 and that of hydrogen is 2.1. The molecule is tetrahedral, with each C–H bond formed from a $2sp^3$ hybrid orbital on the carbon atom, and with the bonds at the tetrahedral angle (109.5°) from each other. The dipole contributions from the four bonds cancel each other so that the molecule is nonpolar.

Exercise 21.5

Describe the bonding in ammonia, NH_3, including the conformation of the molecule and a statement about the dipole moment of the molecule. How do you think the actual bond angles deviate from the tetrahedral angle of 109.5°?

PROBLEMS

Section 21.3: The CH_4, NH_3, and H_2O Molecules and the sp^3 Hybrid Orbitals

21.11 Show that the $2sp^3$ hybrid orbitals of Eq. (21.10-1) are normalized and are orthogonal to each other.

21.12 Describe the bonding in the HF molecule using sp^3 hybrids for the fluorine instead of sp hybrids. Which description fits better with the VSEPR theory?

21.13 Describe the bonding in the F_2 molecule using sp^3 hybrids instead of the orbitals used in Table 20.2. Which description fits better with the VSEPR theory?

21.14 Using LCAOMOs made with hybrid orbitals, describe the bonding and molecular shape of each of the molecules or ions:

a. SO_4^{2-}

b. BF_3

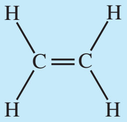
c. $HClO_4$

21.4 Molecules with Multiple Bonds

According to the description in Chapter 20, the double bond in C_2 consists of two pi bonds. We now construct approximate wave functions for larger molecules containing double bonds.

EXAMPLE 21.4

Describe the bonding in ethene (ethylene), which has the following structural formula



Solution

The VSEPR theory predicts C–C–H bond angles of 120°, approximately equal to the experimental bond angles of 122°. We place the molecule in the xy plane with the double bond on the x axis. We rotate the axes for one carbon by 180° to make the orbital regions of two of the $2sp^2$ hybrids on the two carbons point toward each other and overlap. We construct a C–C sigma bonding orbital from these two $2sp^2$ hybrid orbitals and denote it by 1σ. We construct a C–H bonding orbital from each of the other $2sp^2$ hybrids and a hydrogen $1s$ orbital, placing the hydrogen atoms in the xy plane with 120° bond angles. Denote these bonding orbitals by σA, σB, σC, and σD. The second C–C bonding orbital is a linear combination of the two unhybridized $2p_z$ orbitals and is a pi orbital. Denote this orbital by 1π. The molecule must be planar for the two unhybridized $2p_z$ orbitals to have maximum overlap.

The electron configuration of the molecule in the ground-state is

$$(1sA)^2(1sB)^2(1\sigma)^2(1\pi)^2(\sigma A)^2(\sigma B)^2(\sigma C)^2(\sigma D)^2$$

Since the nuclei must be placed on the symmetry axes of the hybrid orbitals to have good overlap, the C–C–H bond angles equal 120°, in agreement with the VSEPR prediction. The double bond consists of a sigma bond and a pi bond.

Exercise 21.6

Describe the bonding in diatomic carbon using hybrid orbitals like those used in ethene. Do you think this description would be superior to that in Section 20.3?

We now model a carbon–carbon triple bond as a sigma bond and two pi bonds.

EXAMPLE 21.5

Describe the bonding in ethyne (acetylene), C_2H_2, which has the Lewis dot structure:

$$\mathrm{H:C:::C:H}$$

The molecule is experimentally found to be linear at each carbon in its equilibrium conformation.

Solution

Assuming the Born–Oppenheimer approximation and the experimental conformation, we orient the molecule on the z axis. Acetylene is isoelectronic with N_2, which also has a triple bond. In the simple LCAOMO description of N_2 of Chapter 20 we assigned the first eight electrons to the $\sigma_g 1s$, $\sigma_u^* 1s$, $\sigma_g 2s$, and $\sigma_u^* 2s$ orbitals. Only the LCAOMOs made from the $2p$ orbitals were involved in the bonding. Two electrons were assigned to the $\sigma_G 2p_z$ orbital, two to the $\pi_u 2p_x$ orbital, and two to the $\pi_u 2p_y$ orbital, making a triple bond that consists of a sigma bond and two pi bonds.

We cannot make a similar description for acetylene. Since the $2p$ orbitals are all involved in the C–C bonds, there are no orbitals left to form the C–H bonds. A better description is obtained by constructing two $2sp$ hybrids on each carbon. The orbital regions of the $2sp$ hybrids on the same atom point in opposite directions along the z axis. We form a carbon–carbon sigma bonding orbital from the two $2sp$ hybrid orbitals that overlap between the carbon atoms. We call this the 1σ bonding orbital. There is also an antibonding orbital, but we will not need to occupy it. The carbon–carbon pi bonds are constructed from the unhybridized

$2p_x$ and $2p_y$ orbitals, exactly as with the N_2 molecule. On each carbon atom, this leaves a $2sp$ hybrid orbital with an orbital region that is directed along the z axis away from the C–C bond. We place the hydrogen atoms on the z axis, achieving maximum overlap. From the $2sp$ hybrid on carbon A and a hydrogen $1s$ orbital we form a carbon–hydrogen σ bonding orbital that we call σ_A. From the $2sp$ hybrid on carbon B and a hydrogen $1s$ orbital we form a carbon–hydrogen σ bonding orbital that we call σ_B. The electron configuration is now

$$(1sA)^2(1sB)^2(1\sigma)^2(\pi_u 2p_x)^2(\pi u 2p_y)^2(\sigma A)^2(\sigma B)^2$$

where we place four electrons in the nonbonding inner-shell carbon $1s$ orbitals instead of using the $\sigma_g 1s$ and $\sigma_u^* 1s$ LCAOMOs. The triple bond consists of a sigma bond made from two hybrid sp orbitals and two pi bonds that are made from unhybridized p orbitals.

Exercise 21.7

Describe the bonding in N_2 using LCAOMOs similar to those used in the description of acetylene. Why is this description superior to the previous description of N_2 in Chapter 20?

The energy-localized orbitals for double and triple bonds do not correspond to a sigma bond plus pi bonds. The three energy-localized orbitals in the triple bond in acetylene (ethyne) have the same energy and have the same shape, with the orbital regions lying 120° from each other around the bond axis. These energy-localized orbitals are sometimes called "banana orbitals" because of their shape.[3] These orbitals are superior to our description of the triple bond as a sigma and two pi bonds, since they allow the electrons to be as far from each other as possible. However, our goal is simply to provide a way to describe chemical bonding without calculation, and our method is adequate for that purpose.

Fourth- and Fifth-Order Bonds

Elements in the second row of the period table do not form higher-order bonds than triple bonds, but elements in the higher rows can form higher-order bonds, which can be represented with linear combinations using d orbitals as well as s and p orbitals. A fifth-order bond has been reported between two chromium(I) ions.[4]

PROBLEMS

Section 21.4: Molecules with Multiple Bonds

21.15 Write an approximate LCAOMO wave function without antisymmetrization for the formaldehyde molecule, using no more than two atomic orbitals in an LCAOMO. Place the C–O bond on the z axis and the H atoms in the yz plane. Use hybrid orbitals where appropriate. Specify which atomic orbitals make up each LCAOMO and identify each with an index and the designation σ or π. Give the shape of the molecule.

21.16 Using LCAOMOs made with hybrid orbitals, describe the bonding and molecular shape of each of the molecules:

a. $H_2C{=}C{=}CH_2$

b. NO_2

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[3] Levine, *op. cit.*, p. 527 (note 2).
[4] T. Nguyen, *Science*, **310**, 844 (2005).

21.17 Using LCAOMOs made with hybrid orbitals, describe the bonding and molecular shape of each of the molecules or ions:

a. HNO_2

b. NO_3^-

c. SO_4^{2-}

21.18 Using LCAOMOs made with hybrid orbitals, describe the bonding and molecular shape of each of the molecules or ions:

a. C_2H_2

b. C_2N_2

c. S_2^{2-}

21.5 The Valence-Bond Description of Polyatomic Molecules

If the molecular orbital wave function of a molecule has no unpaired electrons and no occupied antibonding orbitals it can be replaced by a simple valence-bond wave function that is obtained by replacing each pair of bonding molecular spin orbitals with a bonding factor such as that of Eq. (20.3-7). The hybrid orbitals were originally defined to be used in valence-bond wave functions and are used in much the same way as we have used them in LCAOMOs. The criteria for forming a good valence-bond bonding factor are the same as those for forming a good bonding molecular orbital: The two atomic orbitals should have the same symmetry around the bond axis, they should have roughly equal energies, and they should have considerable overlap. In early applications of the valence-bond theory the strength of a bond was assumed to be proportional to the value of its overlap integral.

To give a simple description of the bonding in the water molecule using the valence-bond method it is necessary only to specify that two nonbonding electrons occupy the oxygen $1s$ space orbital, four nonbonding electrons occupy two oxygen $2sp^3$ hybrid space orbitals, and four electrons occupy two bonding factors, each constructed from an oxygen $2sp^3$ hybrid and a hydrogen $1s$ orbital. The corresponding unnormalized valence-bond wave function is

$$\begin{aligned}\Psi_{\mathrm{VB}} = {} & \psi_{1s\mathrm{O}}(1)\psi_{1s\mathrm{O}}(2)\psi_{2sp^3(1)}(3)\psi_{2sp^3(1)}(4)\psi_{2sp^3(4)}(5)\psi_{2sp^3(4)}(6)\\ & \times [\psi_{2sp^3(2)}(7)\psi_{1s\mathrm{A}}(8) + \psi_{1s\mathrm{A}}(7)\psi_{2sp^3(2)}(8)]\\ & \times [\psi_{2sp^3(3)}(9)\psi_{1s\mathrm{B}}(10) + \psi_{1s\mathrm{B}}(9)\psi_{2sp^3(3)}(10)]\end{aligned} \tag{21.5-1}$$

where we have omitted the spin factors. The subscript $1s$A stands for the $1s$ orbital on one hydrogen atom and the subscript $1s$B stands for the $1s$ orbital on the other hydrogen atom.

This wave function corresponds to nonpolar covalent bonds. We can add an ionic term with both electrons on the oxygen atom:

$$\Psi_{\mathrm{MVB}} = c_{\mathrm{VB}}\Psi_{\mathrm{VB}} + c_{\mathrm{I}}\Psi_{\mathrm{I}} \tag{21.5-2}$$

where Ψ_{I} is the completely ionic wave function in which each bonding factor is replaced by a factor with both bonding electrons occupying the hybrid orbital on the oxygen atom. The values of the coefficients c_{VB} and c_{I} would be determined by minimizing the variational energy.

Exercise 21.8

Write the expression for Ψ_{I} in Eq. (21.5-2).

The ionic character of a bond can also be represented by placing an ionic term in each bonding factor instead of making an ionic term for the entire wave function. The space factor of the first bonding factor in the water molecule wave function would become

$$[\psi_{2sp^3(2)}(7)\psi_{1s\mathrm{A}}(8) + \psi_{1s\mathrm{A}}(7)\psi_{2sp^3(2)}(8) + c\psi_{2sp^3(2)}(7)\psi_{2sp^3(2)}(8)] \qquad (21.5\text{-}3)$$

with a similar factor for the other bond. An optimum value for the coefficient c would be obtained by minimizing the variational energy of the molecule.

Exercise 21.9

Using the valence-bond method, give a description of the bonding in

a. Ammonia
b. Methane
c. Hydrogen fluoride

The simple wave functions for diatomic molecules obtained in Chapter 20 can be improved by using hybrid orbitals, both in the LCAOMO method and the valence-bond method.

EXAMPLE 21.6

Write a simple valence-bond wave function for the ground-state of diatomic F_2 using $2sp^3$ hybrid orbitals.

Solution

Orient the coordinate axes so that each atom has a hybrid orbital region pointing at the other atom. Make the bonding factor with one of the hybrid orbitals on each atom and use the other three for lone pairs. Denote the hybrids involved in the bond as $2sp^3(1)\mathrm{A}$ and $2sp^3(1)\mathrm{B}$. We omit the spin factors. Use the $1s$ and the other $2sp^3$ orbitals as nonbonding orbitals. Without complete antisymmetrization, the wave function is

$$\begin{aligned}\Psi = {} & \psi_{1s\mathrm{A}}(1)\alpha(1)\psi_{1s\mathrm{A}}(2)\beta(2)\psi_{1s\mathrm{B}}(3)\alpha(3)\psi_{1s\mathrm{B}}(4)\beta(4)\psi_{2sp^3(2)\mathrm{A}}(5)\alpha(5)\\ & \times \psi_{2sp^3(2)\mathrm{A}}(6)\beta(6)\psi_{2sp^3(3)\mathrm{A}}(7)\alpha(7)\psi_{2sp^3(3)\mathrm{A}}(8)\beta(8)\psi_{2sp^3(4)\mathrm{A}}(9)\alpha(9)\\ & \times \psi_{2sp^3(4)\mathrm{A}}(10)\beta(10)\psi_{2sp^3(2)\mathrm{B}}(11)\alpha(11)\psi_{2sp^3(2)\mathrm{B}}(12)\beta(12)\\ & \times \psi_{2sp^3(3)\mathrm{B}}(13)\alpha(13)\psi_{2sp^3(3)\mathrm{B}}(14)\beta(14)\psi_{2sp^3(4)\mathrm{B}}(15)\alpha(15)\psi_{2sp^3(4)\mathrm{B}}(16)\beta(16)\\ & \times [\psi_{2sp^3(1)\mathrm{A}}(17)\psi_{2sp^3(1)\mathrm{B}}(18) + \psi_{2sp^3(1)\mathrm{B}}(17)\psi_{2sp^3(1)\mathrm{A}}(18)]\\ & \times [\alpha(17)\beta(18) - \beta(17)\alpha(18)]\end{aligned}$$

This wave function is probably superior to that used in Chapter 20 without hybrid orbitals, since it allows the lone pair electrons to be farther from each other on the average, and thus probably more nearly resembles the energy-localized wave function.

Exercise 21.10

Construct an LCAOMO wave function for diatomic fluorine using the hybrid orbitals.

Valence-bond descriptions of multiple bonds are also similar to the simple LCAOMO description. A double bond consists of a sigma bond and a pi bond, and a triple bond consists of a sigma bond and two pi bonds. Each bonding factor replaces one LCAOMO, but nonbonding orbitals are the same in both methods. There are no analogues to antibonding orbitals in the simple valence-bond method, so molecules with unpaired electrons such as O_2 also cannot be well described in the simple valence-bond method. The extended valence-bond methods mentioned in Chapter 20 are more versatile.

EXAMPLE 21.7

Describe the bonding in the ethyne (acetylene) molecule, using the valence-bond method.

Solution

Four electrons occupy the two carbon 1*s* space orbitals. Two electrons occupy a carbon–carbon sigma bonding factor made from a 2*sp* hybrid on each carbon, and four electrons occupy two carbon–hydrogen sigma bonding factors made from a 2*sp* hybrid orbital on a carbon atom and a 1*s* orbital on a hydrogen atom. The last four electrons occupy two carbon–carbon pi bonding factors, one made from the $2p_x$ on each carbon atom and one made from the $2p_y$ orbital on each carbon atom, making a triple carbon–carbon bond. The molecule is linear.

Exercise 21.11

Using the valence-bond method, describe the bonding in the propene (propylene) molecule. Give the bond angles around each carbon.

Other Types of Hybrid Orbitals

In addition to the *sp*, sp^2, and sp^3 hybrid orbitals, there are hybrid orbitals that include *d* orbitals, either from the same shell as the *s* and *p* orbitals or from the next lower shell. If one *d* space orbital is included in addition to the four space orbitals of the *s* and *p* subshells, five hybrid space orbitals can be constructed. These are called sp^3d hybrids if the *d* orbital is from the same shell as the *s* and *p* orbitals or dsp^3 hybrids if the *d* orbital is from the next lower shell. The symmetry axis of one orbital points along the positive *z* axis, that of another points along the negative *z* axis, and three point in the *xy* plane in directions 120° from each other. This geometry is called “trigonal bipyramidal,” and is included in the simple VSEPR theory for five charged regions. The sp^3d orbitals can be used to construct sigma LCAO molecular orbitals or valence-bonding factors for molecules such as IF_3, PF_5, SF_4, and so on, that have five pairs of electrons in the valence shell of the central atom.

EXAMPLE 21.8

Describe the bonding in the iodine trifluoride molecule. Apply the VSEPR rule that lone pairs require more space than bonding pairs of electrons and are therefore placed in equatorial rather than axial positions.

Solution

The valence shell of the iodine atom is the fifth shell, and the 4d subshell is full, so the d orbitals in the hybrid orbitals are from the same shell. We denote the five 5sp^3d hybrids as follows: The orbital region of $\psi_{5sp^3d(1)}$ points in the direction of the positive z axis, that of $\psi_{5sp^3d(2)}$ points in the direction of the negative z axis, that of $\psi_{5sp^3d(3)}$ points in the direction of the positive x axis, that of $\psi_{5sp^3d(4)}$ points between the positive y axis and the negative x axis with an angle of 120° from that of $\psi_{5sp^3d(3)}$, and that of $\psi_{5sp^3d(5)}$ points between the negative y axis and the negative x axis with an angle of 120° from that of both $\psi_{5sp^3d(3)}$ and $\psi_{5sp^3d(4)}$. We place the fluorine atoms on the positive and negative z axis and on the positive x axis. In each fluorine atom we form 2sp^3 hybrids and orient them so that one of the orbital regions points toward the iodine atom. We form three sigma bonds with a 5sp^3d hybrid on the iodine atom and a 2sp^3 hybrid on a fluorine atom. The other orbitals on the fluorine atoms are occupied by nonbonding electrons. All of the inner-shell orbitals on the iodine atom are occupied by nonbonding electrons, as are the remaining hybrids on the iodine atom, $\psi_{5sp^3d(4)}$ and $\psi_{5sp^3d(5)}$. This description should agree fairly well with the energy-localized wave function since it allows the lone pairs maximum separation from bonds and other lone pairs.

Hybrid orbitals can be formed from one s orbital, two p orbitals, and one d orbital. These orbitals point in the directions of the x and y axes, and correspond to a square planar electron geometry. If the d orbital is from the same shell as the s and p orbitals, these orbitals are called sp^2d orbitals, and if the d orbital is from the next lower shell, they are called dsp^2 orbitals. There are various platinum complexes that exhibit square planar molecular geometry. Hybrid orbitals can also be formed from two d orbitals, one s orbital, and three p orbitals. These orbitals are called sp^3d^2 if the d subshell is from the same shell as the s and p orbitals or d^2sp^3 if the d subshell is from the shell below that of the s and p orbitals. These six orbitals have symmetry axes pointing along the positive and negative Cartesian coordinate axes, the directions of the apices of a regular octahedron, and the electron geometry or molecular geometry is called octahedral. When these hybrids are used in a molecule wave function, all of the bond angles are equal to 90°. Examples of molecules with this "octahedral" electron geometry are SF_6, XeF_4, and various complexes of transition metals.

PROBLEMS

Section 21.5: The Valence-Bond Description of Polyatomic Molecules

21.19 Using the modified valence-bond method, describe the bonding of the $BeCl_2$ molecule. Predict the degree of ionic character in the bonds. Look up the electronegativity of Be if necessary.

21.20 Using the valence-bond method describe the bonding in H_2CO (formaldehyde or methanal).

21.21 *cis*-Diamminedichloroplatinum (II) (cisplatin) is a chemotherapy drug that is commonly used against testicular cancer. The molecule has a square planar conformation with the two chlorines and the two ammonias bonded to the platinum atom with the chlorines adjacent to each other and the ammonias adjacent to each other, explaining the *cis* designation. Describe the bonding in cisplatin, using appropriate hybrid orbitals.

21.22 It was once thought that the inert gases could not form chemical bonds, but it is not difficult to form compounds of xenon with fluorine and oxygen. Describe the bonding in XeF_4, using appropriate hybrid orbitals. You can use the VSEPR theory to determine the electron geometry and the molecular geometry.

21.23 Describe the bonding in $XeOF_4$, using appropriate hybrid orbitals. You can use the VSEPR theory to establish the electron geometry and the molecular geometry.

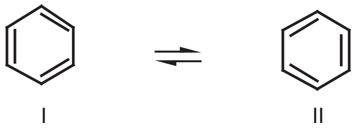
21.6 Delocalized Bonding

In our qualitative descriptions of chemical bonding we have used LCAOMOs made from two atomic orbitals and valence-bond factors containing two atomic orbitals. In this section we discuss molecules for which this description is unsatisfactory.

The Valence-Bond Method and Resonance

We consider the benzene molecule (C_6H_6) as an example. A simple valence-bond wave function for benzene has alternating single C–C bonds and double C=C bonds. It is an experimental fact that double bonds are shorter than single bonds, so this wave function conflicts with the experimental fact that the benzene molecule is hexagonal in shape with six C–C bonds of the same length. This deficiency is remedied in the valence-bond method by the use of *resonance*. To illustrate this method we place the benzene molecule in the xy plane and orient the coordinate system at each carbon so that its $2sp^2$ orbital regions point in the directions of the C–C bond and the C–H bonds. We first construct a simple valence-bond wave function with alternating single bonds and double bonds between the carbon atoms. The single bonds are sigma bonds made from two $2sp^2$ hybrids, and each double bond consists of a sigma bond made from $2sp^2$ hybrids and a pi bond made from unhybridized $2p_z$ orbitals.

To obtain a better representation of benzene, we construct another valence-bond wave function with the double bonds in the other locations. We represent the two structures by abbreviated structural formulas as follows:



where the carbon atoms are located at the corners of the hexagons and the hydrogen atoms have been omitted. These structures are called *resonance structures*. It is customary to write a double-headed arrow between resonance structures.

We construct a wave function that is a linear combination:

$$\Psi = c_{\mathrm{I}}\Psi_{\mathrm{I}} + c_{\mathrm{II}}\Psi_{\mathrm{II}} \tag{21.6-1}$$

where the valence-bond wave functions corresponding to structures I and II are called Ψ_{I} and Ψ_{II}. This representation of the wave function as a linear combination of wave functions for different resonance structures is the mathematical expression of resonance. Neither formula alone represents the structure of the molecule, and the linear combination corresponds to a "blending" of the two structural formulas, giving six C–C bonds that are intermediate between single and double bonds.

Because a more flexible variation trial function must give a lower energy than a less flexible function, the optimized energy calculated from the function of Eq. (21.6-1) will be lower than that with a wave function corresponding to one resonance structure. In this case the two coefficients c_{I} and c_{II} will be equal to each other when optimized. Various other resonance structures have been constructed for benzene, including some with "long bonds" across the ring. Terms in the wave function corresponding to such resonance structures would have smaller coefficients after optimization, and we omit them.

The difference between the variational energy calculated with a wave function including resonance and that calculated with a single resonance structure is called the *resonance energy*. The same name is sometimes applied to the difference between the correct nonrelativistic ground-state energy and that calculated with a single resonance structure. An experimental estimate of the resonance energy for benzene is obtained from the difference between the enthalpy change of hydrogenation of benzene and three times the enthalpy change of hydrogenation of ethylene.

EXAMPLE 21.9

Estimate the resonance energy of benzene using the thermodynamics techniques of Part 1.

Solution

We calculate enthalpy changes of hydrogenation of benzene at 298 K using enthalpy changes of formation:

$$C_6H_6(g) + 3H_2(g) \longrightarrow C_6H_{12}(g)$$

$$\begin{aligned}\Delta H^\circ &= \Delta_f H^\circ(C_6H_{12}) - \Delta_f H^\circ(C_6H_6) - 3(0)\\ &= -123.1\ \mathrm{kJ\ mol^{-1}} - (82.93\ \mathrm{kJ\ mol^{-1}}) = -206.0\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

We do the same for ethylene:

$$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$$

$$\Delta H^\circ = \Delta_f H^\circ(C_2H_6) - \Delta_f H^\circ(C_2H_4) - 3(0) = 137.15\ \mathrm{kJ\ mol^{-1}}$$

$$\begin{aligned}\text{Resonance energy of benzene} &= 3(137.15\ \mathrm{kJ\ mol^{-1}}) - 206.0\ \mathrm{kJ\ mol^{-1}}\\ &= 205\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

The LCAOMO Treatment of Delocalized Bonding

To treat molecules such as benzene or butadiene in the LCAOMO method we must abandon our policy of including only two atomic orbitals in our molecular orbitals. In a complete Hartree–Fock–Roothaan treatment or variational treatment, we would choose a basis set of atomic orbitals and would use linear combinations that contain all of the basis functions. Delocalized canonical orbitals would result, as with BeH_2.

Energy localization should turn all of the sigma bonding orbitals into localized orbitals, but this is not the case with the pi orbitals.

We assume that the localized sigma bonds and the delocalized pi bonds can be treated separately. We place the benzene molecule in the xy plane as in the valence-bond treatment. We use the carbon $1s$ orbitals as nonbonding (inner-shell) orbitals. As our basis functions for the sigma bonds we use the three carbon $2sp^2$ hybrids in the xy plane for each carbon atom and a $1s$ orbital on each hydrogen atom. We orient the coordinate system at each carbon atom so that two of the $2sp^2$ hybrid orbital regions point in the directions of the C–C bonds and one points in the direction of the C–H bond. Each C–C sigma bonding orbital is made from two $2sp^2$ hybrid orbitals on adjacent carbons. Each C–H bonding orbital is made from a $2sp^2$ carbon hybrid orbital and a $1s$ orbital on a hydrogen atom. The benzene molecule has 42 electrons. Twelve electrons occupy the nonbonding carbon $1s$ orbitals, twelve occupy the localized C–C bonding orbitals, and twelve occupy the localized C–H bonding orbitals. This leaves six electrons to occupy the pi orbitals.

We take the six unhybridized $2p_z$ atomic orbitals as the basis functions for the delocalized pi orbitals. We denote the $2p_z$ orbitals by $\psi_1, \psi_2, \ldots, \psi_6$ where the subscript indicates which carbon atom is involved. We construct delocalized LCAOMOs:

$$\varphi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + c_4\psi_4 + c_5\psi_5 + c_6\psi_6 = \sum_{j=1}^{6} c_j\psi_j \tag{21.6-2}$$

Since there are six basis functions, there can be six independent LCAOMOs.

The Hückel Method

The Hückel method is an approximation scheme for finding the coefficients in the delocalized LCAOMOs. It is called a *semiempirical method*, because various quantities are not calculated explicitly, but are assigned values to agree with experiment. We assume that the Hamiltonian is a sum of effective one-electron Hamiltonian operators, $\widehat{H}_{\text{eff}}$, in which all attractions and repulsions are expressed in some approximate way, so that the wave function will be a product of orbitals and each orbital can be treated separately. We apply the variation method, minimizing the orbital energy W obtained from the wave function φ in Eq. (21.6-2):

$$W = \frac{\int \varphi^* \widehat{H}_{\text{eff}} \varphi d^3\mathbf{r}}{\int \varphi^* \varphi d^3\mathbf{r}} \tag{21.6-3}$$

This orbital energy is expressed in terms of the c coefficients. To minimize the energy with respect to all of the c coefficients the variation energy W is differentiated with respect to each of the coefficients and each derivative is set equal to zero. Six simultaneous equations are obtained. There is a condition on the simultaneous equations that must be satisfied for them to have a usable solution. This condition is expressed in an equation called a *secular equation*, which can be solved for six values of the variational energy W. Each of these values is substituted into the simultaneous equations, leading to a set of coefficients for each of the six delocalized orbitals.

The simultaneous equations and the secular equation contain a number of integrals involving the effective Hamiltonian and the basis functions. In a semiempirical method

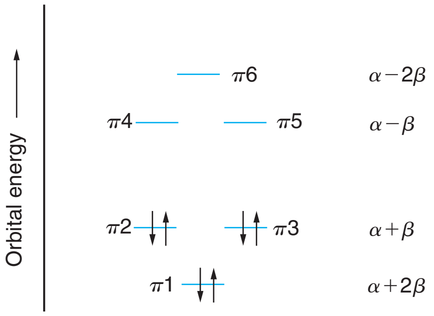


Figure 21.8 Orbital Energies of the Delocalized Pi Orbitals in Benzene by the Hückel Method.

The Hückel method was developed in the 1930s by Erich Hückel, 1896–1980, a German chemist who was also the co-inventor of the Debye–Hückel theory of electrolyte solutions.

such as the Hückel method, one does not evaluate such integrals, but assigns values to them at the end of the calculation to obtain agreement with experiment. The approximation scheme used for the various integrals is described in Appendix H, and the calculations are carried out for the allyl radical. The benzene calculation is similar, but more tedious.

Figure 21.8 shows the orbital energies of the six LCAOMOs.[5] The pattern of the energy levels has the same shape as the molecule. This correspondence occurs in the Hückel solution for all single-ring aromatic molecules. The integral β turns out to be negative, so that the lowest value of W for benzene is

$$W_1 = \alpha + 2\beta \tag{21.6-4}$$

When each value of W is substituted into the simultaneous equations a different set of c_j coefficients is obtained for each value of W, so that there are six different delocalized space orbitals. When the value of W in Eq. (21.6-4) is substituted into the simultaneous equations, we find that the normalized lowest-energy LCAOMO is

$$\varphi_1 = \sqrt{\frac{1}{6}}\,[\psi_1 + \psi_2 + \psi_3 + \psi_4 + \psi_5 + \psi_6] \tag{21.6-5}$$

This orbital has no nodes between the carbon atoms, and an electron moves around the entire molecule if it occupies this orbital. Other LCAOMOs are obtained from the other values of W, which actually represent either relative minima or relative maxima in W. Figure 21.9 shows a view of the orbital regions of the six LCAOMOs. Since each of the $2p_z$ basis functions has a nodal plane in the xy plane, each LCAOMO has this nodal plane. The sign shown in the figure applies to the region above the plane. The broken lines represent vertical nodal planes for the other LCAOMOs. A nodal plane can occur between two carbon atoms or it can pass through a carbon nucleus if the coefficient for the $2p_z$ orbital of that carbon atom vanishes.

Our results follow the general rule that a higher energy corresponds to a larger number of nodes. In addition to the nodal plane in the plane of the molecule, there are no nodal surfaces in the lowest-energy orbital, one nodal plane in each of the next two orbitals (which are degenerate), two nodal planes in the next two orbitals (also degenerate), and three nodal planes in the highest-energy orbital. Without doing any calculations, we might have been able to guess the pattern of the energy levels and the pattern of nodes in the delocalized orbitals from the possible nodal patterns.

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[5] I. N. Levine, *op. cit.*, p. 634ff (note 2).

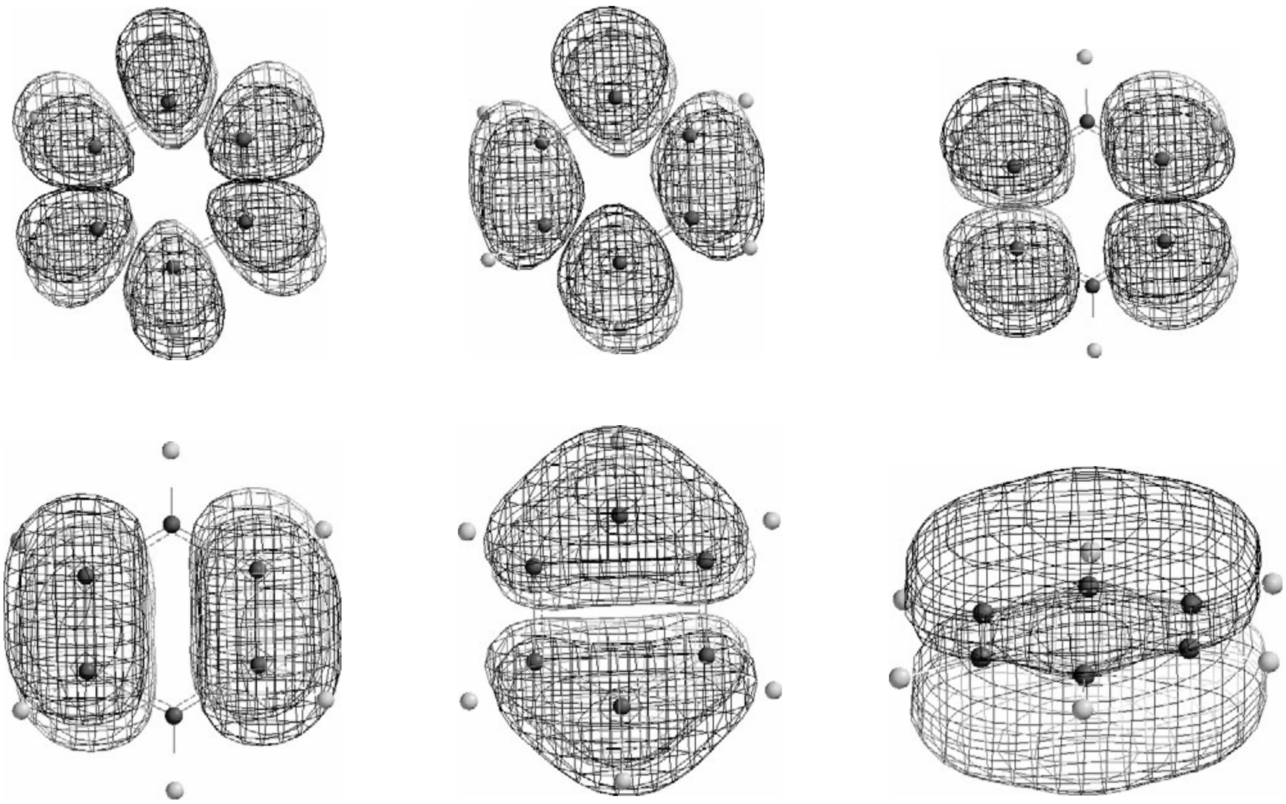


Figure 21.9 The Orbital Regions of the Delocalized Pi Orbitals in Benzene by the Hückel Method. Positive regions are in black and negative regions are in gray.

There are six electrons to occupy the delocalized space orbitals. By the Aufbau principle, in the ground-state each of the three lowest-energy space orbitals is occupied by two electrons with opposite spins, as depicted by arrows in Figure 21.8. Although these orbitals do not have simple angular momentum properties, we refer to them as pi orbitals.

In the first excited state, an electron in one of the highest occupied molecular orbitals (HOMOs) is promoted to one of the lowest unoccupied molecular orbitals (LUMOs), increasing the energy of the molecule by $2|\beta|$. This transition can be observed spectroscopically, and the value of β can be determined.

EXAMPLE 21.10

From the fact that benzene absorbs strongly at wavelengths near 180 nm, estimate the value of β.

Solution

$$2|\beta| = \frac{hc}{\lambda} = \frac{(6.6261 \times 10^{-34}\ \text{J s})(2.9979 \times 10^{8}\ \text{m s}^{-1})}{180 \times 10^{-9}\ \text{m}} = 1.10 \times 10^{-18}\ \text{J}$$

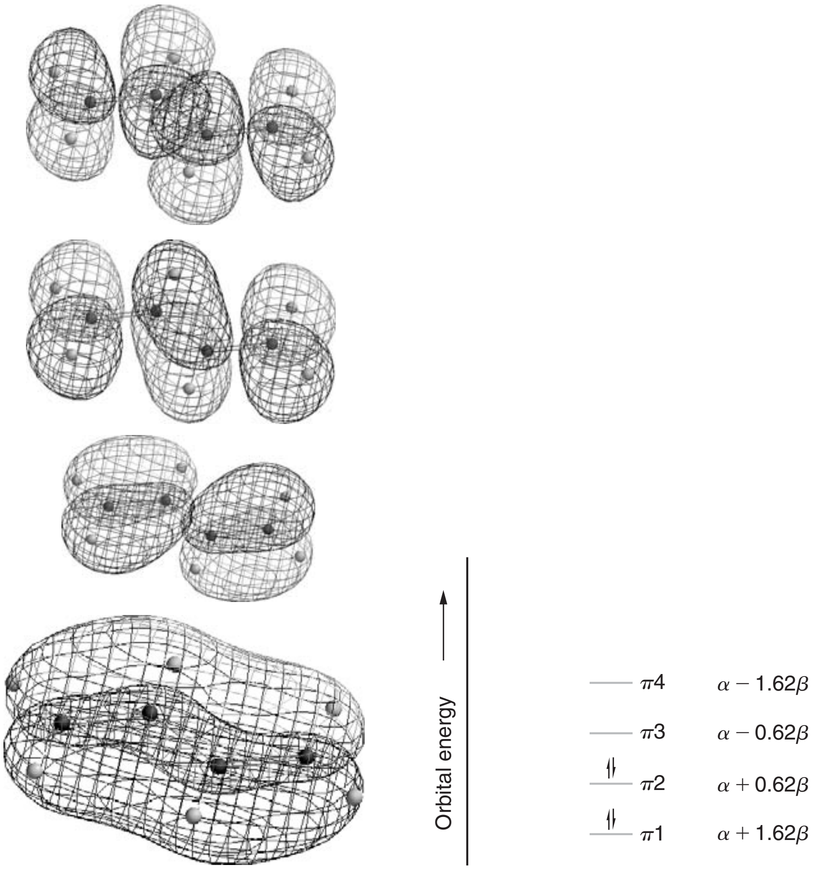
$$\beta = -5.5 \times 10^{-19}\ \text{J},\ \text{which is equivalent to –3.4 eV or –330 kJ mol}^{-1}$$

EXAMPLE 21.11

Without calculations, predict the energies and the shapes of the delocalized pi molecular orbitals for *trans*-1,3-butadiene.

Solution

With the planar molecule located in the xy plane, there are four unhybridized $2p_z$ carbon orbitals to act as basis functions for the delocalized orbitals. We assume that the LCAO-MOs have different numbers of vertical nodal surfaces in addition to the nodal plane in the xy plane: no nodes, one node, two nodes, and three nodes. There is only one symmetrical way to have each number of nodes, with the lowest-energy orbital not having any vertical nodal surfaces, the next-lowest-energy orbital having one vertical nodal surface, and so on. Since there is only one obvious way to have each number of nodes, the energy levels are nondegenerate. Figure 21.10 shows the results of a Hückel calculation, bearing out our predictions.



(a) (b)

Figure 21.10 Results of the Hückel Molecular Orbital Calculation for 1,3-Butadiene. (a) The orbital regions for the 1,3-butadiene Hückel molecular orbitals. (b) The orbital energies of these orbitals. In part a, positive regions are in black and negative regions are in gray.

Exercise 21.12

a. Describe the pi LCAOMOs in the cyclobutadiene molecule, C_4H_4, assuming a square structure. Use $2sp^2$ hybrid orbitals for the sigma bonds, although they do not quite fit. There are two ways to make a single node in a LCAOMO (either horizontal or vertical). Give the electron configuration of the ground-state of the molecule.

b. Describe the bonding using the valence-bond method, using the resonance structures:

c. Describe the bonding using the valence-bond method, assuming the single structure with alternating single and double bonds. The correct structure more nearly resembles one of these resonance structures with bonds of unequal length. The molecule is not aromatic.[6]

PROBLEMS

Section 21.6: Delocalized Bonding

21.24 The motion of the pi electrons around the benzene molecule is sometimes represented as de Broglie waves moving around a circular ring. Take the carbon–carbon distance in the ring as 139 pm, and take the lowest-energy electron state to have a de Broglie wavelength equal to the circumference of the ring, the next to have a de Broglie wavelength equal to half of the circumference, and so on. Find the energy and wavelength of the photons absorbed in the longest-wavelength ultraviolet absorption and compare with the experimental wavelength of 180 nm.

21.25 Using the valence-bond method with resonance, describe the bonding in CO_3^{2-}.

21.26 Describe the bonding of the CO_3^{2-} ion using LCAOMOs. Place the nuclei in the $x-y$ coordinate plane and make delocalized orbitals with the unhybridized p_z orbitals on all four atoms, trying to guess where the nodes are in the lowest-energy delocalized orbitals.

21.27 Sketch the orbital regions that you would expect for the pi electrons in the allyl radical, C_3H_5.

21.28 Sketch the orbital regions that you expect for the pi electrons in cyclobutadiene, C_4H_4.

21.29 Using the valence-bond method, with resonance where appropriate, describe the bonding in the molecules:

- **a.** HNO_3
- **b.** SO_2

21.30 Using the valence-bond method, describe the bonding and molecular shape of

- **a.** 1,3,5-hexatriene
- **b.** NO_2^-
- **c.** CH_3 (methyl radical)

21.31 Carry out the Hückel calculation for the cyclopropenyl radical, C_3H_3, by hand. Notice the similarity with the analysis of the allyl radical in Appendix H. Sketch the orbital region of the lowest-energy LCAOMO. Note that the next-lowest LCAOMOs are degenerate so that different linear combinations can be chosen. Choose two that are eigenfunctions of a vertical reflection operator passing through one of the carbon atoms.

21.32 Carry out the Hückel calculation for the cyclopropenyl cation, $C_3H_3^+$. How does it differ from the analysis of the cyclopropenyl radical?

21.33 Use the energy level expressions for benzene and for 1,3-butadiene to obtain two different values for the parameter β in the Hückel theory, using the fact that the strongest ultraviolet absorption in benzene is at a wavelength 180 nm, while the strongest ultraviolet absorption in 1,3-butadiene is at 217 nm. Compare these values with an accepted value of $\beta = -2.71$ eV[7] and explain why the values do not agree.

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[6] I. N. Levine, *op. cit.*, p. 639 (note 2); T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, 3rd ed., Harper and Row, New York, 1987, pp. 43–44.

[7] D. J. Royer, *Bonding Theory*, McGraw-Hill, New York, 1968, p. 162.

21.34 Obtain access to any of the common computer programs that will solve the Hückel molecular orbital problem for various molecules. You will have to find out how the necessary information is put into the computer.

a. Run the program for benzene and for 1,3,5-hexatriene. Compare the results and explain the differences.

b. Run the program for cyclobutadiene and for 1,3-butadiene. Compare the results and explain the differences.

21.35 Obtain access to any of the common computer programs that will carry out the Hückel method. You will have to find out how the necessary information is put into the computer. Run the program for cyclooctatetraene and for 1,3,5,7-octatetraene. Compare the results and explain the differences.

21.7 The Free-Electron Molecular Orbital Method

In the free-electron molecular orbital (FEMO) method delocalized molecular orbitals are represented by particle-in-a-box wave functions. As an example, we discuss the pi electrons in 1,3-butadiene, assuming that the sigma-bond framework has been separately treated. The experimental carbon–carbon bond lengths are 146 pm for the center bond and 134 pm for two outer bonds.[8] The orbital regions must extend beyond the nuclei at the ends of the molecule, so we assign the length of the box in which the pi electrons move to be the sum of the three bond lengths plus one additional bond length at each end. If the extra bond length is taken as the average of the two bond lengths, a total box length of 694 pm (6.94 Å) is obtained.

The energy eigenfunctions and energy levels of a particle in a box are given by Eqs. (15.3-10) and (15.3-11):

$$\psi = \psi_n = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right), \tag{21.7-1}$$

$$E = E_n = \frac{h^2 n^2}{8ma^2} \tag{21.7-2}$$

where a is the length of the box and n is a quantum number (a positive integer). The energy values are nondegenerate. Since we have four electrons, the Aufbau principle gives the ground-state wave function (including only the pi electrons) without antisymmetrization as

$$\Psi_{gs} = \psi_1(1)\alpha(1)\psi_1(2)\beta(2)\psi_2(3)\alpha(3)\psi_2(4)\beta(4) \tag{21.7-3}$$

The ground-state pi-electron energy is

$$E_{gs} = \frac{h^2}{8ma^2}(1^2 + 1^2 + 2^2 + 2^2) = \frac{10h^2}{8ma^2} \tag{21.7-4}$$

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[8] K. Kuchitsu, F. Tsutomu, and Y. Morino, *J. Mol Struct.*, **37**, 2074 (1962).

EXAMPLE 21.12

Using the FEMO method, calculate the wavelength of the light absorbed when 1,3-butadiene makes the transition from the ground-state to the first excited state.

Solution

This transition is the promotion of one electron from $n = 2$ to $n = 3$, so

$$\Delta E = \frac{h^2}{8ma^2}(9-4) = \frac{(5)(6.6261 \times 10^{-34}\,\mathrm{J\,s})^2}{(8)(9.109 \times 10^{-31}\,\mathrm{kg})(6.94 \times 10^{-10}\,\mathrm{m})^2}$$

$$= 6.25 \times 10^{-19}\,\mathrm{J}$$

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.6261 \times 10^{-34}\,\mathrm{J\,s})(2.9979 \times 10^{8}\,\mathrm{m\,s^{-1}})}{6.25 \times 10^{-19}\,\mathrm{J}}$$

$$= 3.18 \times 10^{-7}\,\mathrm{m} = 318\,\mathrm{nm}$$

This is in fairly poor agreement with the experimental value of 217 nm, but it is remarkable that the agreement is not worse than this. Better results could be attained by adding more or less than a full bond length at each end of the carbon–carbon chain.

Exercise 21.13

Modify the length of the “box” to recover the experimental wavelength of 217 nm for 1,3-butadiene. What fraction of a bond added at the ends of the box does this correspond to? Could this fraction be negative?

PROBLEMS

Section 21.7: The Free-Electron Molecular Orbital Method

21.36 Using the same value of β as obtained for benzene in Example 21.10, find the wavelength of the lowest-energy electronic transition in 1,3-butadiene according to the Hückel method. Compare with the experimental value of 217 nm.

21.37 Using the same bond lengths as with 1,3-butadiene, find the reciprocal wavelength of the longest-wavelength electronic transition of 1,3,5-hexatriene according to the FEMO method. Compare with the experimental value, 24,000 cm^{-1}.

21.38 Using the same bond lengths as with 1,3-butadiene, find the wavelength of the longest-wavelength electronic transition of 1,3,5,7-octatetraene according to the FEMO method.

21.39 In the free-electron molecular orbital model, the electrons actually move in three dimensions. For 1,3-butadiene represent the electrons as particles in a three-dimensional box with a length in the x direction equal to 694 pm, width in the y direction equal to 268 pm, and height in the z direction equal to the width. Find the wavelength of the photons absorbed in the longest-wavelength absorption due to changes in the quantum numbers n_y and n_z. Explain why the representation as a one-dimensional box can successfully be used to understand the near-ultraviolet spectrum.

21.8 Applications of Symmetry to Molecular Orbitals

Our treatment of polyatomic molecules thus far has not exploited the symmetry properties of the molecules. We have largely restricted our descriptions of chemical bonding to orbitals made from no more than two atomic orbitals, and have included hybrid orbitals in our basis functions to achieve this goal. The approximate LCAO molecular orbitals that we have created are not necessarily eigenfunctions of any symmetry operators belonging to the molecule.

Consider the H_2O molecule. We now construct a basis set containing linear combinations of atomic orbitals that are eigenfunctions of the symmetry operators that belong to the molecule. We orient the molecule with the center of mass at the origin, the oxygen atom on the z axis and the hydrogen atoms in the yz plane, and with the z axis bisecting the bond angle. The symmetry operators that belong to the H_2O molecule are the identity operator, the $\widehat{C}_{2z}$ operator, a $\hat{\sigma}_v$ reflection with its symmetry element in the plane of the molecule (the yz plane), and a $\hat{\sigma}_v$ operator with its symmetry element perpendicular to the plane of the molecule (the xz plane). The canonical orbitals resulting from a Hartree–Fock–Roothaan calculation can be eigenfunctions of all of these operations.

We begin with a minimal basis set that contains the oxygen $1s$, $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals and the $1s$ orbitals of the two hydrogen atoms. The oxygen orbitals are eigenfunctions of these four operators, but the two hydrogen $1s$ orbitals are not. We replace the hydrogen $1s$ orbitals by linear combinations that are eigenfunctions of the symmetry operators:

$$\psi_{a_1} = \psi_{1s\mathrm{Ha}} + \psi_{1s\mathrm{Hb}} \tag{21.8-1}$$

$$\psi_{b_2} = \psi_{1s\mathrm{Ha}} - \psi_{1s\mathrm{Hb}} \tag{21.8-2}$$

We call these new basis functions *symmetry orbitals* or *symmetry-adapted basis functions*. The labels on these linear combinations are explained in Appendix I. The new basis set consists of the oxygen orbitals ψ_{1s}, ψ_{2s}, ψ_{2p_x}, ψ_{2p_y}, ψ_{2p_z}, and the symmetry orbitals ψ_{a_1} and ψ_{b_2}. The canonical orbitals will be simpler linear combinations of these basis orbitals than if we used the original basis set.

Exercise 21.14

Find the eigenvalue of each basis orbital for each of the operators that belong to the H_2O molecule.

The LCAO molecular orbitals are written in the form

$$\psi = c_{1s\mathrm{O}}\psi_{1s\mathrm{O}} + c_{2s\mathrm{O}}\psi_{2s\mathrm{O}} + c_{2p_z\mathrm{O}}\psi_{2p_z\mathrm{O}} + c_{2p_y\mathrm{O}}\psi_{2p_y\mathrm{O}} + c_{2p_x\mathrm{O}}\psi_{2p_x\mathrm{O}} + c_{a_1}\psi_{a_1} + c_{b_2}\psi_{b_2} \tag{21.8-3}$$

Only basis orbitals of the same symmetry can be included in any one LCAO molecular orbital if it is to be an eigenfunction of the symmetry operators. The a_1 basis function can combine with the $1s$, $2s$, and $2p_z$ functions on the oxygen. The b_2 basis function can combine with the $2p_y$ function on the oxygen, and the $2p_x$ function on the oxygen cannot combine with any of the other basis functions. Table 21.2 contains the values of the coefficients determined by the Hartree–Fock–Roothaan method for the seven canonical molecular orbitals, using Slater-type orbitals (STOs) as basis functions, with

Table 21.2 SCF Orbitals for H_2O

MO	$c_{1s\mathrm{O}}$	$c_{2s\mathrm{O}}$	$c_{2p_z\mathrm{O}}$	$c_{2p_y\mathrm{O}}$	$c_{2p_x\mathrm{O}}$	c_{a_1}	c_{b_2}
1_{a1}	1.000	0.015	0.003	0	0	−0.004	0
2_{a1}	−0.027	0.820	0.132	0	0	0.152	0
1_{b2}	0	0	0	0.624	0	0	0.424
3_{a1}	−0.026	−0.502	0.787	0	0	0.264	0
1_{b1}	0	0	0	0	1.000	0	0
4_{a_1}	0.08	0.84	0.70	0	0	−0.75	0
2_{b_2}	0	0	0	0.99	0	0	−0.89

From M. Pitzer and D. P. Merrifield, *J. Chem. Phys.*, **52**, 4782 (1970).

the lowest-energy orbitals at the top of the table. The orbital designations are explained in Appendix H. There are ten electrons, so that by the Aufbau principle each of the first five orbitals is occupied by two electrons. The $1a_1$ orbital is nearly the same as the nonbonding inner-shell oxygen $1s$ orbital. The $1b_1$ orbital is identical with the oxygen $2p_x$ orbital, and contains a lone pair. The other occupied orbitals extend over the entire molecule.

Exercise 21.15

Sketch an approximate orbital region for the $1b_2$ LCAOMO in Table 21.2. Is this a bonding, a nonbonding, or an antibonding orbital?

This description is somewhat different from the ideas presented in a general chemistry course and with our earlier simple description, in which four electrons are shared between pairs of atoms and four electrons constitute two "lone pairs." If energy-localized orbitals are formed, they have orbital regions primarily concentrated between pairs of atoms and correspond to localized sigma bonds between the oxygen atom and the hydrogen atoms.[9]

PROBLEMS

Section 21.8: Applications of Symmetry to Molecular Orbitals

21.40 Construct symmetry-adapted basis orbitals for the BeH_2 molecule from the minimal basis set used in Section 21.1. How do the LCAOMOs in Table 21.1 relate to these basis orbitals?

21.41 List the symmetry operations that belong to *trans*-1,3-butadiene in its equilibrium nuclear conformation. Construct a set of symmetry-adapted basis orbitals for the delocalized pi orbitals of this molecule. Specify the symmetry operators of which each of the basis orbitals is an eigenfunction and give the corresponding eigenvalues.

21.42 List the symmetry operations that belong to *cis*-1,3-butadiene in its equilibrium nuclear conformation. Construct a set of symmetry-adapted basis orbitals for the delocalized pi orbitals of this molecule. Specify the symmetry operators of which each of the basis orbitals is an eigenfunction and give the corresponding eigenvalues.

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[9] I. N. Levine, *op. cit.*, pp. 513–514 (note 2).

21.43 List the symmetry operations that belong to benzene in its equilibrium nuclear conformation. Specify the symmetry operators of which each of the Hückel orbitals is an eigenfunction and give the corresponding eigenvalues.

21.44 **a.** List the symmetry operators that belong to the N_2O molecule if it has the structure NON.

b. List the symmetry operators that belong to the N_2O molecule if it has the structure NNO.

21.45 Consider a tennis ball or a baseball, ignoring any trademarks or logos. List the symmetry operators that belong to this object.

21.9 Groups of Symmetry Operators

For many molecules, the equilibrium nuclear conformations have useful symmetry properties. In Section 20.1 we introduced several symmetry operators: The identity operator, the inversion operator, reflection operators, and rotation operators. We now add *improper rotations*, which are equivalent to ordinary rotations followed by a reflection through a plane perpendicular to the axis of rotation. The rotation axis is the symmetry element, and the axis and the reflection plane both include the origin. As with ordinary rotations, we consider only counterclockwise rotations such that an integral number of applications of the rotation yield a complete rotation of 360°. An operator that produces a full rotation with n operations is denoted by $\widehat{S}_n$. For example, an $\widehat{S}_4$ operator with the z axis as its symmetry element will rotate by 90° about the z axis and reflect through the xy plane:

$$\widehat{S}_{4z}(x, y, z) = (x', y', z') = (-y, x, -z) \tag{21.9-1}$$

Sometimes the presence of one symmetry operator implies the presence of another. If a molecule has an S_4 axis, it also has a C_2 axis, since the square of the $\widehat{S}_{4z}$ operator is the same as the $\widehat{C}_{2z}$ operator:

$$\widehat{S}_{4z}{}^2(x, y, z) = \widehat{C}_{2_z}(x, y, z) = (-x, -y, z) \tag{21.9-2}$$

If n is an even integer,

$$\widehat{S}_n^n = \widehat{E} \quad (n \text{ even}) \tag{21.9-3}$$

If n is an odd integer

$$\widehat{S}_n^n = \widehat{\sigma} \quad (n \text{ odd}) \tag{21.9-4}$$

where the $\widehat{\sigma}$ operator has the same reflection plane as the $\widehat{S}_n$ operator. An $\widehat{S}_1$ operation has the same effect as the reflection operation, and an $\widehat{S}_2$ operation is equivalent to the inversion operator $\widehat{i}$. The lowest-order improper rotation that is not equivalent to another operator is $\widehat{S}_3$.

EXAMPLE 21.13

Find the location to which the point (x, y, z) is moved by the $\widehat{S}_4$ operator around the y axis.

Solution

The rotation moves the point from (x, y, z) to $(z, y, -x)$. The reflection through the xz plane moves the point to $(z, -y, -x)$.

Exercise 21.16

Find the coordinates of the point to which the point (1, 2, 3) is moved by the $\widehat{S}_3$ operator whose symmetry element is the x axis.

A symmetry operator that does not change the potential energy when applied to the electrons of a molecule commutes with the electronic Hamiltonian in the Born–Oppenheimer approximation and is said to belong to the molecule. To test whether a symmetry operator belongs to a molecule in its equilibrium nuclear conformation, we can apply the symmetry operator to all of the nuclei. If a symmetry operator belongs to a molecule, it either leaves each nucleus in its original location or moves it to the original location of a nucleus of the same isotope of the same element. We can also test the symmetry operator by applying it to the electrons without moving the nuclei and determine whether this changes the potential energy, but this is usually less convenient.

EXAMPLE 21.14

Find the improper rotations that belong to the ethane molecule, C_2H_6, in the staggered conformation.

Solution

We place the molecule so that a hydrogen atom bonded to the upper carbon atom is in the xz plane with a positive value of x and a hydrogen atom bonded to the lower carbon atom is in the xz plane with a negative value of x. There is an S_3 axis coinciding with the z axis. A rotation of 180° about the y axis exchanges these two hydrogens and also exchanges two other pairs of hydrogens. The reflection through the xz plane exchanges the four hydrogens not in the xz plane, so the $\widehat{S}_{2y}$ operator with the y axis as its element belongs to the molecule. There are two additional $\widehat{S}_2$ operators with axes perpendicular to planes containing hydrogen nuclei, so there are three $\widehat{S}_2$ operators that belong to the molecule as well as the $\widehat{S}_3$ operator.

We can think of a symmetry operator as a mathematical operator that can operate both on points and functions, or we can think of a *symmetry operation* as a means of moving a point in three-dimensional space. The effect of the symmetry operator on a point is the same as the effect of the symmetry operation. A symmetry operation will be denoted by the same symbol as a symmetry operator without the caret (^). When operating on the nuclei of a molecule we will sometimes use the terms “symmetry operators” and “symmetry operations” interchangeably.

EXAMPLE 21.15

List the symmetry operations that belong to the H_2O molecule in its equilibrium nuclear conformation.

Solution

There is a C_2 axis that bisects the bond angle, and we orient the molecule so that this symmetry axis coincides with the z axis. There is a σ_v reflection plane in the plane of the molecule, which we place in the yz plane, and there is another σ_v plane perpendicular to the plane of the molecule, in the xz plane. As with any molecule there is also the identity operation, E.

Exercise 21.17

a. List the symmetry operations that belong to the ammonia molecule, NH_3.

b. List the symmetry operations that belong to the ethane molecule, C_2H_6, in its eclipsed conformation. Place the molecule with the C–C bond on the z axis with two hydrogens in the xz plane.

Group Theory

A mathematical **group** is a set of objects called members with a single rule for combining two members of the group to produce another member of the group. We call the member that is produced the *product* of the first two members. In the mathematics of group theory, any well-defined rule for combining two members of the group can be used. In our application of group theory the members of the groups are symmetry operators and the rule for combining two members of the group is operator multiplication. The product of two operators is a third operator that is equivalent to successive application of the two operators with the operator on the right operating first.

The following requirements must be met for the set of members to be a group:

1. If **A** and **B** are members of the group, and if **C** is the product **AB**, then **C** must be a member of the group.
2. The group must contain the identity, **E**, which is defined such that if **A** is a member of the group

$$\mathbf{AE} = \mathbf{EA} = \mathbf{A} \tag{21.9-5}$$

3. If **A** is a member of the group its inverse $\mathbf{A}^{-1}$ must be a member of the group. The inverse of **A** is defined such that

$$\mathbf{AA}^{-1} = \mathbf{A}^{-1}\mathbf{A} = \mathbf{E} \tag{21.9-6}$$

4. The associative law must hold:

$$\mathbf{A}(\mathbf{BC}) = (\mathbf{AB})\mathbf{C} \tag{21.9-7}$$

It is not necessary that the members of the group commute with each other. It is possible that

$$\mathbf{AB} \neq \mathbf{BA} \quad \text{(possible, but not necessary)} \tag{21.9-8}$$

If all the members of the group commute with each other, the group is called *abelian*. It is a fact that the symmetry operators belonging to any symmetrical object form a mathematical group.

Abelian groups are named after Niels Henrik Abel, 1802–1829, a great Norwegian mathematician who was the first to show that a general fifth-degree algebraic equation does not necessarily have a radical expression as a solution.

EXAMPLE 21.16

Show that the symmetry operations belonging to the H_2O molecule form a group.

Solution

Figure 21.11a shows the H_2O nuclear framework in the yz plane oriented as in Example 21.15. The hydrogen atoms are labeled H_A and H_B. The symmetry operators that belong to the molecule are $\widehat{E}$, $\widehat{C}_2$, $\widehat{\sigma}_{vyz}$, reflection through the yx plane and $\widehat{\sigma}_{vxz}$, reflection through the xz plane.

Condition 1. The product of any two members of the group must be a member of the group. The multiplication table of the group is shown in Table 21.3, in terms of the symmetry operations. The operations listed in the first row of the table are to be used as the right factor in a product, and the operations in the first column of the table are to be used as the left factor in the product. The product $\sigma_{yz}C_2$ is obtained as follows: The C_2 operation interchanges the positions of the hydrogen nuclei, as shown in Figure 21.11b. The σ_{yz} reflects through the plane of the nuclei and does not move the nuclei. The nuclei are now in the positions that either the C_2 or the σ_{xz} would have put them, and we have to decide which of these operations is equivalent to the product $\sigma_{yz}C_2$. In order to decide, we consider a coordinate system that moves with the nuclei. A reflection turns a right-handed coordinate system into a left-handed coordinate system. Since the two operations reverse the handedness of the coordinate system as would σ_{xz}, we conclude that

$$\sigma_{yz}C_2 = \sigma_{xz} \tag{21.9-9}$$

A simpler analysis is to notice that σ_{yz} is not the same as E, so that $\sigma_{yz}C_2$ is not the same as C_2. The action of the σ_{xz} operation is shown in Figure 21.11c. The products of other pairs of operations are obtained similarly.

Condition 2. The group does contain the identity operation, E.

Condition 3. The inverse of every member is in the group, because each member of this group is its own inverse.

Condition 4. The group operation is associative, because operator multiplication is associative.

Exercise 21.18

Verify several of the entries in Table 21.3, the multiplication table for this group.

Point Groups and Schoenflies Symbols

A group that consists of point symmetry operations is called a *point group*. A unique symbol called a *Schoenflies symbol* is assigned to each point group. The Schoenflies symbol of the point group of the H_2O molecule is C_{2v}. This symbol indicates that the molecule has a C_2 rotation axis and two vertical mirror planes. You can specify the symmetry properties of a molecule like H_2O or SO_2 quickly to a knowledgeable person

Table 21.3 Multiplication Table for the H_2O Molecule

	E	C_2	σ_{yz}	σ_{xz}
E	E	C_2	σ_{yz}	σ_{xz}
C_2	C_2	E	σ_{xz}	σ_{yz}
σ_{yz}	σ_{yz}	σ_{xz}	E	C_2
σ_{xz}	σ_{xz}	σ_{yz}	C_2	E

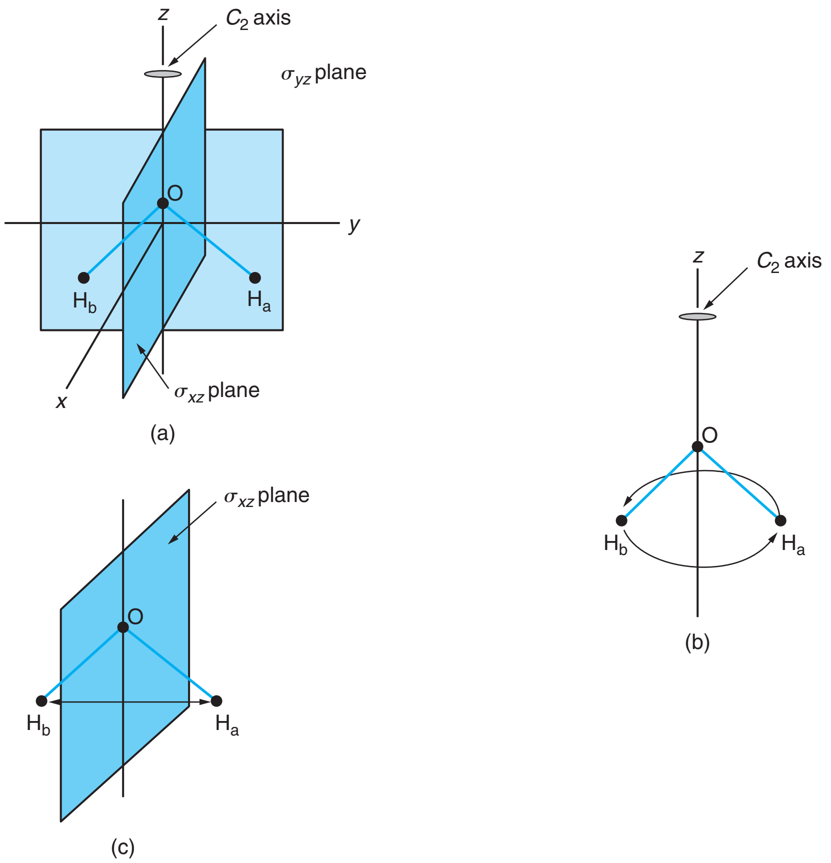

Figure 21.11 The H_2O Molecule. (a) The molecule in the standard location in the coordinate system. The symmetry elements C_2, σ_{xz}, and σ_{yz} are shown. (b) The action of the C_2 operation on the nuclei. (c) The action of the σ_{xz} operation on the nuclei.

by saying that it has C_{2v} symmetry. The NH_3 molecule belongs to the C_{3v} point group, which contains the operations E, C_3, C_3^2, and three σ_v operations.

There are many different point groups. Table 21.4 shows some common point groups with their Schoenflies symbols, a list of the symmetry operations in each group, and a representative molecule belonging to each group. A rotation axis of order greater than 2 implies the presence in the group of more than one operation for that axis. For example, a C_3 operation corresponds to a counterclockwise rotation of 120°. The group must include its inverse, which is a rotation of 120° in the clockwise direction. This inverse is equivalent to C_3^2, corresponding to a rotation of 240° in the counterclockwise direction, so C_3^2 must be a member of any group containing C_3. These two operations are listed as $2C_3$. Benzene has a six-fold axis so that in order to include all the operations and their inverses for this axis, the group must include C_6, C_6^2, C_6^3, C_6^4, and C_6^5. These are listed as $2C_6$, $2C_3$, and C_2, where $2C_6$ indicates C_6 and C_6^5, $2C_3$ indicates C_6^2 (same as C_3) and C_6^4 (same as C_3^2), and where C_2 indicates C_6^3.

The main part of the Schoenflies symbol is a capital letter. There is a capital C if there are no two-fold axes perpendicular to the principal rotation axis (the axis of largest value of n) or a capital D if there are such two-fold axes. There is a subscript that denotes the value of n for the highest-order rotation axis. A subscript v indicates the presence of vertical mirror planes, and a subscript h denotes the presence of a horizontal

Table 21.4 Examples of Some Point Groups

Schoenflies Symbol	Symmetry Operations	Example Molecule
C_1	E	CIBrClF
C_s	E, σ	$H_2C{=}CClBr$
C_i	E, i	HClBrC−CHClBr (staggered conformation)
C_2	E, C_2	H_2O_2
C_{2v}	$E, C_2, 2\sigma$	H_2O, SO_2
C_{3v}	$E, 2C_3, 3\sigma$	NH_3
C_{4v}	$E, 2C_4, C_2, 2\sigma_v, 2\sigma_d$	$XeOF_4$
$C_{\infty v}$	$E, C\infty, \sigma_v$	HF
D_{3h}	$E, 2C_3, 3C_2, 3\sigma_v, \sigma_h$	BF_3
D_{6h}	$E, 2C_6, 2C_3, C_2, C_2', 3C_2'', i, 2S_3, 2S_6, \sigma_h, 3\sigma_d, 3\sigma_v$	C_6H_6
$D_{\infty h}$	$E, C_\infty, C_2, \sigma_h, \sigma_v, i$	H_2
T_d	$E, 8C_3, 3C_2, 6S_4, 6\sigma_d$	CCl_4
O_h	$E, 8C_3, 6C_2', 6C_4, 3C_2, i, 6S_4, 8S_6, 3\sigma_d, 3\sigma_h$	SF_6

mirror plane. For example, the group C_{4v} has a C_4 axis, four vertical mirror planes, and the identity operation E. The group C_1 contains only the identity operation E. The C_s group contains only a reflection plane and E. The T_d group is the group of tetrahedral molecules such as CH_4, and the O_h group is the group of octahedral molecules such as SF_6. These groups contain many symmetry operations, which the interested reader is invited to list.

Exercise 21.19

Think of a molecule belonging to each of the point groups:

a. C_{4v}
b. C_{3v} (other than NH_3)
c. D_{3h}

Figure 21.12 represents a scheme for assigning a molecule to a point group. This type of diagram is called a *decision tree* or a *flow chart*. It is assumed that the user can assign linear molecules, tetrahedral molecules, and octahedral molecules to their groups without use of the decision tree. To use the decision tree, one starts at the top of the diagram with knowledge of the equilibrium nuclear conformation. One looks at the questions at each branching point and answers yes or no to whether a particular symmetry element is present. After each answer one proceeds along the appropriate branch to the next question. There are two places where there is a choice between three alternatives, which must be considered from left to right. The use of this decision tree is illustrated in the following example:

EXAMPLE 21.17

Assign the benzene molecule to a point group.

Solution

The molecule in its equilibrium conformation is in the shape of a regular hexagon of 6 carbon atoms, with a hydrogen atom bonded to each carbon atom, forming a second regular

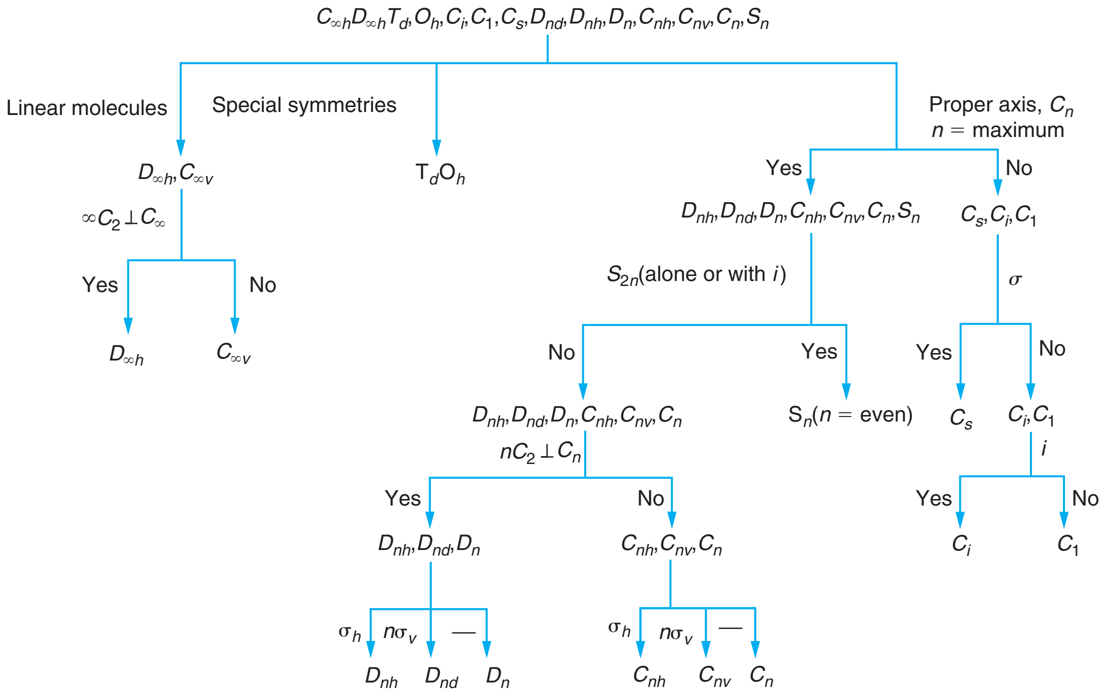

Figure 21.12 Flow Chart (Decision Tree) for the Assignment of a Molecule to a Point Group. To use this chart, start at the top and follow the path that corresponds to the answer to each question.

hexagon in the same plane. Starting at the top of the figure, we eliminate the categories of linear, tetrahedral or octahedral molecules, and move to the right side. There is a proper C_6 axis so we answer “yes” and move to the left branch. Although there is an S_6 axis, is does not occur alone or with inversion so we answer “no” and move to the left branch. There are six C_2 axes perpendicular to the C_6 axis so we answer “yes” and move to the left branch. Next we have three choices, which are to be examined from left to right. The molecule does have a σ_h plane of symmetry, so we arrive at the point group D_{6h}. If there had not been a σ_h plane of symmetry, we would have asked if there were six σ_v planes. If so, the group would be D_{6d}. The benzene molecule does have six σ_v planes, but you must ask about the σ_h plane before asking about the σ_v planes, and the presence of the σ_h plane means that it belongs to the D_{6h} group.

Exercise 21.20

Using the decision tree of Figure 21.12, assign the following molecules to point groups:

a. 1,1-Dichloroethene
b. *trans*-1,2-Dichloroethene
c. *cis*-1,2-Dichloroethene

Some Elementary Applications of Group Theory

Once a molecule has been assigned to a point group we can draw some conclusions about it. If a molecule has a dipole moment, any symmetry operation belonging to the molecule will leave the dipole moment unchanged, since it can at most exchange nuclei of the same type. Only if the dipole moment vector is contained in all of the symmetry elements can there be a nonzero dipole moment. Any molecule with a dipole moment must belong to one of the groups C_1, C_s, C_n, or C_{nv}, where n can be any integer. A molecule with a center of symmetry or a horizontal mirror plane cannot have a dipole moment.

Another immediate conclusion involves optical activity. Any molecule that cannot be superimposed on its mirror image possesses an *enantiomorph*, which is an isomer that is like the mirror image of the first molecule. Two enantiomorphs rotate plane polarized light in opposite directions and are said to be *optically active*. Any molecule that has no symmetry elements or has only proper rotation axes can be optically active. The only groups that meet these criteria are C_1, C_n, and D_n, where n can be any integer. Any molecule with an inversion center, a reflection plane, or an S_n axis cannot be optically active.

There are numerous more advanced applications of group theory. It is possible to determine without calculation whether an overlap integral will vanish, what the degeneracy of an energy level is, whether a transition between certain electronic or vibrational states can be accompanied by emission or absorption of radiation, and so on. These applications use the representations of groups, which are briefly introduced in Appendix I.

PROBLEMS

Section 21.9: Groups of Symmetry Operators

21.46 Show that the group of operations belonging to the water molecule is abelian (all operations commute with each other).

21.47 **a.** Obtain the multiplication table for the C_{3v} point group.

b. Show that it satisfies the conditions to be a group only if C_3^2 is included in the group.

c. Show that the group is not abelian.

21.48 What is the symmetry operator that is equivalent to the product $\hat{i}\widehat{\sigma}_h$? Is this the same as the product $\hat{\sigma}_h\hat{i}$?

21.49 What is the symmetry operator that is equivalent to the product $\widehat{C}_2\hat{i}$? Is it the same as the product $\hat{i}\widehat{C}_2$?

21.50 Write the function that is equal to $\widehat{C}_{4_z}\psi_{2p_x}$.

21.51 List all of the symmetry operators that belong to the formaldehyde (CH_2O) molecule in its equilibrium conformation. Assign it to a point group.

21.52 Write the function that is equal to $\widehat{C}_{2_z}\psi_{2p_x}$.

21.53 List all of the symmetry operations that belong to the BH_3 molecule. Assign it to a point group, using Figure 21.12.

21.54 Construct the multiplication table for the $D_{\infty h}$ point group. Omit the C_∞ and S_∞ operations.

21.55 Construct the multiplication table for the C_{4v} point group.

21.56 Assign the following molecules to point groups:

a. Dichlorodibromomethane

b. Toluene

c. Naphthalene

21.57 Assign the following molecules to point groups:

a. 1,4-Dichlorobenzene

b. 1,2-Dichlorobenzene

c. Tetrachloroethene

21.58 Using the decision tree of Figure 21.12, assign the following molecules to point groups:

a. Ethane (staggered)

b. Ethane (eclipsed)

c. Cyclohexane (boat conformation)

21.59 Assign a tennis ball or a baseball to a point group.

21.60 The N_2O molecule is linear. Assign it to a point group

a. If it has the structure NON,

b. If it has the structure NNO.

21.61 Tell which of the following molecules and ions will have nonzero dipole moments:

a. SO_4^{2-}

b. BF_3

c. $HClO_4$

Explain your answers.

21.62 Tell which of the following molecules and ions will have nonzero dipole moments:

a. $H_2C{=}C{=}CH_2$

b. NO_2

c. CO_2

21.63 Show geometrically that the dipole moment of a tetrahedral molecule such as carbon tetrachloride vanishes. Place the bonds on alternate diagonals of a cube centered at the origin and with faces perpendicular to the Cartesian coordinate axes.

21.10 More Advanced Treatments of Molecular Electronic Structure. Computational Chemistry

Our discussion of molecular electronic structure has been extremely crude compared with current quantum chemistry practice. Over the past several decades modern digital computers have made calculations possible that previously could only be dreamed of. Dewar and Storch have written a review article comparing the results of different semiempirical and ab initio methods in calculating enthalpy changes of reactions.[10] At the time this article was published (1985), no method had given accuracy that is adequate for quantitative chemical purposes for anything but a few small molecules. However, considerable progress has been made since that time.

Semiempirical Methods

There are a number of semiempirical methods, each with its own set of approximations. These methods are analogous to the Hückel method described in Section 21.6 but are more sophisticated. Some use the variation method, but more use the Hartree–Fock–Roothaan method. All of them represent the molecular orbitals as linear combinations of a set of basis functions. There are simultaneous equations to be solved for the coefficients in the linear combinations. These equations contain numerous integrals, including matrix elements of one-electron Hamiltonians such as those in Appendix H for the Hückel method, overlap integrals, and integrals representing expectation values of electron–electron repulsions. These integrals contain only basis functions, so that they can be evaluated numerically if the Hamiltonian is known. In semiempirical methods approximations are used to avoid explicit calculation of some or all of the integrals. Two types of approximations are invoked: The first is the assumption that certain integrals can be approximated by zero, and the second is a scheme to assign approximate values to other integrals such that results agree with experimental data, as was done in the Hückel method.

The Extended Hückel Method

The extended Hückel method was pioneered by Wolfsberg and Helmholz.[11] It is not restricted to the electrons in pi orbitals and can treat molecules that are not planar

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[10] M. J. S. Dewar and D. M. Storch, *J. Am. Chem. Soc.*, **107**, 3898 (1985).

[11] M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

and that do not necessarily have conjugated systems of bonds. All of the valence-shell electrons are included in the treatment, but inner-shell electrons are assumed to be separately treated. A minimal set of basis functions is used that includes all atomic orbitals in the valence shell of every atom.

The procedure is based on the variation method. The Hamiltonian for the valence electrons is assumed to be a sum of effective one-particle Hamiltonians, which are not explicitly represented. Approximations are invoked that differ somewhat from those of the simple Hückel method. The electron–electron repulsive energy is neglected, but the overlap integrals are explicitly calculated. The matrix elements of the effective Hamiltonian, Eq. (H-5) of Appendix H, are approximated using various formulas. The elements with $a = b$ (the diagonal elements) are set equal to the valence-state ionization potential (VSIP) of the given orbital, which is the energy required to remove one electron from the valence shell of the atom. Wolfsberg and Helmholz approximated the off-diagonal elements by the mean of the VSIP of each orbital times a fixed constant times the overlap integral:

$$H_{\mathrm{ab}} = \frac{1}{2}K\left(H_{\mathrm{aa}}^{\mathrm{eff}} + H_{\mathrm{bb}}^{\mathrm{eff}}\right)S_{\mathrm{ab}} \tag{21.10-1}$$

The constant K has been assigned various values from 1 to 3. A value of 1.75 is common. A slightly different version is employed by Ballhausen and Gray, who use the geometric mean instead of the arithmetic mean in approximating H_{ab}.[12]

The extended Hückel method can be used to find the conformation of lowest energy by repeated calculations with different conformations. Reasonable results are obtained, and the resulting conformations are sometimes used as starting points for more sophisticated calculations.

Exercise 21.21

Use a software package such as CAChe or Spartan to find the equilibrium (lowest-energy) conformation for the following molecules, using the extended Hückel method:

a. H_2CO (formaldehyde or methanal)
b. C_2H_6 (ethane)
c. CH_3COCH_3 (acetone or propanone)

The Pariser–Pople–Parr method

The Pariser–Pople–Parr method is the simplest implementation of the self-consistent field method. Like the Hückel method, it treats only the electrons in delocalized pi orbitals in planar molecules and represents these orbitals as linear combinations of basis functions that include only the unhybridized p orbitals. All overlap integrals are assumed to vanish, as in the Hückel method, but not all of the integrals representing electron–electron repulsions are assumed to vanish. Two notations are used for these integrals:

$$(rt|su) = \langle rt|\frac{1}{r_{12}}|su\rangle = \int\int f_r^*(1)\, f_t^*(2)\frac{1}{r_{12}}\, f_s(1)\, f_u(2)dq_1dq_2 \tag{21.10-2}$$

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[12] C. J. Ballhausen and H. B. Gray, *Molecular Orbital Theory*, W. A. Benjamin, New York, 1964, p. 118.

An approximation called *zero differential overlap* is invoked to set some of these integrals to zero. The name is somewhat confusing because the approximation is not applied to overlap integrals but to these electron–electron repulsion integrals. This approximation sets integrals like that of Eq. (21.10-2) equal to zero, unless $r = t$ and $s = u$.

When the LCAOMOs are substituted into the Hartree–Fock equations and the above approximations are applied, a set of equations for the coefficients in the linear combinations is obtained. These equations are called the Roothaan equations.[13] The Roothaan equations are solved by iteration, and the results are the orbital energies and the values of the coefficients for each of the LCAOMOs.

Other Semiempirical Methods

There are a number of other semiempirical methods that use the Hartree–Fock–Roothaan self-consistent field approach. They differ from each other in the scheme used to decide which integrals to approximate by zero and in the scheme used to assign values to the other integrals. Some methods are named according to the type of integrals that are assumed to vanish, such as the CNDO method (complete neglect of differential overlap), the INDO method (intermediate neglect of differential overlap), the NDDO method (neglect of diatomic differential overlap), MNDO (modified neglect of differential overlap), and the MINDO method (modified intermediate neglect of differential overlap). Two common methods that are based on the MNDO method are the AM1[14] and PM3[15] methods, which are included in a package of programs called MOPAC.[16] The CAChe software package contains the MOPAC package as well as additional programs. Other methods are named for approximations of different sorts, such as the PCILO method (perturbative configuration interaction using localized orbitals) and the DIM method (diatomics in molecules). Table 21.5 summarizes some characteristics of several semiempirical methods.

Exercise 21.22

Using a software package, such as CAChe or Spartan, that contains either the AM1 or PM3 method, find the equilibrium conformation of the molecules in Exercise 21.21. Construct and view the orbital regions and compare your results with the results using the extended Hückel method.

Ab Initio Methods

The principal differences between ab initio and semiempirical calculations is that ab initio methods evaluate all of the integrals numerically instead of relying on experimental information to assign values to integrals. The term ab initio means “from the beginning.” If a large enough set of well-chosen basis functions is used, the results of ab initio Hartree–Fock–Roothaan calculations can nearly replicate the Hartree–Fock

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[13] I. N. Levine, *op. cit.*, p. 429ff (note 2).

[14] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985).

[15] J. J. P. Stewart, *J. Comp. Chem.*, **10**, 209 (1989); **10**, 221 (1989).

[16] The MOPAC package of programs was originally available from the Quantum Chemistry Program Exchange at Indiana University, and is included in the CAChe package.

Table 21.5 Comparison of Semiempirical Molecular Orbital Methods

	H	EH	PPP	CNDO	INDO	NDDO	MNDO	MINDO
1	p	v	p	v	v	v	v	v
2	p	g	p	g	g	g	g	g
3	n	n	y	y	y	y	y	y
4	e	a	a	a	a	a	a	a
5	y	n	n	n	n	n	n	n
6	z	c	z	z	z	z	z	z
7	n	n	y	y	y	y	y	y
8	n	n	c	c	i	d	d	i
9	n	y	y	y	y	y	y	y

Methods considered:

H = Hückel, EH = extended Hückel, PPP = Pariser–Pople–Parr, CNDO = complete neglect of differential overlap, INDO = intermediate neglect of differential overlap, NDDO = neglect of diatomic differential overlap, MNDO = modified neglect of differential overlap, MINDO = modified intermediate neglect of differential overlap. Note: AM1 and PM3 are MNDO methods that differ only in the way constants are chosen to approximate various integrals.

Characteristics considered:

1. Type of electrons explicitly treated (p = π only, v = valence only)
2. Molecular geometry that can be treated (p = planar only, g = general)
3. Is it a self-consistent field calculation? (y = yes, n = no)
4. How are matrix elements of H^{eff} obtained? (a = approximated by some formula, e = fit from experimental data)
5. Are some off-diagonal matrix elements of H^{eff} assumed to vanish?
6. How are overlap integrals treated? (z = assumed to vanish, c = calculated)
7. Are electron–electron repulsions included in the Hamiltonian? (y = yes, n = no)
8. How are electron–electron repulsion terms handled? (n = not included, c = zero differential overlap (ZDO) approximation applied to all integrals, i = ZDO not applied to one-center integrals, d = ZDO not applied to one-center integrals nor to a two-center integral if both orbitals of an electron are on the same nucleus)
9. Can the method be used to optimize molecular geometry? (y = yes, n = no)

orbitals, which are the best possible set of orbitals. Various kinds of basis functions are in common use. An important criterion is the speed with which computers can evaluate the integrals occurring in the calculation. It is found that Slater-type orbitals (STOs) require less computer time than hydrogen-like orbitals. These orbitals contain the same spherical harmonic functions as the hydrogen-like orbitals, but their radial factors are exponential functions multiplied by powers of r instead of by polynomials in r. There are rules for guessing appropriate values for the exponents.[17]

In addition to Slater-type orbitals, *Gaussian orbitals* have been widely used. The correct spherical harmonic functions are used for the angular factors, but the radial factor is approximated by

$$R(r) \propto e^{-br^2} \tag{21.10-3}$$

where b is a constant. Such Gaussian functions are not very good representations of radial factors, but allow for even more rapid computer evaluation of integrals than Slater-type orbitals. Some basis sets contain linear combinations of several Gaussian

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[17] I. N. Levine, *op. cit.*, p. 624 (note 2).

functions that simulate Slater-type orbitals. For example, in the STO-3G basis set, each Slater-type orbital is represented approximately by a linear combination of three Gaussian functions.

Since the best single-configuration product of molecular orbitals still contains the correlation error, configuration interaction (CI) is used to improve the energies. This means that the wave function, instead of being a Slater determinant corresponding to a particular electron configuration, is a linear combination of Slater determinants, each corresponding to a different configuration. The CI procedure appears to converge slowly, and numerous configurations are required to obtain nearly complete elimination of the correlation energy. Up to a million configurations have been used in some calculations, but the use of many configurations requires a large amount of computer time.

Most of the methods we have mentioned rely on the Hartree–Fock–Roothaan method. The principal shortcoming of this method is that the only way to eliminate the correlation error is by using configuration interaction, which is rather inefficient. We now mention some computational methods that have been devised to provide a more efficient way to eliminate the correlation error.

The Density Functional Method

This method was mentioned in Chapter 19, and has become a common method in quantum chemical research. Detailed discussion of it is beyond the scope of this book.[18] It has been found that the approximation schemes that have been developed work at least as well as Hartree–Fock–Roothaan methods with configuration interaction for most molecular properties such as bond lengths and energies of molecular ground states.

The Møller-Plesset Perturbation Method

The Møller-Plesset perturbation method was introduced around 1975. It differs from the ordinary perturbation method introduced in Chapter 19 in that the unperturbed wave function is taken to be the Hartree–Fock wave function without configuration interaction. The perturbation term is taken as the difference between the Hartree–Fock potential and the actual interelectron repulsion potential.[19] Calculations are usually carried out to second order but calculations to the fourth order have been done.

The Coupled-Cluster Method

This method introduces electron correlation by expressing configuration interaction in a particular way. The correct wave function Ψ is represented as

$$\Psi = \exp(\widehat{T})\Phi_0 \tag{21.10-4}$$

where Φ_0 is the ground-state Hartree–Fock wave function. The exponential of the operator $\widehat{T}$ is represented by a Taylor series expression, as mentioned in Problem 16.4

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[18] I. N. Levine, *op. cit.*, p. 573ff (note 2) and references cited therein.

[19] I. N. Levine, *op. cit.*, p. 563ff (note 2) and references cited therein.

of Chapter 16.

$$\exp(\widehat{T}) = 1 + \widehat{T} + \frac{1}{2!} + \widehat{T}^2 + \frac{1}{3!}\widehat{T}^3 + \cdots \tag{21.10-5}$$

The operator $\widehat{T}$ is itself a sum of terms that corresponds to excitation of one electron to a previously unoccupied orbital, excitation of two electrons to previously unoccupied orbitals, and so on. We do not discuss the method, which is discussed in some graduate-level quantum chemistry textbooks.[20]

Molecular Mechanics

Molecular mechanics is a branch of calculational chemistry that has achieved considerable success in predicting geometries of molecules and reactive intermediates without any use of quantum mechanics. The potential energy of the molecule is expressed as a sum of functions of the bond lengths and angles, using various empirical formulas for different bonds. Different formulas have been developed by Allinger and others, using trial and error and curve-fitting techniques. These sets of formulas are known by different acronyms such as MM2, MM3, MMFF94, AMBER, and so on.[21] The potential energy functions are built into a computer program, which then carries out the process of finding the conformation of minimum potential energy by varying bond distances and angles. For a molecule containing many atoms the energy minimization can be a difficult problem, and various techniques exist for its solution.[22]

Since the energy change in a chemical reaction is a small fraction of the total energy of the molecules, the total energies must be calculated to very high accuracy in order to get a good approximation to the energy change of a chemical reaction. The energy change in a reaction is typically near 500 kJ mol^{-1} (about 5 eV per molecule) while the total energies of the molecules might be several thousand eV per molecule (several hundred thousand kJ mol^{-1}). Achieving an error of 10% in the energy change of reaction requires an uncertainty of less than a tenth of a percent in the molecular energies. This degree of accuracy is not yet routinely achievable.

There are some things that are inherently very difficult to observe experimentally, and any quantum chemical calculation giving information about such a process can be useful. For example, the elementary steps in a chemical reaction might take place in 10^{-13} second or less, making experimental study difficult. Quantum-chemical calculations giving the energies and geometries (bond angles and lengths) of reactive intermediates can be a source of such information, even if great accuracy is not achieved.

Quantum Chemistry Software

With presently available programs, it is possible for any student of chemistry to carry out a calculation in a few seconds that would have constituted a Ph.D. dissertation fifty

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[20] I. N. Levine, *op. cit.*, p. 568ff (note 2).

[21] N. L. Allinger and L. Yan, *J. Am. Chem. Soc.*, **115**, 11918 (1993); T. A. Halgren, *J. Comput. Chem.*, **20**, 730 (1999).

[22] U. Burkert and N. L. Allinger, *Molecular Mechanics.* ACS Monograph 177, American Chemical Society, Washington, DC, 1982.

years ago. The following is a list of some programs that were available in 2008. All of these programs can carry out geometry optimization, which means finding conformations of minimum energy. Websites that are available in 2008 are given, but these are subject to change.

ArgusLab This program carries out ab initio and semiempirical Hartree–Fock calculations on a Windows machine (no Macintosh version is available). The AM1 and PM3 methods are available for semiempirical calculations. This program is provided free for academic use, but other users must pay a licensing fee. The program is available at http://www.planaria-software.com.

AMPAC This is a comprehensive program that carries out semiempirical molecular orbital calculations by a variety of methods. It can locate transition states by any of several procedures and can treat solvated molecules. It does not include ab initio calculations, but is compatible with Gaussian 03. As of 2008 information is available at http://www.semichem.com/ampac.

CAChe This title of this package of programs is an abbreviation for Computer Assisted Chemistry. The package carries out semiempirical calculations, molecular mechanics calculations, and ab initio calculations with various sets of basis functions. Vibrational and electronic spectra can be calculated and transition states can be determined. Configuration interaction calculations can be carried out. As of 2008 information is available at http://cachesoftware.com.

Chem3D This program is part of a package of programs called ChemOffice that includes ChemDraw and ChemFinder. It carries out molecular mechanics calculations with the MMR formulas, and can also carry out molecular dynamics calculations, which are basically integration of classical equations of motion. There is a trial version that can be used for two weeks without charge, and there is also a demonstration version that can be used indefinitely but cannot save or print files. Information is available at http://www.cambridgesoft.com.

GAMESS This program originated with the research group of M. S. Gordon at the Ames Laboratory at Iowa State University.[23] It is a free program, and can carry out a variety of ab initio calculations, as well as electron correlation corrections by means of configuration interaction, second-order perturbation, and coupled-cluster approaches. Density-functional calculations can also be carried out as can generalized valence-bond calculations. As of 2008, it is available at http://www.msg.chem.iastate.edu/gamess/.

Gaussian This program is said to be the most widely used calculational chemistry program. It has existed in various versions, each labeled by the year in which it appeared. As of 2003, the newest version is Gaussian 03 and the previous version was Gaussian 98. It is capable of carrying out just about every kind of quantum chemistry calculation. Information is available at http://www.gaussian.com.

Hyperchem This program carries out ab initio, density functional, semiempirical, and molecular mechanics calculations. Molecular dynamics calculations can be carried out, giving classical trajectories for reactive collisions. A student version is available at reduced cost. Information is available at http://www.hyper.com.

Jaguar This is a high-speed ab initio program. Information is available at http://www.schrodinger.com.

MOPAC This package of programs is the most widely used semiempirical program. It is claimed that it is capable of handling polypeptides and DNA. It is incorporated

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[23] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Hguyen, S. Su, T. L. Winduw, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.*, **14**, 1347–1363 (1993).

into the CAChe package of programs. As of 2004 the latest version is called MOPAC 2002. Information is available at http://www.schrodinger.com.

Q-Chem This is a program that requires high-level workstations such as DEC alpha and IBM workstations. As of 2004, a version using a Macintosh G4 or G5 with OS X is being developed. Information is available at http://www.q-chem.com.

Spartan This is probably the most widely used program for undergraduate instruction and has appeared in versions for Macintosh and Windows computers. As of 2004, the latest version is called Spartan'06 for Windows, and earlier versions were called PCSpartan Pro and MacSpartan Pro. The new version contains a database with the results of calculations on over 50,000 organic molecules. Semiempirical and ab initio calculations are available, with several basis sets. Density functional methods can be carried out. Molecular mechanics calculations are carried with the MMFF94 formulas. NMR chemical shifts can be calculated, as can vibrational and electronic spectra. Vibrational normal modes are exhibited as movies. Information is available at http://www.wavefun.com.

Any of these programs can be used without detailed knowledge of the calculations carried out by the program. A more complete list is available at http://cmm.info.nih.gov/modeling/universal_software.html

PROBLEMS

Section 21.10: More Advanced Treatments of Molecular Electronic Structure. Computational Chemistry

21.64 **a.** Find the equilibrium conformation of ethylene (ethene, C_2H_4) using semiempirical calculations with either the AM1 or PM3 parameters. Compare the bond angles with the experimental bond angles and with the experimental C–C–H bond angle of 122°.

b. Can you find bonding C–C orbitals in your results that resemble the sigma and pi bonding orbitals used in our crude analysis in Example 21.4? Explain.

21.65 Use a computer program such as CAChe or Spartan to find the semiempirical approximations to the SCF orbitals for benzene, using several methods, such as AM1, PM3, and extended Hückel. Compare your orbitals with those obtained using the Hückel method. Calculate the wavelength of the lowest-energy transition (from the highest occupied MO to the lowest unoccupied MO) for each method. Compare the values with the experimental value 180 nm and with each other.

21.66 Use a computer program such as CAChe or Spartan that carries out ab initio calculations for benzene, using several different basis sets. Compare your orbitals with those obtained using the Hückel method. Calculate the wavelength of the lowest-energy transition (from the highest occupied MO to the lowest unoccupied MO) for each basis set. Compare the values with the experimental value of 180 nm and with each other.

21.67 Use a computer program such as CAChe or Spartan to find the conformation of minimum energy for *trans*-1,3-butadiene, using a semiempirical method such as AM1 or PM3. Compare the bond angles with those predicted by the use of the $2sp^2$ hybrid orbitals. Inspect the orbital regions and try to determine whether the orbitals are eigenfunctions of any symmetry operators.

21.68 Use a computer program such as Spartan that will carry out ab initio calculations to find the conformation of minimum energy for *trans*-1,3-butadiene. Compare the bond angles with those predicted by the use of the $2sp^2$ hybrid orbitals. Inspect the orbital regions and try to determine if the orbitals are eigenfunctions of any symmetry operators. Compare your results with those of Problem 21.67 if you did that problem.

21.69 Use a computer program such as CAChe or Spartan to find the conformation of minimum energy for *cis*-1,3-butadiene, using a semiempirical method such as AM1 or PM3. Compare the bond angles with those predicted by the use of the $2sp^2$ hybrid orbitals. Inspect the orbital regions and try to determine whether the orbitals are eigenfunctions of any symmetry operators. Compare your results with those for *trans*-1,3-butadiene.

21.70 Using an available computational chemistry program, carry out a semiempirical calculation for the carbonate ion, CO_3^{2-}. Compare your LCAOMOs with those obtained by the simple "guesswork" LCAOMO analysis.

21.71 Use a computer program such as CAChe or Spartan to find the semiempirical approximations to the SCF orbitals for cyclooctatetraene (C_8H_8), using several methods, such as AM1, PM3, extended Hückel, and so on. Does the molecule appear to be aromatic?

21.72 Use a computer program such as CAChe or Spartan to find the semiempirical approximations to the SCF orbitals for 1,3,5,7-octatetraene (C_8H_{10}), using several methods, such as AM1, PM3, extended Hückel, and so on.

21.73 Using a program that carries out molecular mechanics, find the equilibrium conformation of each of the following molecules. Compare the bond angles and bond lengths with those obtained with AM1 or PM3 semiempirical methods.

a. H_2CO

b. $CHCl_3$

21.74 Using a program that carries out molecular mechanics, find the equilibrium conformation of each of the following molecules. Compare the bond angles and bond lengths with those obtained with AM1 or PM3 semiempirical methods.

a. C_2H_4

b. CH_3Cl

21.75 Using a program that carries out molecular mechanics, find the equilibrium conformation of *trans*-1,3-butadiene. Compare the bond angles and bond lengths with those obtained with AM1 or PM3 semiempirical methods.

Summary of the Chapter

In this chapter, we have discussed the quantum mechanics of electrons in polyatomic molecules using the Born–Oppenheimer approximation, which is the assumption that the nuclei are stationary as the electrons move. Approximate LCAOMOs for polyatomic molecules were constructed as linear combinations of only two atomic orbitals, conforming to these three general criteria. In the case of the water molecule, it was found that sp^3 hybrid atomic orbitals could produce a satisfactory wave function with a bond angle of 109.5°. The sp^2 hybrid orbitals were useful in constructing LCAOMOs for molecules with double bonds, such as ethene, with the second bond being represented by an LCAOMO made from unhybridized $2p$ orbitals. The sp hybrid orbitals were used in molecules with triple bonds, such as ethyne, with two bonds represented by LCAOMOs made from unhybridized $2p$ orbitals.

Delocalized bonding was described in the valence-bond method by use of the concept of resonance. In the molecular orbital description, delocalized LCAOMOs are used. For example, in the benzene molecule, six of the electrons occupy delocalized orbitals.

A brief introduction to group theory was presented, along with two elementary applications: Determining whether a molecule could be polar and whether it could be optically active.

A brief survey of some of the modern semiempirical molecular orbital methods was presented. These methods can be carried out using commercially available computer software that is relatively easy to use.

ADDITIONAL PROBLEMS

21.76 The N_2O molecule is linear and might have either of the two structures NNO or NON.

a. Using simple Lewis electron dot formulas, decide which structure is more likely, using the formal charge criterion from your general chemistry course.

b. Describe the bonding in the molecule for both of the structures and see if you can decide on the correct structure independently of part a.

21.77 Using either the LCAOMO method or the valence-bond method, describe the bonding in the following molecules.

Include a specification of the molecular geometry, which means the shape of the molecule not including the nonbonding electron pairs.

a. Sulfur hexafluoride, SF_6.

b. Xenon difluoride, XeF_2.

c. Phosphorus trichloride, PCl_3.

21.78 The methylene radical (carbene), CH_2, is said to be linear, whereas CCl_2 is thought to be bent, with a bond angle near 120°. Assuming this to be true, describe the bonding in both molecules and explain the difference in shape. Which molecule will have unpaired electrons?

21.79 The crystal field theory is an approximate theory for complex ions with a transition metal atom in the center and several atoms or groups (ligands) bonded around it. The ligands are approximately represented as point charges.

a. If six negative charges are octahedrally arranged about an iron(II) ion, say which of the real $3d$ orbitals will have their energies raised by a greater amount and which will have their energies raised by a lesser amount.

b. If the energy difference in part a is small, the $3d$ orbitals will be occupied as though they were at the same energy, and if the energy difference is large, the lower-energy $3d$ orbitals will be preferentially occupied in the ground-state. In each case, use Hund's first rule to determine the number of unpaired $3d$ electrons in the iron.

21.80 Calculations[24] indicate that the C–H bonds in methane might have the opposite polarity from that predicted by the electronegativity difference, with each bond having a dipole moment possibly as large as 1.67 debye with a net positive charge on the carbon atom. If each sigma C–H bonding orbital is represented by

$$C(\psi_{2sp^3\mathrm{C}} + c_{\mathrm{H}}\psi_{1s\mathrm{H}})$$

estimate the value of the coefficient c_{H}, assuming the bond polarity given above. Neglect the overlap integral in the calculation.

21.81 The infrared spectrum of methonium ion, CH_5^+, has recently been observed.[25] Using one of the available computational chemistry programs, carry out a semiempirical or ab initio calculation to find its equilibrium conformation and its predicted infrared spectrum.

21.82 Using one of the available computational chemistry programs, carry out a semiempirical or ab initio calculation on the hydroxyl radical, OH, to obtain its LCAOMOs and its electronic spectrum.

21.83 The hydroxyl radical, OH, is important in atmospheric chemistry. Describe the bonding in this radical using hybrid orbitals as appropriate. What orbital is occupied by the unpaired electron?

21.84 Using one of the available computational chemistry programs, carry out a semiempirical or ab initio calculation on the cyclopropenyl cation, $C_3H_3^+$, to obtain its equilibrium conformation, its LCAOMOs, and its electronic spectrum.

21.85 The dipole moment of chloromethane is 1.87 debye. Assume that the C–H bond has length 111 pm and that the C–Cl bond has length 178 pm. Estimate the net charge on each atom, assuming a tetrahedral molecular geometry and assuming that the carbon atom has a net charge of zero.

21.86 Compare the electronic structures of BeH_2, BH_2, CH_2 and H_2O. How many unpaired electrons are there in BH_2? How many in CH_2? Explain your answer.

21.87 Consider the two molecules, BH_3 and NH_3.

a. Describe the bonding in each, using the simple LCAOMO approach of using two atomic orbitals in each LCAOMO. Use the appropriate hybrid atomic orbitals in the LCAO molecular orbitals.

b. Explain why the molecules have different shapes.

c. In the gas phase, a mixture of these two substances undergoes a Lewis acid-base reaction to form an adduct with a coordinate covalent bond. Describe the bonding in this molecule, using the simple LCAOMO approach with the appropriate hybrid atomic orbitals.

d. Compare the adduct of part c to ethane, C_2H_6.

e. Would the adduct of part c be polar or nonpolar? Justify your answer in terms of electronegativity and in terms of orbital energy levels.

f. To which point group does each molecule belong?

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[24] A. E. Reed and F. Weinhold, *J. Chem. Phys.*, **84**, 2428 (1986).

[24] S. Borman, *Chem. Eng. News*, **83**, 45, July 25, 2005.

21.88 Using one of the available computational chemistry programs, carry out a semiempirical or ab initio calculation for

a. NH_3

b. BH_3

c. The adduct of NH_3 and CH_3
Compare your results with those of the previous problem.

21.89 Identify each statement as either true or false. If a statement is true only under special circumstances, label it as false.

a. Hybrid orbitals are used to allow reasonable approximate molecular orbitals to be written as linear combinations of only two atomic orbitals.

b. Every orbital must be an eigenfunction of every operator that belongs to the molecule.

c. If the self-consistent field method were carried out to exact consistency, correct wave functions and correct energy eigenvalues would be obtained.

d. Configuration interaction is one way to reduce the correlation error.

e. In a variation wave function, introducing explicit dependence on electron–electron distances is one way to reduce the correlation error.

f. The symmetry operators that belong to any object form a mathematical group.

g. Only abelian groups can correspond to molecules in their equilibrium conformations.

h. The *sp* hybrid orbitals can be used only with linear molecules.

i. The sp^2 hybrid orbitals can be used only with trigonal planar molecules.

j. The Hückel method is used only for planar molecules with delocalized orbitals.

22

Translational, Rotational, and Vibrational States of Atoms and Molecules

PRINCIPAL FACTS AND IDEAS

1. Atoms have translational and electronic energy.
2. The electronic energy of atoms can usually be ignored.
3. The translational energy of an atom can be represented as that of a structureless particle.
4. Molecules have translational, electronic, rotational, and vibrational energy. The translational energy can be represented as that of a structureless particle.
5. The Born–Oppenheimer approximation is used to separate the electronic motion from the rotational and vibrational motion of molecules.
6. The Born–Oppenheimer energy acts as a potential energy for vibration.
7. In homonuclear diatomic molecules, only half of the values of J, the rotational quantum number, are permitted. In polyatomic molecules $1/\sigma$ of the conceivable rotational states are permitted, where σ is the symmetry number of the molecule.
8. The population of molecular states is governed by the Boltzmann probability distribution.

22.1 The Translational States of Atoms

The energy eigenfunction of a hydrogen atom is given in Eq. (17.1-17) as a product of the center-of-mass factor ψ_c and the relative factor ψ:

$$\Psi = \psi_c(x_c, y_c, z_c)\psi(x, y, z) \tag{22.1-1}$$

where x_c, y_c, and z_c are the Cartesian coordinates of the center of mass of the nucleus and electron, and x, y, and z are the Cartesian coordinates of the electron relative to the nucleus. We now relabel the center-of-mass factor ψ_c as ψ_{tr} and call it the *translational factor*. The relative motion was equivalent to the motion of a fictitious particle with a mass equal to the reduced mass of the electron and nucleus. If the reduced mass is replaced by the electronic mass, the motion is the same as a the motion of an electron around a stationary nucleus (a good approximation). We now relabel the relative factor ψ as ψ_{el} and call it the *electronic factor*.

The energy of a hydrogen atom is given by Eq. (17.1-20)

$$E_{total} = E_c + E_{rel} = E_{tr} + E_{el} \tag{22.1-2}$$

where we now relabel the center-of-mass energy E_c as the translational energy E_{tr}, and relabel the relative energy E_{rel} as the electronic energy E_{el}.

For multielectron atoms, we treated the electronic motion with the assumption that the nucleus is stationary. This is a good approximation because the nucleus is much more massive than the electrons and moves much more slowly, allowing the electrons to follow it to a new position almost as though it had always been there. We can still study the motion of the nucleus. If an atom is not confined in a container its center of mass obeys the time-independent Schrödinger equation of a free particle, Eqs. (15.3-40) and (17.1-18). The solution of the Schrödinger equation for this translational motion is given by Eq. (15.3-41). The translational energy is given by Eq. (15.3-42), and is not quantized.

If an atom is confined in a rectangular box its center of mass cannot move completely up to the walls of the box because of the electrons in the atom. However, if the box is much larger than the size of an atom it will be an excellent approximation to apply the formulas that apply to a particle of zero size to the translation of an atom in a box. The translational energy eigenfunctions would be represented by the normalized version of Eq. (15.3-21):

$$\psi_{tr} = \sqrt{\frac{8}{abc}}\sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_y\pi y}{b}\right)\sin\left(\frac{n_z\pi z}{c}\right) \tag{22.1-3}$$

where a, b, and c are the dimensions of the box and n_x, n_y, and n_z are three quantum numbers, which we now call the *translational quantum numbers*. The translational energy is given by Eq. (15.3-22):

$$E_{tr} = \frac{h^2}{8M}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \tag{22.1-4}$$

where M is the total mass of the atom.

The electronic energy levels of any atom other than the hydrogen atom cannot be represented by any simple formula, and we will usually rely on experimental data for the energy eigenvalues. The electronic energy levels are very widely spaced compared with translational energy levels.

EXAMPLE 22.1

The energy difference between the ground state and first excited electronic level of a hydrogen atom is 10.2 eV. Compare this energy difference with the spacing between the ground state and first excited translational level of a hydrogen atom in a cubical box 0.100 m on a side.

Solution

The ground translational state corresponds to $n_x = n_y = n_z = 1$, which we denote by (111). The first excited level consists of the states denoted by (112), (121), and (211), so the energy difference is

$$\begin{aligned}\Delta E = E_{112} - E_{111} &= \frac{h^2}{8ma^2}(6-3)\\ &= \frac{(6.6261 \times 10^{-34}\,\mathrm{J\,s})^2}{8(1.674 \times 10^{-27}\,\mathrm{kg})(0.100\,\mathrm{m})^2}(6-3)\left(\frac{1\,\mathrm{eV}}{1.6022 \times 10^{-19}\,\mathrm{J}}\right)\\ &= 6.14 \times 10^{-20}\,\mathrm{eV}\end{aligned}$$

which is smaller than the electronic excitation energy by a factor of approximately 10^{-20}.

Exercise 22.1

Calculate the difference in energy between the ground state and the first excited translational level of a xenon atom in a box 0.100 m on each side. Express it in joules and in electron volts. Compare it with the corresponding value for a hydrogen atom in Example 22.1, and also compare it with the excitation energy to the first excited electronic level of the xenon atom, 8.315 eV.

Since the translational energy levels are very closely spaced, the translational quantum numbers of the states occupied at room temperature can be very large.

EXAMPLE 22.2

According to gas kinetic theory, the average translational energy of the atoms of a gas is equal to

$$\langle E_{\mathrm{tr}} \rangle = \frac{3k_{\mathrm{B}}T}{2} \tag{22.1-5}$$

where k_{B} is Boltzmann's constant, $1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}}$, and where T is the absolute temperature.

a. For a hydrogen atom in the box of Example 22.1 with translational energy equal to $3k_{\mathrm{B}}T/2$ at 298 K, find the value of the three translational quantum numbers, assuming them to be equal to each other.

b. Find the change in energy if one of the translational quantum numbers is increased by unity from its value in part a. Find the ratio of this change to the translational energy and to the energy of the first excited electronic state, 10.2 eV.

Solution

a.

$$\frac{3k_BT}{2} = \frac{3}{2}(1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}})(298\,\mathrm{K}) = 6.17 \times 10^{-21}\,\mathrm{J} = \frac{h^2}{8Ma^2}\left(3n_x^2\right)$$

$$n_x = \left[\frac{8(1.674 \times 10^{-27}\,\mathrm{kg})(0.100\,\mathrm{m})^2(6.17 \times 10^{-21}\,\mathrm{J})}{3\left(6.6261 \times 10^{-34}\,\mathrm{J\,s}\right)^2}\right]^{1/2}$$

$$= [6.27 \times 10^{17}]^{1/2} = 7.92 \times 10^8$$

b.

$$\Delta E = \frac{h^2}{8Ma^2}\left[(n_x+1)^2 - n_x^2\right]$$

$$= \frac{(6.6261 \times 10^{-34}\,\mathrm{J\,s})^2}{8\left(1.674 \times 10^{-27}\,\mathrm{kg}\right)(0.100\,\mathrm{m})^2}(2n_x + 1)$$

$$= (3.278 \times 10^{-39}\,\mathrm{J})(2(7.92 \times 10^8) + 1)$$

$$= 5.19 \times 10^{-30}\,\mathrm{J} = 3.24 \times 10^{-11}\,\mathrm{eV}$$

$$\text{Ratio of } \Delta E \text{ to } E = \frac{5.19 \times 10^{-30}\,\mathrm{J}}{6.17 \times 10^{-21}\,\mathrm{J}} = 8.41 \times 10^{-10}$$

$$\text{Ratio of } \Delta E \text{ to the electronic energy} = \frac{3.24 \times 10^{-11}\,\mathrm{eV}}{10.2\,\mathrm{eV}} = 3.18 \times 10^{-12}$$

PROBLEMS

Section 22.1: The Translational States of Atoms

22.1 Repeat the calculation of Example 22.1 for a box 1.00 m on a side. Compare your answer with that of Example 22.1 and comment on any qualitative difference.

22.2 Find the values of the three translational quantum numbers (assumed equal) of a xenon atom in a cubical box 0.200 m on a side if the translational energy is equal to 8.315 eV, the excitation energy to the first excited electronic level.

22.3 If a gaseous CH_4 molecule has a translational energy equal to $3k_BT/2$ at 298.15 K, what are the values of the three translational quantum numbers if the molecule is contained in a cubical box 0.100 m on a side? Assume the three quantum numbers to be equal to each other.

22.4 Find the values of the three translational quantum numbers (assumed equal) of a xenon atom in a cubical box 20.00 m on a side if the translational energy is equal to 8.315 eV, the excitation energy to the first excited electronic level.

22.5 **a.** For a xenon atom in a cubical box with side 0.100 m, find the values of the translational quantum numbers (assumed equal) if the energy is equal to $3k_BT/2$ at 298 K. Compare your values with those of Example 22.2.

b. Find the change in energy if one of the translational quantum numbers is increased by unity from its value in part a. Find the ratio of this change to the translational energy. Compare your values with those of Example 22.2.

c. The first excited electronic level of xenon is 8.315 eV above the ground level. Find the ratio of the energy change in part b to this energy difference.

22.2 The Nonelectronic States of Diatomic Molecules

We assume that the Born–Oppenheimer Schrödinger equation for the electrons of a diatomic molecule has been solved repeatedly for different internuclear distances, giving the electronic energy, E_{el}, as a function of the internuclear distance, r_{AB}. The Born–Oppenheimer energy is the sum of the electronic energy and the nuclear–nuclear repulsion energy, $\mathcal{V}_{\mathrm{nn}}$:

$$E_{\mathrm{BO}} = E_{\mathrm{el}} + \mathcal{V}_{\mathrm{nn}} \tag{22.2-1}$$

For a diatomic molecule, the nuclear–nuclear repulsion energy is given by

$$\mathcal{V}_{\mathrm{nn}} = \frac{e^2 Z_{\mathrm{A}} Z_{\mathrm{B}}}{4\pi\varepsilon_0 r_{\mathrm{AB}}} = \mathcal{V}_{\mathrm{nn}}(r_{\mathrm{AB}}) \tag{22.2-2}$$

where e is the charge on a proton, Z_{A} is the number of protons in nucleus A, Z_{B} is the number of protons in nucleus B, and where the internuclear distance is given by a three-dimensional version of the theorem of Pythagoras:

$$r_{\mathrm{AB}} = [(x_{\mathrm{B}} - x_{\mathrm{A}})^2 + (y_{\mathrm{B}} - y_{\mathrm{A}})^2 + (z_{\mathrm{B}} - z_{\mathrm{A}})^2]^{1/2} \tag{22.2-3}$$

The Born–Oppenheimer energy depends only on r_{AB}

$$E_{\mathrm{BO}} = E_{\mathrm{el}}(r_{\mathrm{AB}}) + \mathcal{V}_{\mathrm{nn}}(r_{\mathrm{AB}}) = \mathcal{V}(r_{\mathrm{AB}})$$

Because E_{BO} depends only on nuclear position, it acts like a potential energy for nuclear motion, and we denote it as $\mathcal{V}(r_{\mathrm{AB}})$.

The Hamiltonian operator for nuclear motion is now

$$\widehat{H}_{\mathrm{nuc}} = \frac{-\hbar^2}{2m_{\mathrm{A}}}\nabla_{\mathrm{A}}^2 + \frac{-\hbar^2}{2m_{\mathrm{B}}}\nabla_{\mathrm{B}}^2 + \mathcal{V}(r_{\mathrm{AB}}) + \mathcal{V}_{\mathrm{ext}} \tag{22.2-4}$$

where ∇_{A}^2 and ∇_{B}^2 are the Laplacian operators for the nuclear coordinates. The electrons in the molecule have been removed from the problem and act only as a source of the potential energy function $\mathcal{V}(r_{\mathrm{AB}})$. If the molecule is not in any container $\mathcal{V}_{\mathrm{ext}}$ is equal to a constant that we can set equal to zero. If the molecule is in a container the collision of a molecule with the container wall will be slightly different for different rotational and vibrational states of the molecule. If the container is large compared with the size of the molecule, it should be a good approximation to ignore this fact and to assume that $\mathcal{V}_{\mathrm{ext}}$ is equal to zero if the center of mass of the molecule is inside the container and approaches infinity outside of the container.

Since $\mathcal{V}_{\mathrm{ext}}$ depends only on the center-of-mass coordinates, $\widehat{H}_{\mathrm{nuc}}$ can be separated into a center-of-mass term and a relative term in the same way as is discussed in

Appendix E and was applied to the hydrogen atom in Chapter 17. We relabel the center-of-mass term as the translational term, $\widehat{H}_{\mathrm{tr}}$:

$$\widehat{H}_{\mathrm{nuc}} = \widehat{H}_{\mathrm{c}} + \widehat{H}_{\mathrm{rel}} = \widehat{H}_{\mathrm{tr}} + \widehat{H}_{\mathrm{rel}} \tag{22.2-5}$$

$$\widehat{H}_{\mathrm{tr}} = \frac{-\hbar^2}{2M}\nabla_{\mathrm{c}}^2 + \mathscr{V}_{\mathrm{ext}}(x_{\mathrm{c}}, y_{\mathrm{c}}, z_{\mathrm{c}}) \tag{22.2-6}$$

$$\widehat{H}_{\mathrm{rel}} = \frac{-\hbar^2}{2\mu}\nabla^2 + \mathscr{V}(r) \tag{22.2-7}$$

where we now drop the subscript AB on the internuclear distance. The sum of the masses of the two nuclei is denoted by M and their reduced mass is denoted by μ:

$$M = m_{\mathrm{A}} + m_{\mathrm{B}} \tag{22.2-8}$$

$$\mu = \frac{m_{\mathrm{A}} m_{\mathrm{B}}}{m_{\mathrm{A}} + m_{\mathrm{B}}} \tag{22.2-9}$$

We neglect the mass of the electrons compared with the nuclei and consider M to the mass of the entire molecule. The operator ∇_{c}^2 is the Laplacian operator for the center-of-mass coordinates and the operator ∇ is the Laplacian operator for the relative coordinates. The x coordinate of the center of mass is

$$x_{\mathrm{c}} = \frac{m_{\mathrm{A}} x_{\mathrm{A}} + m_{\mathrm{B}} x_{\mathrm{B}}}{M} \tag{22.2-10}$$

and the relative x coordinate is

$$x = x_{\mathrm{B}} - x_{\mathrm{A}} \tag{22.2-11}$$

The y and z coordinates are similarly defined.

Since the Hamiltonian operator in Eq. (22.2-5) contains the two terms in Eq. (22.2-6) and Eq. (22.2-7) it can be solved by the separation of variables, yielding one Schrödinger equation for $\widehat{H}_{\mathrm{tr}}$ and one Schrödinger equation for $\widehat{H}_{\mathrm{rel}}$. We assume that the molecule is contained in a rectangular box. The Schrödinger equation for $\widehat{H}_{\mathrm{tr}}$ is like that of a structureless particle in the box, and the particle-in-a-box energy wave functions and the particle-in-a-box energy eigenvalues from Chapter 15 can be used. We now focus on the Schrödinger equation for $\widehat{H}_{\mathrm{rel}}$, which can be solved by a second separation of variables in the same way as was done for the hydrogen atom.

The relative Hamiltonian $\widehat{H}_{\mathrm{rel}}$ gives the same Schrödinger equation as in Eq. (17.2-2) since that equation applies to any two-body system in which $\mathscr{V}$ depends only on r. We now omit the subscript AB on r. This equation is solved by the trial function of Eq. (17.2-3):

$$\psi_{\mathrm{rel}}(r, \theta, \phi) = R(r)Y(\theta, \phi) \tag{22.2-12}$$

The Y factor represents the same spherical harmonic functions as in Chapter 17, which are eigenfunctions of $\widehat{L}^2$, the operator for the square of the angular momentum. Substitution of $\psi_{\mathrm{rel}} = R(r)Y(\theta, \phi)$ into the time-independent Schrödinger equation and division by $R(r)Y(\theta, \phi)$ gives Eq. (17.2-5):

$$-\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu r^2}{\hbar^2}(\mathscr{V} - E_{\mathrm{rel}}) + \frac{1}{\hbar^2}\frac{1}{Y}\widehat{L}^2 Y = 0 \tag{22.2-13}$$

To solve this equation for the nuclear motion of a diatomic molecule, we must have a representation of the potential energy function $\mathscr{V}(r)$.

The Rigid Rotor

The rigid rotor is a model system that consists of two nuclei with fixed internuclear distance equal to r_e. No vibration is possible. Because r is fixed at the value r_e, the derivatives with respect to r in Eq. (22.2-13) do not occur, and because $\mathscr{V}$ depends only on r, the potential energy has a constant value that we set equal to zero:

$$\mathscr{V} = \mathscr{V}(r_e) = \text{constant} = 0 \tag{22.2-14}$$

Equation (22.2-13) now becomes

$$\frac{1}{2\mu r_e^2}\widehat{L}^2 Y = E_{\text{rel}} Y \tag{22.2-15}$$

This equation is the same as Eq. (17.2-6) except for the factor $1/2\mu r_e^2$. It is satisfied by the spherical harmonic function Y_{JM} of Section 17.2, which we now denote as the rotational wave function ψ_{rot}:

$$\psi_{\text{rot}} = Y_{JM}(\theta, \phi) = \Theta_{JM}(\theta)\Phi_M(\phi) \tag{22.2-16}$$

It is customary to use the letters J and M for the quantum numbers instead of l and m for rotational states:

$$J = 0, 1, 2, \ldots \tag{22.2-17a}$$

$$M = J, J-1, \ldots, -J+1, -J \tag{22.2-17b}$$

From the angular momentum eigenvalues in Eq. (17.2-27),

$$\boxed{E = E_J = \frac{\hbar^2}{2\mu r_e^2} J(J+1) \quad \text{(rigid rotor)}} \tag{22.2-18}$$

The degeneracy of the energy level for a given value of J is equal to the number of possible values of M (J positive values, J negative values, plus one zero value):

$$g_J = (2J+1) \tag{22.2-19}$$

Figure 22.1 shows the first few energy levels. The degeneracies are depicted by placing a line segment for each value of M.

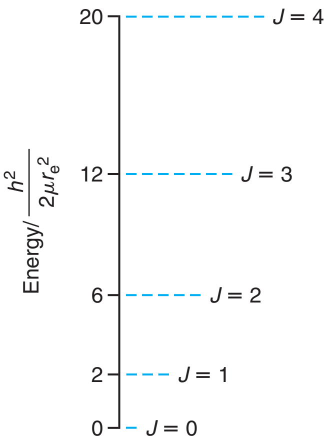

Figure 22.1 Energy Levels of the Rigid Rotor.

EXAMPLE 22.3

Assume that the carbon monoxide molecule is a rigid rotor with $r_e = 1.128 \times 10^{-10}$ m. Find the rotational energy for $J = 0$ and $J = 1$.

Solution

$$\mu = \frac{(12.000\,\text{amu})(15.9949\,\text{amu})}{12.000\,\text{amu} + 15.9949\,\text{amu}}\left(\frac{1\,\text{kg}}{6.02214 \times 10^{26}\,\text{amu}}\right)$$

$$= 1.1385 \times 10^{-26}\,\text{kg}$$

$$E_0 = 0$$

$$E_1 = \frac{h^2}{8\pi\mu r_e^2}(1)(2) = 2.412 \times 10^{-22}\,\text{J}$$

Exercise 22.2

Find the frequency and wavelength of the radiation absorbed if a carbon monoxide molecule makes a transition from the $J = 0$ state to one of the $J = 1$ states. In which region of the electromagnetic spectrum does this radiation lie?

The Rotation and Vibration of Diatomic Molecules

In order to discuss vibration as well as rotation, we abandon the rigid rotor model. Using the eigenvalue of $\widehat{L}^2$ from Eq. (17.2-27) we can write Eq. (22.2-13) in the form

$$-\frac{d}{dr}r^2\frac{dR}{dr} + \frac{2\mu r^2}{\hbar^2}(\mathcal{V} - E)R + J(J+1)R = 0 \tag{22.2-20}$$

where we now omit the subscript on the relative energy E_{rel}. To proceed we need a representation of the potential energy $\mathcal{V}(r)$. Curves that schematically represent $\mathcal{V}(r)$ for two electronic states are depicted in Figure 22.2. These curves conform to the general pattern that the state of higher energy has the longer equilibrium internuclear distance and a weaker bond. We represent $\mathcal{V}(r)$ as a power series in the variable $x = r - r_{\mathrm{e}}$, where r_{e} is the value of r at the minimum in $\mathcal{V}$:

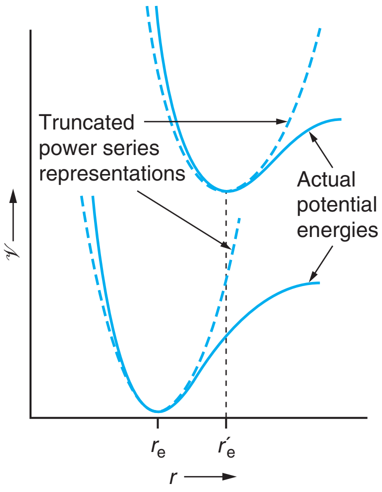

Figure 22.2 Vibrational Potential Energy for a Typical Diatomic Molecule in Two Electronic States.

$$\mathcal{V}(r) = \mathcal{V}(x) + \left(\frac{d\mathcal{V}}{dr}\right)_{r_{\mathrm{e}}} x + \frac{1}{2!}\left(\frac{d^2\mathcal{V}}{dr^2}\right)_{r_{\mathrm{e}}} x^2 + \cdots \tag{22.2-21}$$

where the subscript 0 means that the derivatives are evaluated at $x = 0$. The function $\mathcal{V}(r)$ is at a minimum if $x = 0$, so the first derivative vanishes. To a fairly good approximation, we truncate the series at the quadratic term and write

$$\mathcal{V}(r) = \mathcal{V}_{\mathrm{e}} + \frac{1}{2!}\left(\frac{d^2\mathcal{V}}{dx^2}\right)_0 x^2 = \mathcal{V}_{\mathrm{e}} + \frac{1}{2}kx^2 \tag{22.2-22}$$

where we use the same symbol for $\mathcal{V}$ whether it is expressed as a function of r or of x and where $\mathcal{V}_{\mathrm{e}} = \mathcal{V}(r_{\mathrm{e}})$. The quantity k is a force constant like the one that we introduced for the harmonic oscillator in Chapter 15. The function of Eq. (22.2-22) is called a *harmonic potential*. The parabolas representing the harmonic potential are included in Figure 22.2.

The radial Schrödinger equation is now

$$\frac{d}{dr}r^2\frac{dR}{dr} - J(J+1)R + \frac{2\mu r^2}{\hbar^2}\left(E - \mathcal{V}_{\mathrm{e}} - \frac{kx^2}{2}\right)R = 0 \tag{22.2-23}$$

We define a new dependent variable

$$S(r) = rR(r) \tag{22.2-24}$$

The derivative of Eq. (22.2-23) is

$$\frac{d}{dr}r^2\frac{dR}{dr} = \frac{d}{dr}r^2\frac{dS/r}{dr} = \frac{d}{dr}r^2\left(\frac{1}{r}\frac{dS}{dr} - \frac{S}{r^2}\right) = \frac{d}{dr}\left(r\frac{dS}{dr} - S\right)$$

$$= r\frac{d^2S}{dr^2} + \frac{dS}{dr} - \frac{dS}{dr} = r\frac{d^2S}{dr^2}$$

so that Eq. (22.2-23) becomes

$$\frac{\hbar^2}{2\mu}\left(\frac{rd^2S}{dr^2}-\frac{J(J+1)rS}{r^2}\right)+\left(E-\mathscr{V}_{\mathrm{e}}-\frac{kx^2}{2}\right)rS=0$$

$$\frac{\hbar^2}{2\mu}\left(\frac{d^2S}{dr^2}-\frac{J(J+1)S}{r^2}\right)+\left(E-\mathscr{V}_{\mathrm{e}}-\frac{kx^2}{2}\right)S=0 \qquad (22.2\text{-}25)$$

We express $1/r^2$ as a power series in x:

$$\frac{1}{r^2}=\frac{1}{(r_{\mathrm{e}}+x)^2}=\frac{1}{r_{\mathrm{e}}^2}\left(1-\frac{2x}{r_{\mathrm{e}}}+\frac{3x^2}{r_{\mathrm{e}}^2}+\cdots\right) \qquad (22.2\text{-}26)$$

If x is quite small compared with r_{e}, it is a fairly good approximation to keep only the first term of this series:

$$\frac{1}{r^2}\approx\frac{1}{r_{\mathrm{e}}^2} \qquad (22.2\text{-}27)$$

Using this approximation and the fact that $d^2S/dx^2=d^2S/dr^2$, Eq. (22.2-25) becomes

$$-\frac{\hbar^2}{2\mu}\frac{d^2S}{dx^2}+\frac{kx^2}{2}S=\left(E-\mathscr{V}_{\mathrm{e}}-\frac{\hbar^2}{2\mu r_{\mathrm{e}}^2}J(J+1)\right)S \qquad (22.2\text{-}28)$$

Equation (22.2-28) is the same as the harmonic oscillator Schrödinger equation of Eq. (15.4-1), except for the presence of the two constant terms subtracted from the energy eigenvalue. The function S is the same as the harmonic oscillator energy eigenfunction, given by Eqs. (15.4-10), (15.4-11), and so on. The energy eigenvalue E for the relative energy is the harmonic oscillator energy eigenvalue of Eq. (15.4-8) plus the two constant terms. (See Problem 15.6 for the effect of adding a constant to a potential energy function.)

$$E=E_{vJ}=h\nu_{\mathrm{e}}\left(v+\frac{1}{2}\right)+\frac{\hbar^2}{2\mu r_{\mathrm{e}}}J(J+1)+\mathscr{V}_{\mathrm{e}} \qquad (22.2\text{-}29a)$$

$$=E_{\mathrm{vib},v}+E_{\mathrm{rot},J}+\mathscr{V}_{\mathrm{e}} \qquad (22.2\text{-}29b)$$

The energy eigenvalue is a harmonic oscillator energy eigenvalue plus a rigid rotor energy eigenvalue, plus a constant, $\mathscr{V}_{\mathrm{e}}$.

The quantity ν_{e} is the oscillator frequency of Eq. (14.2-29) except that in our case we have a reduced mass μ instead of a mass m:

$$\nu_{\mathrm{e}}=\frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \qquad (22.2\text{-}30)$$

We can express the rotational energy in terms of the equilibrium *moment of inertia* of the diatomic molecule:

$$I_{\mathrm{e}}=\mu r_{\mathrm{e}}^2 \qquad (22.2\text{-}31)$$

The quantum number v can equal 0, 1, 2, …, and the quantum number J can also equal 0, 1, 2, …. We refer to the approximation of Eq. (22.2-29) as the *rigid rotor–harmonic oscillator approximation*.

The wave function for the relative motion of the nuclei is now

$$\psi_r = \Theta_{JM}(\theta)\Phi_M(\phi)\frac{S_v(r - r_e)}{r} = \psi_{\text{rot},JM}(\theta, \Phi)\psi_{\text{vib},v}(x) \qquad (22.2\text{-}32)$$

The rotational wave function is the same spherical harmonic function that occurred with the hydrogen atom or the rigid rotor:

$$\psi_{\text{rot},JM} = \Theta_{JM}(\theta)\Phi_M(\phi) \qquad (22.2\text{-}33)$$

The vibrational wave function is equal to a harmonic oscillator wave function divided by r, the internuclear distance.

$$\psi_{\text{vib},v} = R(r) = \frac{S_v}{r} = \frac{\Psi_{\text{HO},v}}{r} \qquad (22.2\text{-}34)$$

The wave function is given in the Born–Oppenheimer approximation by the wave function for relative nuclear motion times the translational wave function times the electronic wave function:

$$\psi_{\text{tot}} = \psi_{\text{tr}}\psi_{\text{rel}}\psi_{\text{el}} = \psi_{\text{tr}}\psi_{\text{rot}}\psi_{\text{vib}}\psi_{\text{el}} \qquad (22.2\text{-}35)$$

The energy is the translational energy plus the relative energy in Eq. (22.2-29).

$$E = E_{\text{tr}} + E_{\text{vJ}} = E_{\text{tr}} + h\nu_e\left(v + \frac{1}{2}\right) + \frac{\hbar^2}{2I_e}J(J+1) + \mathcal{V}_e \qquad (22.2\text{-}36)$$

We write this as

$$E_{\text{tot}} = E_{\text{tr}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{el}} \qquad (22.2\text{-}37)$$

where

$$E_{\text{tr}} = E_{n_x n_y n_z} = \frac{h^2}{8M}\left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right] \qquad (22.2\text{-}38)$$

$$E_{\text{vib}} = h\nu_e\left(v + \frac{1}{2}\right) \qquad (22.2\text{-}39)$$

$$E_{\text{rot}} = \frac{\hbar^2}{2I_e}J(J+1) \qquad (22.2\text{-}40)$$

$$E_{\text{el}} = \mathcal{V}_e = \mathcal{V}(r_e) = E_{\text{BO}}(r_e) \qquad (22.2\text{-}41)$$

The electronic energy E_{el} is equal to a constant. The rest of the Born–Oppenheimer energy was taken as the potential energy of vibration. Sometimes the zero-point vibrational energy is included in the constant electronic energy, so that

$$E_{\text{el}} = \mathcal{V}_e + \frac{h\nu_e}{2} \quad \text{(alternate version)} \qquad (22.2\text{-}42)$$

and

$$E_{\text{vib}} = h\nu_e v \quad \text{(alternate version)} \qquad (22.2\text{-}43)$$

The electronic energy E_{el} for the electronic ground state is usually assigned the value zero, which makes E_{el} equal to a different positive constant for each excited level.

EXAMPLE 22.4

For a carbon monoxide molecule in a cubical box 0.100 m on a side, compare the spacing between the ground state and the first excited level for translation, rotation, vibration, and electronic motion. The equilibrium bond length is 1.128×10^{-10} m, and the vibrational frequency is $6.505 \times 10^{13}\ \text{s}^{-1}$ for the ground electronic state. The excitation energy to the first excited electronic state is 6.036 eV.

Solution

We assume the most common isotopes, ^{12}C and ^{16}O, for which $M = 4.469 \times 10^{-26}$ kg and $\mu = 1.138 \times 10^{-26}$ kg. For translation,

$$E_{211} - E_{111} = \frac{h^2}{8Ma^2}(6-3) = \frac{(6.6261 \times 10^{-34}\ \text{J s})(3)}{8(4.469 \times 10^{-26}\ \text{kg})(0.100\ \text{m})^2}$$

$$= 3.68 \times 10^{-40}\ \text{J} = 2.30 \times 10^{-21}\ \text{eV}$$

For rotation,

$$E_1 - E_0 = \frac{\hbar^2}{2I_{\text{e}}}(2-0) = \frac{h^2}{8\pi^2 \mu r_{\text{e}}^2}(2-0)$$

$$= \frac{\left(6.6261 \times 10^{-34}\ \text{J s}\right)^2(2)}{8\pi^2\left(1.138 \times 10^{-26}\ \text{kg}\right)\left(1.128 \times 10^{-10}\ \text{m}\right)^2}$$

$$= 7.68 \times 10^{-23}\ \text{J} = 4.79 \times 10^{-4}\ \text{eV}$$

For vibration,

$$E_1 - E_0 = h\nu_{\text{e}}\left(\frac{3}{2} - \frac{1}{2}\right) = h\nu_{\text{e}}$$

$$= (6.6261 \times 10^{-34}\ \text{J s})(6.505 \times 10^{13}\ \text{s}^{-1}) = 4.310 \times 10^{-20}\ \text{J} = 0.269\ \text{eV}$$

The rotational level spacing is larger than the translational level spacing by a factor of 10^{17}, the vibrational energy level spacing is larger than the rotational level spacing by a factor of about 600, and the electronic level spacing is larger than the vibrational level spacing by a factor of about 20.

The results of Example 22.4 are typical. The translational levels are much closer together than the rotational levels, which are quite a bit closer together than the vibrational levels, which are in turn quite a bit closer together than the electronic levels, which are typically spaced by several electron volts.

The energy level expression of Eq. (22.2-29) is only a first approximation. The power series expression for the vibrational potential energy function V was truncated at the quadratic term and the internuclear distance was replaced by its equilibrium value. One additional term of the power series can be kept or an alternate representation of the potential energy can be used.[1] The most commonly used representation is the *Morse function*

$$\mathscr{V}(r) = \mathscr{V}(r_e) + D_e\left(1 - e^{-a(r-r_e)}\right)^2 \tag{22.2-44}$$

where D_e is the *dissociation energy*, which is equal to the energy required to dissociate the molecule from the state of minimum $\mathscr{V}$. The parameter a determines the curvature of the function and is equal to $k/(2D_e)$. The values of these parameters must be determined for each substance. Figure 22.3a depicts the Morse function for the CO molecule. The Schrödinger equation for the Morse function has been solved.[2] It has also been treated in second-order perturbation theory.[3]

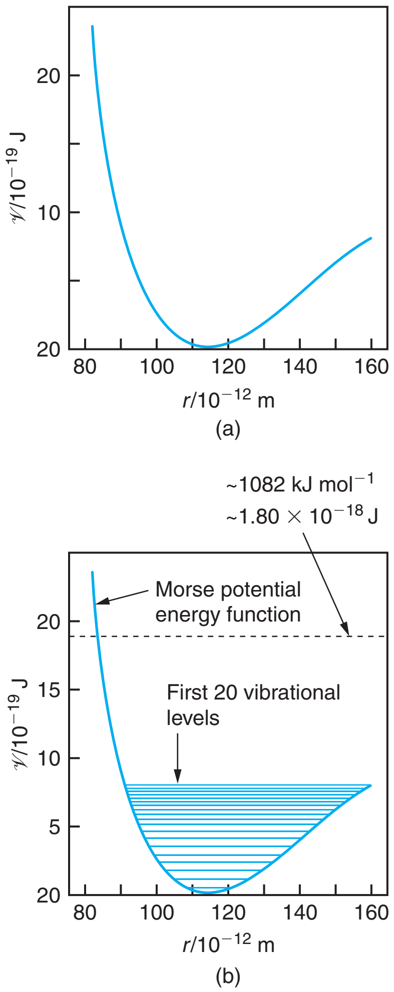

Figure 22.3 The Vibrational Potential Energy and Energy Levels of the CO Molecule. (a) The vibrational potential energy represented by the Morse function. (b) The first 20 vibrational energy levels for the Morse potential. The Morse potential parameters for CO are $D_e = 11.2$ eV $= 1.80 \times 10^{-18}$ J and $a = 2.2994 \times 10^{10}$ m^{-1}. The force constant for the harmonic potential is $k = 1900$ N m^{-1}.

Exercise 22.3

a. Using the general relation between potential energy and force, Eq. (E-6) of Appendix E, obtain a formula for the force on a nucleus in a diatomic molecule described by the Morse potential function.

b. Show that D_e is equal to the difference in potential energy between the minimum and the value for large r.

c. Show that r_e is the value of r at the minimum and show that there is no force if $r = r_e$.

Corrections for anharmonicity, for centrifugal stretching, and for interaction between vibration and rotation can be added to the energy level expression, giving for the energy of vibration and rotation

$$\begin{aligned} E_{vJ} = {} & h\nu_e\left(v + \frac{1}{2}\right) - h\nu_e x_e\left(v + \frac{1}{2}\right)^2 + hB_e J(J+1) \\ & - h\mathscr{D}J^2(J+1)^2 - h\alpha\left(v + \frac{1}{2}\right)J(J+1) \end{aligned} \tag{22.2-45}$$

The constant parameters in this expression are all positive and are given for the Morse potential by[4]

$$\alpha = \frac{3h^2\nu_e}{16\pi^2\mu r_e^2 D_e}\left(\frac{1}{ar_e} - \frac{1}{a^2r_e^2}\right) \tag{22.2-46}$$

$$x_e = \frac{h\nu_e}{4D_e} \tag{22.2-47}$$

$$B_e = \frac{\hbar}{4\pi I_e} = \frac{h}{8\pi^2 I_e} \tag{22.2-48}$$

$$\mathscr{D} = \frac{4B_e}{\nu_e^2} \tag{22.2-49}$$

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[1] J. C. Davis, Jr., *Advanced Physical Chemistry*, The Ronald Press, New York, 1965, p. 285.

[2] P. M. Morse, *Phys. Rev.*, **34**, 57 (1929).

[3] B. A. Pettit, *J. Chem. Educ.*, **75**, 1170 (1998).

[4] J. C. Davis, *op. cit.*, p. 351 (note 1).

The term containing the parameter $\mathscr{D}$ causes the corrected levels to be more closely spaced for larger values of the rotational quantum number J than for smaller values of J. It corresponds to centrifugal stretching of the molecule, which increases the value of the moment of inertia for larger values of J. This effect is typically small, and the term in $\mathscr{D}$ can be neglected except for highly accurate work. The term containing the parameter x_e causes the corrected energy levels to be more closely spaced for larger values of the vibrational quantum number v and is a correction for the anharmonicity of the potential energy function. The term containing the parameter α contains both the vibrational and rotational quantum numbers, and expresses the interaction of vibration and rotation. The origin of this interaction can be seen in Figure 22.3b. For larger values of v the classically allowed region of the vibrational coordinate moves to the right in the figure, so that the moment of inertia is larger for larger values of v, lowering the rotational energy below that of the uncorrected expression.

EXAMPLE 22.5

Calculate the energy of the $v = 2$, $J = 2$ level of the CO molecule using the values of the parameters: $\nu_e = 6.5049 \times 10^{13}\ \text{s}^{-1}$, $x_e = 6.124 \times 10^{-3}$, $B_e = 5.7898 \times 10^{10}\ \text{s}^{-1}$, $\mathscr{D} = 1.83516 \times 10^{5}\ \text{s}^{-1}$, $\alpha = 5.24765 \times 10^{8}\ \text{s}^{-1}$.

Solution

$$\begin{aligned}
E/h &= \nu_e(5/2) - \nu_e x_e(5/2)^2 + B_e(2)(3) - \mathscr{D}(36) - \alpha(5/2)(6) \\
&= (6.5049 \times 10^{13}\ \text{s}^{-1})(5/2) - (3.9836 \times 10^{11}\ \text{s}^{-1})(5/2)^2 \\
&\quad + (5.7898 \times 10^{10}\ \text{s}^{-1})(6) - (1.83516 \times 10^{5}\ \text{s}^{-1})(36) \\
&\quad - (5.24765 \times 10^{8}\ \text{s}^{-1})(5/2)(6) \\
&= 1.6262 \times 10^{14}\ \text{s}^{-1} - 2.4897 \times 10^{12}\ \text{s}^{-1} + 3.4739 \times 10^{11}\ \text{s}^{-1} \\
&\quad - 6.6066 \times 10^{6}\ \text{s}^{-1} - 7.8715 \times 10^{9}\ \text{s}^{-1} \\
&= 1.6047 \times 10^{14}\ \text{s}^{-1}
\end{aligned}$$

$$E = (6.6261 \times 10^{-34}\ \text{J s})(1.6047 \times 10^{14}\ \text{s}^{-1}) = 1.0633 \times 10^{-19}\ \text{J}$$

The α term is fairly small and the $\mathscr{D}$ term is insignificant to five significant digits. The $\nu_e x_e$ term is large compared with the main rotational term (the J term), but is fairly small compared with the ν_e term.

The energy levels are often given in terms of energies divided by hc, where c is the speed of light and h is Planck's constant. This quantity has the dimensions of reciprocal wavelength, and its difference for two levels is equal to the reciprocal of the wavelength of the photon emitted or absorbed in a transition between these levels. It is sometimes called the *term* of the energy level, and denoted by T.

$$\begin{aligned}
T_{vJ} = \frac{E_{vJ}}{hc} &= \widetilde{\nu}_e\left(v + \frac{1}{2}\right) + \widetilde{\nu}_e x_e\left(v + \frac{1}{2}\right)^2 + \widetilde{B}_e J(J+1) \\
&\quad - \widetilde{\mathscr{D}} J^2(J+1)^2 - \widetilde{\alpha}\left(v + \frac{1}{2}\right)J(J+1) \qquad (22.2\text{-}50)
\end{aligned}$$

The terms are commonly given in reciprocal centimeters, sometimes called *wave numbers*. When you use these values, you must remember to convert to reciprocal meters or to use the speed of light in centimeters per second. The parameters in this equation are marked with a tilde (~) to distinguish them from the parameters in Eq. (22.2-45). These parameters are equal to the other parameters divided by c, the speed of light. Table A.22 in Appendix A gives the values of parameters in cm^{-1} for several diatomic molecules. Some reference books use the same letters without a tilde to represent the parameters in Eq. (22.2-50) and the Greek letter ω is sometimes used instead of $\widetilde{\nu}$.

EXAMPLE 22.6

a. Using the expression of Eq. (22.2-50), find the wavelength and frequency of the light absorbed when carbon monoxide molecules make the transition from the $v = 0$, $J = 0$ state to the $v = 1$, $J = 1$ state.

b. Find the wavelength for the same transition, neglecting the terms in $\widetilde{\alpha}$ and $\widetilde{\mathscr{D}}$.

c. Find the wavelength for the same transition, neglecting the terms in $\widetilde{\nu}_e x_e$, $\widetilde{\alpha}$, and $\widetilde{\mathscr{D}}$.

Solution

a. From Table A.22,

$$\begin{aligned}
\widetilde{\nu}_e &= 2169.8\,\text{cm}^{-1}\\
\widetilde{B}_e &= 1.931\,\text{cm}^{-1}\\
\widetilde{\mathscr{D}}_e &= 0.0612 \times 10^{-4}\,\text{cm}^{-1}\\
\widetilde{\alpha}_e &= 0.0175\,\text{cm}^{-1}\\
\widetilde{\nu}_e x_e &= 13.29\,\text{cm}^{-1}\\
\frac{E_{vJ}}{hc} &= \widetilde{\nu}_e\left(v+\frac{1}{2}\right) + \widetilde{\nu}_e x_e\left(v+\frac{1}{2}\right)^2 + \widetilde{B}_e J(J+1) - \widetilde{\mathscr{D}}_e J^2(J+1)^2\\
&\quad - \widetilde{\alpha}_e\left(v+\frac{1}{2}\right)J(J+1)
\end{aligned}$$

$$\begin{aligned}
\frac{1}{\lambda} = \frac{\Delta E}{hc} &= \frac{E_{11}}{hc} - \frac{E_{00}}{hc} = \widetilde{\nu}_e - 2\widetilde{\nu}_e x_e + 2\widetilde{B}_e - 4\widetilde{\mathscr{D}}_e - 3\widetilde{\alpha}_e\\
&= 2169.8\,\text{cm}^{-1} - 2(13.29\,\text{cm}^{-1}) + 2(1.931\,\text{cm}^{-1}) - 4(0.0612\times 10^{-4}\,\text{cm}^{-1})\\
&\quad - 3(0.0175\,\text{cm}^{-1})\\
&= 2147.0\,\text{cm}^{-1}
\end{aligned}$$

$$\lambda = 4.6576 \times 10^{-4}\,\text{cm} = 4.6576\,\mu\text{m}$$

$$\nu = \frac{c}{\lambda} = \frac{2.9979\times 10^{10}\,\text{cm s}^{-1}}{4.6576\times 10^{-4}\,\text{cm}} = 6.4365\times 10^{13}\,\text{s}^{-1}$$

b.

$$\frac{1}{\lambda} = \frac{\Delta E}{hc} = \frac{E_{11}}{hc} - \frac{E_{00}}{hc} = \widetilde{\nu}_e - 2\widetilde{\nu}_e x_e + 2\widetilde{B}_e$$

$$= 2169.8\,\text{cm}^{-1} - 2(13.29\,\text{cm}^{-1}) + 2(1.931\,\text{cm}^{-1}) = 2147.1\,\text{cm}^{-1} \tag{22.2-51}$$

$$\lambda = 4.6575 \times 10^{-4}\,\text{cm} = 4.6575\,\mu\text{m}$$

$$\nu = \frac{c}{\lambda} = \frac{2.9979\times 10^{10}\,\text{cm s}^{-1}}{4.6576\times 10^{-4}\,\text{cm}} = 6.4365\times 10^{13}\,\text{s}^{-1}$$

c.

$$\frac{1}{\lambda} = \frac{\Delta E}{hc} = \frac{E_{11}}{hc} - \frac{E_{00}}{hc} = \widetilde{\nu}_e - 2\widetilde{B}_e$$
$$= 2169.8\,\text{cm}^{-1} + 2(1.931\,\text{cm}^{-1}) = 2173.7\,\text{cm}^{-1}$$
$$\lambda = 4.6005 \times 10^{-4}\,\text{cm} = 4.6005\,\mu\text{m}$$
$$\nu = \frac{c}{\lambda} = \frac{2.9979 \times 10^{10}\,\text{cm s}^{-1}}{4.6005 \times 10^{-4}\,\text{cm}} = 6.5164 \times 10^{13}\,\text{s}^{-1}$$

PROBLEMS

Section 22.2: The Nonelectronic States of Diatomic Molecules

22.6 Compare the energy level spacings for a Cl_2 molecule in a cubical box 0.200 m on a side. Its vibration frequency is $1.694 \times 10^{13}\ \text{s}^{-1}$ and its equilibrium bond length for the ground electronic state is 1.988×10^{-10} m. The energy of the first excited electronic state observed in the gas phase is 2.162 eV above that of the ground electronic state.

22.7 **a.** Calculate the reduced mass of the H_2 molecule.

b. From data in Table A.22 of the appendix, calculate the value of the force constant for the H_2 molecule.

c. Make an accurate graph of the vibrational wave function for the ground state of the H_2 molecule in the rigid-rotor-harmonic-oscillator approximation. Use picometers (pm) for the scale on the horizontal axis and use arbitrary units on the vertical axis. Comment on the difference between this graph and that of a harmonic oscillator wave function.

22.8 **a.** Calculate the rotational energy of a hydrogen molecule in the $\nu = 0, J = 1$ state and in the $\nu = 0, J = 2$ state. Make the calculation once without correction terms and once with correction terms.

b. Repeat the calculation of part a for HD(^{1}H^{2}H) without the correction terms.

22.9 Find the value of the rotational quantum number J if a nitrogen molecule has a rotational energy equal to k_BT at 298.15 K. Find the degeneracy of this level.

22.10 Find a formula for the rotational frequency (number of revolutions per second) of a rigid diatomic molecule assuming that classical mechanics holds, but that the angular momentum has the magnitude $\hbar\sqrt{J(J+1)}$. Compare this with the frequency of a photon absorbed when a quantum-mechanical molecule makes a transition from J to $J + 1$. Show that the two frequencies are nearly equal for large values of J.

22.11 Using information on the normal H_2 molecule, find the frequency of vibration of the HD molecule, where D is deuterium, ^{2}H. Compare with the vibrational frequency of normal H_2.

22.12 Using information on the normal H_2 molecule, find the frequency of vibration of the D_2 molecule, where D is deuterium, ^{2}H. Compare with the vibrational frequency of normal H_2.

22.13 **a.** Using the expression of Eq. (22.2-50), find the wavelength and frequency of the light absorbed when carbon monoxide molecules make the transition from the $\nu = 0, J = 1$ state to the $\nu = 1, J = 0$ state.

b. Find the wavelength for the same transition, neglecting the terms in $\widetilde{\alpha}$ and $\widetilde{D}$.

c. Find the wavelength for the same transition, neglecting the terms in x_e, $\widetilde{\alpha}$ and $\widetilde{D}$.

22.14 Calculate the percent change in the rotational and vibrational energies of an HCl molecule if

a. ^{35}Cl is replaced by ^{37}Cl.

b. ^{1}H is replaced by ^{2}H.

22.15 The dissociation energy is sometimes approximated by determining the point at which two successive vibrational energy levels have the same energy when the x_e correction is included. Estimate the value of D_e for the HCl molecule using this approach. Compare your value with that in Table A.22.

22.16 **a.** From the vibrational frequency in Table A.22, find the value of the force constant for the HF molecule.

b. From the vibrational frequency in Table A.22, find the value of the force constant for the HCl molecule.

c. From the vibrational frequency in Table A.22, find the value of the force constant for the H_2 molecule.

22.17 When electromagnetic radiation is emitted or absorbed by a diatomic molecule in making a transition between different values of the rotational quantum number J, the value of J changes by ± 1.

a. Find the frequency and wavelength of radiation absorbed in the $J = 0$ to $J = 1$ transition for NO.

b. Find the frequency and wavelength of radiation absorbed in the $J = 1$ to $J = 2$ transition for NO.

22.18 When electromagnetic radiation is emitted or absorbed by a diatomic molecule in making a transition between different values of the rotational quantum numbers J and v, the value of J changes by ± 1 and the value of v changes by ± 1.

a. Find the frequency and wavelength of radiation absorbed in the $J = 0$ to $J = 1$, $v = 0$ to $v = 1$ transition for HCl.

b. Find the frequency and wavelength of radiation absorbed in the $J = 1$ to $J = 2$, $v = 0$ to $v = 1$ transition for NO.

22.3 Nuclear Spins and Wave Function Symmetry

If the nuclei in a diatomic molecule have nonzero spins, the wave function in Eq. (22.2-35) must be multiplied by a nuclear spin wave function to be a complete wave function.

$$\psi_{\text{tot}} = \psi_{\text{tr}}\psi_{\text{rot}}\psi_{\text{vib}}\psi_{\text{el}}\psi_{\text{nucspin}} \tag{22.3-1}$$

In the case of homonuclear diatomic molecules (molecules with two nuclei of the same isotope of the same element), the wave function must not pretend to distinguish between the nuclei, which are indistinguishable from each other. The wave function must be symmetric with respect to interchange of the nuclei if they are bosons and must be antisymmetric with respect to interchange of the nuclei if they are fermions.

For our purposes, a nucleus can be considered to be made up of protons and neutrons, collectively called *nucleons*. The mass number given as a left superscript on the symbol for a given isotope is equal to the number of nucleons. Protons and neutrons have a spin quantum number of 1/2, as do electrons, and are therefore fermions. If a nucleus contains an odd number of nucleons, it is a fermion, because exchanging two such nuclei changes the sign of the wave function once for each nucleon. If a nucleus contains an even number of nucleons, it is a boson, because exchanging two such nuclei changes the sign of the wave function an even number of times, leaving the original sign.

The spin angular momentum of a nucleus is denoted by **I** and has the same general properties as any angular momentum. Its magnitude takes on the values

$$|\mathbf{I}| = \hbar\sqrt{I(I+1)} \tag{22.3-2}$$

where I is the spin quantum number, equal to an integer for a boson nucleus and equal to a half-integer for a fermion nucleus. The projection of the spin angular momentum on the z axis takes on the values

$$I_z = \hbar M_I \tag{22.3-3}$$

where M_I is a quantum number ranging from $+I$ to $-I$ in integral steps. If I is an integer, so is M_I, and if $_I$ is a half-integer, so is M_I.

The angular momentum vector **I** is the vector sum of the spin angular momenta of all of the nucleons in the nucleus. A given nucleus can have different spin states, just as a multielectron atom can have different electronic spin states. Very large energies are required to raise nuclei to excited states so that chemists ordinarily encounter nuclei only in their ground states. We therefore regard I as fixed for a particular nucleus. Table A.24 in Appendix A lists the spin quantum numbers for the nuclear ground states of several nuclei. If $I = 0$ there must be an even number of nucleons and the nucleus is a boson. The total wave function must be symmetric with respect to interchange of the nuclei. There is a single nuclear spin function, which is symmetric with respect to interchange of the nuclei. The other factors must combine to give a symmetric function.

If $I = 1/2$, as is the case with ^{1}H, ^{13}C, and some other nuclei, there must be an odd number of nucleons. The nuclei are fermions and the total wave function must be antisymmetric. Each nucleus can occupy nuclear spin functions like those of electrons, denoted by α for spin up and β for spin down, and the diatomic molecule has singlet and triplet nuclear spin states like those of two electrons. The triplet nuclear spin functions for such a diatomic molecule are symmetric:

$$\alpha(\mathrm{A})\alpha(\mathrm{B}), \quad \beta(\mathrm{A})\beta(\mathrm{B}), \quad \sqrt{\frac{1}{2}}[\alpha(\mathrm{A})\beta(\mathrm{B}) + \beta(\mathrm{A})\alpha(\mathrm{B})]$$

where we denote the nuclei by A and B. The singlet spin function is antisymmetric:

$$\sqrt{\frac{1}{2}}[\alpha(\mathrm{A})\beta(\mathrm{B}) - \beta(\mathrm{A})\alpha(\mathrm{B})]$$

The other factors of the total wave function must combine to form an antisymmetric function if they are combined with a triplet nuclear spin function. They must form a symmetric function if they are combined with the singlet spin function. These factors could be symmetrized or antisymmetrized by constructing a two-term wave function, as we did with a two-electron wave function. However, this is unnecessary since the wave functions we have constructed are generally eigenfunctions of symmetry operators, and this fact makes them either symmetric or antisymmetric with respect to exchange of the nuclei. The following sequence of symmetry operations exchanges the nuclei and puts the electrons back in their original positions:

1. Rotate the entire molecule by 180° around an axis perpendicular to the internuclear axis.
2. Reflect the electrons through a plane perpendicular to the axis of rotation that contains the internuclear axis.
3. Invert the electrons through the origin.

Exercise 22.4

Assume that a homonuclear diatomic molecule is located with the nuclei at $(0, 0, z_n)$ and $(0, 0, -z_n)$ and that one electron is at (x, y, z). Show that the above listed operations exchange the nuclei and put the electrons back at their original locations.

We can determine the effect of these operations on each factor of the wave function. The translational factor depends only on the coordinates of the center of mass of the molecule, and is unaffected. The vibrational factor is unaffected because it depends only on r_{AB}, which is a positive scalar quantity that remains unchanged under inversion, rotation, or reflection. The rotational factor of the wave function of a diatomic molecule is a spherical harmonic function. For even values of the rotational quantum number J the spherical harmonic functions are eigenfunctions of the inversion operator with eigenvalue $+1$ (are "gerade"), and for odd values of J they are eigenfunctions with eigenvalue -1 (are "ungerade"). The same eigenvalues apply to a rotation of 180° around an axis perpendicular to the bond axis, because this operation has the same effect on θ and ϕ as does inversion. The rotational factor is unchanged by the operations applied only to the electrons, so the three symmetry operations must change the sign of the electronic factor if J is odd and must not change it if J is even.

Exercise 22.5

Show that the spherical harmonic function Y_{00} is an eigenfunction of the inversion operator with eigenvalue 1, while the spherical harmonic function Y_{11} is an eigenfunction with eigenvalue -1. In spherical polar coordinates the inversion operator replaces θ by $\pi - \theta$ and replaces ϕ by $\pi + \phi$. Show that rotation of 180° around an axis perpendicular to the bond axis gives the same result.

The electronic factor is unaffected by the rotation of the entire molecule, since the electrons simply follow the nuclei according to the Born–Oppenheimer approximation. We have already discussed the effect of a σ_v operation and an inversion operation on the electronic factor in Chapter 20. For a Σ term the superscript $+$ is used to denote eigenfunctions of $\widehat{\sigma}_v$ with eigenvalue $+1$, and a superscript $-$ is used to denote eigenfunctions of $\widehat{\sigma}_v$ with eigenvalue -1. The electronic wave functions are denoted by g if they are eigenfunctions of the inversion operator with eigenvalue $+1$ and by u if the eigenvalue is -1. Functions with eigenvalue $+1$ are said to have *even parity*, and those with eigenvalue -1 are said to have *odd parity*. The reflection and inversion operations change the sign of the electronic factor for a wave function that is $+$ and u or for a wave function that is $-$ and g. Otherwise the sign does not change.

EXAMPLE 22.7

Find the permitted wave functions for H_2 in its electronic ground state.

Solution

The ^{1}H nuclei are protons with $I = 1/2$, so the entire wave function must change sign if the nuclei are exchanged. The ground term symbol is $^1\Sigma_g^+$. The ground-state electronic wave function does not change sign under the three symmetry operations. If the nuclear spin function is the antisymmetric singlet function, the rotational wave function must correspond to even values of J. If the nuclear spin function is one of the triplet functions, which are symmetric, the rotational wave function must correspond to odd values of J.

The form of hydrogen with triplet nuclear spin states and odd values of J is called *orthohydrogen* and the form with singlet nuclear spin state and even values of J is called *parahydrogen*. This terminology can be remembered from the fact that in the *para* form the nuclear spins point in opposite directions, just as do two groups *para* to each other on a benzene ring.

For values of I greater than 1/2, the spin functions are more complicated and we will not discuss them. However, for any specific nuclear spin state of a homonuclear diatomic molecule, either even values of J or odd values of J are permitted. As with hydrogen, only half of the values of J can occur. Both even values of J and odd values of J can occur for a heteronuclear diatomic molecule, because the nuclei are not identical.

Exercise 22.6

For ^{200}Hg, $I = 0$ and the electronic ground state is g and $+$. What values of J can occur with $^{200}Hg_2$?

PROBLEMS

Section 22.3: Nuclear Spins and Wave Function Symmetry

22.19 The common isotope of oxygen, ^{16}O, has $I = 0$. Will $^{16}O_2$ take on even values or odd values of J in the electronic ground state? Determine the term symbol for the electronic ground state. How will the J values differ from the J values of O_2 with one ^{16}O nucleus and one ^{17}O nucleus?

22.20. Fluorine has only one isotope in the earth's crust, ^{19}F, with $I = 1/2$. Refer to Chapter 20 for information about its electronic ground state. Describe the rotational states of F_2 in its electronic ground state.

22.4 The Rotation and Vibration of Polyatomic Molecules

Rotation and vibration are more complicated in polyatomic molecules than in diatomic molecules, and we consider only an approximation that is equivalent to the harmonic oscillator-rigid rotor energy level expression of Eq. (22.2-29). To obtain the energy level expressions, we pretend that the rotating molecule is somehow prevented from vibrating and that the vibrating molecule is prevented from rotating.

Rotation of Polyatomic Molecules

We now assume that all bond lengths and bond angles of a polyatomic molecule are locked at their equilibrium values, so that the molecule cannot vibrate and rotates as a rigid body. The classical rotation of a rigid body is described in terms of *moments of inertia* taken relative to three mutually perpendicular axes that pass through the center of mass of the object. For an object consisting of n mass points, the moment of inertia about an axis is defined to be

$$I_{\text{axis}} = \sum_{i=1}^{n} m_i r_{i(\text{axis})}^2 \tag{22.4-1}$$

where m_i is the mass of the ith mass point and $r_{i(\text{axis})}$ is the perpendicular distance from this mass point to the specified axis. The moments of inertia about the x, y, and z axes are

$$I_x = \sum_{i=1}^{n} m_i\left(y_i^2 + z_i^2\right) \tag{22.4-2a}$$

$$I_y = \sum_{i=1}^{n} m_i\left(x_i^2 + z_i^2\right) \tag{22.4-2b}$$

$$I_z = \sum_{i=1}^{n} m_i\left(x_i^2 + y_i^2\right) \tag{22.4-2c}$$

There are six additional quantities, which are called *products of inertia:*

$$I_{xy} = I_{yx} = \sum_{i=1}^{n} m_i x_i y_i \tag{22.4-3}$$

The other products of inertia, I_{yz}, I_{zy}, I_{xz}, and I_{zx}, are defined analogously. Only three of the products of inertia have distinct values, because $I_{yz} = I_{zy}$ and so on. For calculating the moments of inertia and the products of inertia, we neglect the masses of the electrons and include only the nuclei in the sums since the masses of the electrons are small compared to those of the nuclei.

There is a theorem stating that for any rigid object it is possible to choose a set of perpendicular axes such that all products of inertia vanish. Such axes are called *principal axes*, and the moments of inertia relative to them are called *principal moments of inertia*. For a symmetrical molecule, it is usually possible to assign a set of principal axes by inspection. To do so, place the axes along symmetry elements as much as possible. If there is an axis of symmetry that is at least a three-fold rotation axis (C_n with $n \geq 3$), a set of principal axes is obtained by choosing this rotation axis as one of the axes and placing the other axes in any mutually perpendicular directions. If there is a two-fold rotation axis but no higher-order rotation axis, as with a molecule that has C_{2v} symmetry, a set of principal axes is obtained by choosing the rotational axis as one of the principal axes and placing the other two axes in the reflection planes.

Because the principal axes are defined relative to the molecule and rotate with it, it is customary to call the axes by the letters A, B, and C instead of x, y, and z. By convention, the axes are ordered so that

$$I_A \leq I_B \leq I_C \qquad (22.4\text{-}4)$$

If all three of its principal moments of inertia are equal to each other, an object is called a *spherical top*. The name “top” is apparently chosen because of the rotating toys by that name. A tetrahedral molecule such as methane or an octahedral molecule such as sulfur hexafluoride is a spherical top. Any mutually perpendicular axes passing through the center of mass of a spherical top are principal axes. If two of the principal moments of an object are equal, the object is called a *symmetric top*. A *prolate symmetric top* has a unique moment of inertia that is smaller than the other two. An American football and a rugby ball are prolate symmetric tops if the lacing is ignored. An *oblate symmetric top* has a unique moment that is larger than the other two. A discus is an oblate symmetric top. Any molecule with at least a three-fold rotation axis is either a symmetric top or a spherical top. If all three principal moments of inertia are unequal, the object is called an *asymmetric top*. A bent triatomic molecule such as SO_2 or H_2O is an asymmetric top.

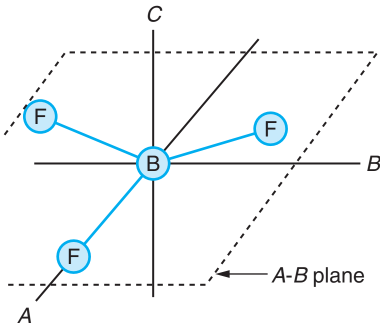

Figure 22.4 The BF_3 Molecule and Its Principal Axes.

EXAMPLE 22.8

Show that BF_3, a trigonal planar molecule, is an oblate symmetric top.

Solution

Orient the molecule as in Figure 22.4, with the molecule in the A–B plane and with one B–F bond on the A axis. Let the bond length be called a.

$$I_A = 2m_F[a\sin(120°)]^2 = 2m_F a^2\left[\frac{1}{2}\sqrt{3}\right]^2 = \frac{3}{2}m_F a^2$$

$$I_B = m_F a^2 + 2m_F[a\cos(120°)]^2 = \frac{3}{2}m_F a^2 = I_A$$

$$I_C = 3m_F a^2 > I_A$$

Exercise 22.7

Show that the methane molecule is a spherical top. Since any mutually perpendicular axes can be chosen, the problem is easier if the hydrogen atoms are placed at alternate corners of a cube that has its faces perpendicular to the coordinate axes and its center at the carbon atom, which is located at the center of mass.

The total angular momentum **L** of any rigid object is the vector sum of the angular momenta of the particles making up the object (see Appendix E for information about angular momentum). The angular momenta of all particles making up a rigid rotating object are in the same direction. The classical rotational energy of a rigid object is given in terms of its angular momentum and its principal moments of inertia by

$$E_{\text{classical}} = \frac{L_A^2}{2I_A} + \frac{L_B^2}{2I_B} + \frac{L_C^2}{2I_C} \tag{22.4-5}$$

where L_A, L_B, and L_C are the components of the vector **L** on the A, B, and C axes. We can write the quantum mechanical rotational energy eigenvalues by replacing the classical variables in Eq. (22.4-5) by their quantum mechanical eigenvalues. Consider a diatomic molecule or linear polyatomic molecule, for which I_A vanishes and for which $I_B = I_C$. There can be no component of angular momentum on the A axis, because all of the nuclei are on this axis. Equation (22.4-5) becomes

$$E_{\text{classical}} = \frac{1}{2I_B}\left(L_B^2 + L_C^2\right) = \frac{L^2}{2I_B} \tag{22.4-6}$$

From Eq. (17.2-28) we have the values that L^2 can assume in quantum mechanics. Substitution of this formula into Eq. (22.4-6) gives

$$E_{\text{qm}} = E_J = \frac{\hbar^2}{2I_B}J(J+1) \tag{22.4-7}$$

where we use the letter J for the quantum number instead of l. For a diatomic molecule, $I = \mu r_e^2$, so Eq. (22.4-7) agrees with Eq. (22.2-18). Equation (22.4-7) also applies to a linear polyatomic molecule such as C_2H_2 or CO_2.

EXAMPLE 22.9

Show that for a rigid diatomic molecule $I_e = \mu r_e^2$.

Solution

Temporarily place the molecule on the z axis with the center of mass at the origin. Denote the masses by m_1 and m_2 and their z coordinates by z_1 and z_2. Let $m_1 = m_2 = M$.

$$I_e = m_1 z_1^2 + m_2 z_2^2$$

$$z_1 = \frac{m_2(z_1 - z_2)}{m_1 + m_2} = \frac{m_2(z_1 - z_2)}{M}, \quad z_2 = \frac{m_2(z_2 - z_1)}{m_1 + m_2} = \frac{m_2(z_2 - z_1)}{M}$$

$$I_e = m_1\left(\frac{m_2(z_1 - z_2)}{M}\right)^2 + m_2\left(\frac{m_1(z_1 - z_2)}{M}\right)^2$$

$$= \frac{m_1 m_2(m_2 + m_1)(z_1 - z_2)^2}{M^2} = \frac{m_1 m_2}{M}(z_1 - z_2)^2 = \mu(z_1 - z_2)^2$$

If the molecule is not oriented on the z axis, the x and y components are similar, so that

$$I_{\mathrm{e}} = \mu r_{\mathrm{e}}^2$$

The possible values of L_z for a diatomic or linear molecule are given by Eq. (17.2-31).

$$L_z = \hbar M \quad (M = 0, \pm 1, \pm 2, \ldots, \pm J) \tag{22.4-8}$$

The energy does not depend on the quantum number M, so the energy level for a particular value of J has a degeneracy of $2J + 1$.

For a spherical top, $I_A = I_B = I_C$. For this case

$$E_{\text{classical}} = \frac{1}{2I_A}\left(L_A^2 + L_B^2 + L_C^2\right) = \frac{1}{2I_A} L^2 \tag{22.4-9}$$

The quantum mechanical energy is

$$E_{\text{qm}} = E_J = \frac{\hbar^2}{2I_A} J(J+1) \tag{22.4-10}$$

This formula is the same as that for the energy of a diatomic or linear molecule, but the degeneracy is not the same. In both cases, there is a quantum number M that specifies the projection of the angular momentum on the z axis (an axis external to the molecule). When there are three independent variables in the expression for the classical kinetic energy, such as the three components of the angular momentum, there are three quantum numbers. In this case, the third quantum number is for the projection of the angular momentum on one of the principal axes, say the A axis. This projection can take on the values

$$L_A = \hbar K \quad (K = 0, \pm 1, \pm 2, \ldots, \pm J) \tag{22.4-11}$$

The quantum number K has the same range of values as M. For a given value of J, there is one state for each value of M and for each value of K, so that the degeneracy is

$$g_J = (2J+1)^2 \quad \text{(spherical top)} \tag{22.4-12}$$

The energy levels of symmetric tops and asymmetric tops can depend on the values of all three quantum numbers J, M, and K.[5] Problems 22.37 and 22.38 display the energy levels of oblate and prolate symmetric tops.

In Section 22.3, we found that only half of the values of the rotational quantum number J occurred for a homonuclear diatomic molecule because of the indistinguishability of the nuclei. In the case of polyatomic molecules the effect of the indistinguishability of identical nuclei is more complicated. We assert without proof that the fraction of the conceivable rotational states that can occur is $1/\sigma$, where σ is called the *symmetry number* of the molecule. The symmetry number is defined as the number of equivalent orientations of the molecule in its equilibrium conformation, which means the number of orientations in which the molecule can be placed and have each nuclear location occupied by a nucleus of the same kind as in the first orientation.

The symmetry number of any homonuclear diatomic molecule equals 2, corresponding to the result that only half of the conceivable values of J can occur. The symmetry number of a heteronuclear diatomic molecule equals unity, as does that of some polyatomic molecules, so that all values of the rotational quantum numbers can occur. The

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[5] G. Herzberg, *Infrared and Raman Spectra*, Van Nostrand Reinhold, New York, 1945, p. 42ff.

symmetry number of BF_3 is 6 (three positions with one side of the molecule upward, and three more positions with the other side up). For this molecule, only one-sixth of the conceivable sets of values of J, K, and M can occur. The symmetry number of methane is 12 (three orientations with each of the four hydrogens upward). Only one-twelfth of the conceivable sets of values of J, M, and K can occur for methane.

Exercise 22.8

Find the symmetry numbers of the molecules in their equilibrium conformations:

a. Chloroform, $CHCl_3$
b. Water, H_2O
c. Benzene, C_6H_6

Vibrations of Polyatomic Molecules

In a polyatomic molecule there are several bond lengths and bond angles that can oscillate about their equilibrium values. However, each bond length or bond angle does not oscillate independently of the others. It turns out that there are collective motions of some or all of the nuclei that can oscillate independently, called *normal modes*. Determining the normal modes is a complicated process, and we give only a brief summary.[6] Some software packages such as CAChe and Spartan carry out the process automatically. We assume that the molecule cannot rotate and is in a fixed orientation. For the first nucleus, let q_1 be the displacement of the nucleus from its equilibrium position in the x direction, let q_2 be its displacement in the y direction, and q_3 be its displacement in the z direction. For the second nucleus, let q_4, q_5, and q_6 be similar displacements, and so on. There are $3n$ such variables if there are n nuclei.

The Born–Oppenheimer energy acts as the vibrational potential energy. We assume a *harmonic potential energy*. That is, we assume that the potential energy depends on the q variables in the following way:

$$E_{\mathrm{BO}} = \mathscr{V}(q_1, q_2, \ldots, q_{3n}) = \mathscr{V}_e + \frac{1}{2}\sum_{i=1}^{3n}\sum_{j=1}^{3n} b_{ij}q_iq_j \tag{22.4-13}$$

where the b's are constants. In addition to terms with $i = j$, "cross terms" occur in which $i \neq j$. The presence of the cross terms make the q coordinates interfere with each other so that they do not vibrate independently. Equation (22.4-13) is analogous to Eq. (22.2-22) and will be a good approximation for small values of the q's.

We now find a transformation to a new set of coordinates such that each new coordinate can oscillate independently from the other new coordinates. The potential energy function must be given by a formula like that of Eq. (22.4-3) without cross terms. The number of such coordinates turns out to be smaller than $3n$, because the Born–Oppenheimer energy of the molecule is independent of its location and orientation. Three coordinates can be used to specify the location of the center of mass of the molecule. For a linear or diatomic molecule, two angular coordinates specify the orientation of the molecule. For a nonlinear molecule, three angular coordinates are required to specify the orientation of the molecule, as shown in Figure 22.5. The angles θ and ϕ specify the direction of an axis (as in spherical polar coordinates) and the angle ψ specifies the angle of rotation about this axis. The Born–Oppenheimer energy can

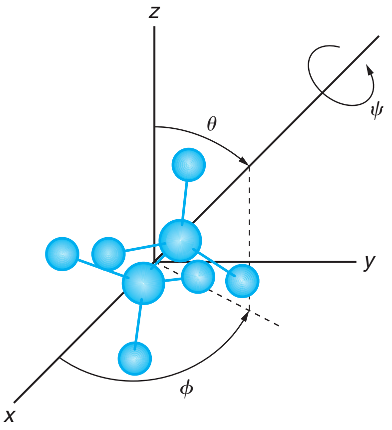

Figure 22.5 Three Angles to Specify the Orientation of a Nonlinear Polyatomic Molecule. The angles θ and ϕ are used to specify the orientation of one molecular axis. The angle ψ is used to specify the angle of rotation about this axis.

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[6] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations*, McGraw-Hill, New York, 1955.

depend on only $3n - 5$ of the new coordinates for a linear molecule, or on $3n - 6$ of them for a nonlinear molecule.

The new coordinates are linear combinations of the q's:

$$w_i = \sum_{j=1}^{3n} c_{ij} q_j \quad (i = 1, 2, \ldots, 3n - 5(6)) \tag{22.4-14}$$

where the c's are constants and where we introduce the notation $3n - 5(6)$ to indicate $3n - 5$ for a linear molecule and $3n - 6$ for a nonlinear molecule. We do not discuss the process by which the c_{ij} coefficients are chosen. The outcome is that

$$\mathscr{V} = \mathscr{V}_{\mathrm{e}} + \frac{1}{2} \sum_{i=1}^{3n-5(6)} \kappa_i w_i^2 \tag{22.4-15}$$

The w coordinates are called *normal coordinates*. The constant κ_i is the effective force constant for the coordinate w_i.

The classical vibrational energy can be written

$$E_{\mathrm{vib}} = \mathscr{K}_{\mathrm{vib}} + \mathscr{V}_{\mathrm{vib}} = \frac{1}{2} \sum_{i=1}^{3n-5(6)} \left[M_i \left(\frac{dw_i}{dt} \right)^2 + \kappa_i w_i^2 \right] + \mathscr{V}_{\mathrm{e}} \tag{22.4-16}$$

where the M's are effective masses for the new coordinates. Equation (22.4-16) is a sum of classical harmonic oscillator energy expressions. According to classical mechanics, each normal coordinate oscillates independently with a characteristic classical frequency given by

$$\nu_i = \frac{1}{2\pi} \sqrt{\frac{\kappa_i}{M_i}} \tag{22.4-17}$$

The motions of the normal coordinates are the *normal modes* of vibration. Since each normal coordinate is a linear combination of the Cartesian coordinates of the nuclei, each normal mode corresponds to a concerted motion of some or all of the nuclei.

When the quantum mechanical Hamiltonian for vibration is constructed from Eq. (22.4-16) there are $3n - 5$ or $3n - 6$ terms, each one of which is a harmonic oscillator Hamiltonian operator. The variables can be separated, and the vibrational Schrödinger equation is solved by a vibrational wave function that is a product of $3n - 5$ or $3n - 6$ factors:

$$\psi_{\mathrm{vib}} = \psi_1(w_1)\psi_2(w_2)\cdots = \prod_{i=1}^{3n-5(6)} \psi_i(w_i) \tag{22.4-18}$$

Each ψ_i factor is a harmonic oscillator wave function. The energy is a sum of harmonic oscillator energy eigenvalues:

$$E_{\mathrm{vib}} = \sum_{i=1}^{3n-5(6)} h\nu_i \left(v_i + \frac{1}{2} \right) = \sum_{i=1}^{3n-5(6)} hc\widetilde{\nu}_i \left(v_i + \frac{1}{2} \right) \tag{22.4-19}$$

where v_1, v_2, ... are vibrational quantum numbers, one for each normal mode, and ν_1, ν_2, and so on, are the frequencies of Eq. (22.4-17). The quantities $\widetilde{\nu}_i$, $\widetilde{\nu}_i$, and so on are the frequencies divided by the speed of light, usually specified in cm^{-1}. Just as in classical mechanics, each normal mode oscillates independently of the others.

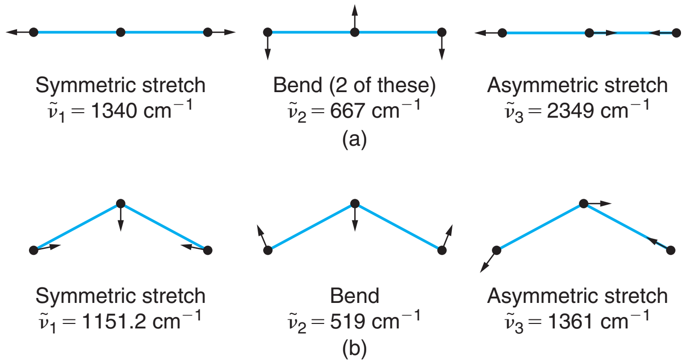

Figure 22.6 Vibrational Normal Modes. (a) Carbon dioxide. (b) Sulfur dioxide.

Figure 22.6 shows schematically the motion corresponding to the four normal modes of carbon dioxide (linear) and the three normal modes of sulfur dioxide (nonlinear), and shows the frequencies divided by the speed of light, given in cm^{-1}. These values are sometimes called "frequencies" and the unit is called "wave numbers." The arrows in the diagrams show the direction of motion of each nucleus away from its equilibrium position during one-half cycle of the concerted motion. As each nucleus oscillates, it first moves in the direction indicated and then reverses.

Each triatomic molecule has a normal mode called a *symmetric stretch* in which both bonds shorten and lengthen simultaneously. There is also an *asymmetric stretch* in which one bond lengthens while the other shortens. A linear triatomic molecule such as carbon dioxide can bend in two perpendicular directions, so there are two *bending modes*, which have the same frequency. A nonlinear triatomic molecule has only one bending mode, because it can bend only in the plane of the molecule. A motion perpendicular to the plane of the molecule would have no restoring force to make it oscillate, and therefore corresponds to a rotation, explaining why there is one more normal mode for a linear molecule than for a nonlinear molecule. There is a common pattern of frequencies for triatomic molecules that is shown in Figure 22.6: Asymmetric stretches usually have the highest frequency, symmetric stretches are often somewhat lower in frequency, and bends nearly always have the lowest frequency. Some software packages such as Spartan generate movies showing the normal mode motions.

For a molecule with more than three atoms, there are numerous normal modes, and we do not attempt to describe all of them. Benzene, with 12 nuclei, has 30 normal modes, including a "breathing mode" in which the ring alternately contracts and swells, and a "pseudorotation" in which a kind of puckered wave moves around the ring. Various techniques, including group theory, are used in studying the normal modes of polyatomic molecules.[7]

In some large molecules, some of the normal modes correspond to relatively large oscillations of one bond length or bond angle while other bond lengths and bond angles do not oscillate or oscillate with smaller amplitudes. The frequency of such a normal mode is often nearly the same for the same pair of elements in different compounds. For example, most hydrocarbons exhibit a C–H stretching frequency in the 2850 cm^{-1} to 3000 cm^{-1} range, and compounds with an O–H bond usually exhibit an O–H stretching frequency in the 3600 cm^{-1} to 3700 cm^{-1} range. Table A.23 of Appendix A lists a few such characteristic frequencies. Organic chemistry textbooks give longer lists.

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[7] I. N. Levine, *Molecular Spectroscopy*, John Wiley and Sons, New York, 1975, p. 427ff.

PROBLEMS

Section 22.4: The Rotation and Vibration of Polyatomic Molecules

22.21 The equilibrium CO bond length in carbon dioxide is 116.15 pm. Find the moment of inertia of CO_2.

22.22 Consider the SF_6 molecule.

- **a.** Specify the shape of the molecule in its equilibrium conformation. List as many of the symmetry operators that belong to the molecule as you can.
- **b.** Assign the principal rotational axes of the molecule. Is the molecule a symmetric top, an asymmetric top, or a spherical top? Estimate the three principal moments of inertia of the molecule. Assume that the bond lengths are equal to $1.82\ \text{Å} = 182$ pm.
- **c.** Write a formula for the rotational energy levels of the molecule in joules and in electron volts. Specify the degeneracies of the levels.
- **d.** How many vibrational normal modes does the molecule have?

22.23 Find the symmetry numbers of the molecules in their equilibrium conformations:

- **a.** Dichloromethane, CH_2Cl_2
- **b.** Toluene, $C_6H_5CH_3$
- **c.** Sulfur hexafluoride, SF_6

22.24 Classify each of the following molecules in its equilibrium conformation as linear, spherical top, prolate symmetric top, oblate symmetric top, or asymmetric top. Give the symmetry number for each molecule.

- **a.** H_2O
- **b.** CO_2
- **c.** CH_3Cl

22.25 Classify each of the following molecules in its equilibrium conformation as linear, spherical top, prolate symmetric top, oblate symmetric top, or asymmetric top. Give the symmetry number for each molecule.

- **a.** $CHCl_3$
- **b.** CH_2Cl_2
- **c.** CCl_4

22.26 Classify each of the following molecules in its equilibrium conformation as linear, spherical top, prolate symmetric top, oblate symmetric top, or asymmetric top. Give the symmetry number for each molecule.

- **a.** C_6H_6
- **b.** C_2H_6 (staggered)
- **c.** C_2H_5Cl
- **d.** C_2H_4
- **e.** C_2H_2
- **f.** *trans*-$C_2H_2F_2$

22.27 Classify each of the following molecules in its equilibrium conformation as linear, spherical top, prolate symmetric top, oblate symmetric top, or asymmetric top. Give the symmetry number for each molecule.

- **a.** CH_2O
- **b.** HCN
- **c.** 1,1-Dichloroethene
- **d.** *cis*-$C_2H_2F_2$
- **e.** C_2H_6 (eclipsed)
- **f.** 1,1,1-Trichloroethane (eclipsed)

22.28 Determine the number of vibrational normal modes for each of the molecules in Problem 22.24.

22.29 Determine the number of vibrational normal modes for each of the molecules in Problem 22.27.

22.30 Determine the number of vibrational normal modes for each of the molecules in Problem 22.25.

22.31 Determine the number of vibrational normal modes for each of the molecules in Problem 22.26.

22.32 Without doing any calculations, assign principal axes for the molecules in parts a–c of Problem 22.27.

22.33 Without doing any calculations, assign principal axes for the molecules in parts d–f of Problem 22.27.

22.34 Without doing any calculations, assign principal axes for the molecules in parts a, b, d, and e of Problem 22.26.

22.35 At high temperatures, the two methyl groups making up the ethane molecule rotate nearly freely with respect to each other about the C–C bond instead of undergoing a torsional vibration relative to each other (this is called *internal rotation*). Assuming free internal rotation, how many vibrational normal modes does ethane have?

22.36 Calculate the three principal moments of inertia for the water molecule, assuming a bond length of 96 pm and a bond angle of 104.5°. You must first find the location of the center of mass in the molecule. Assume its isotopes are ^{16}O and ^{1}H. Pick a product of inertia and show that it vanishes.

22.37 **a.** Calculate the principal moments of inertia for the chloroform molecule, assuming tetrahedral bond angles, a C–H bond length of 111 pm, and a C–Cl bond length of 178 pm. Show that the molecule is an oblate symmetric top.

b. Find the rotational energy of the $J = 1$, $K = 1$ level of chloroform. The energy of an oblate symmetric top is given by the formula[8]

$$E = J(J+1)\frac{\hbar^2}{2I_B} + K^2\left(\frac{1}{I_C} - \frac{1}{I_B}\right)\frac{\hbar^2}{2}$$

22.38 **a.** Calculate the principal moments of inertia for the chloromethane molecule, assuming tetrahedral bond angles, a C–H bond length of 111 pm, and a C–Cl bond length of 178 pm. Show that the molecule is a prolate symmetric top.

b. Find the rotational energy of the $J = 1$, $K = 1$ level of chloromethane. The energy of a prolate symmetric top is given by the formula[9]

$$E = J(J+1)\frac{\hbar^2}{2I_B} + K^2\left(\frac{1}{I_A} - \frac{1}{I_B}\right)\frac{\hbar^2}{2}$$

22.39 Give the number of vibrational normal modes for each molecule:

a. C_6H_6

b. C_2N_2

c. C_2H_4

d. C_2H_6

e. C_8H_{18}

f. C_2H_2

22.40 Give the number of vibrational normal modes for each molecule:

a. SF_6

b. BH_3

c. NH_3

d. C_6H_{12}

e. H_2CO

f. CH_3COCH_3

22.41 The covalent radius of an atom is an average value derived from bond lengths in various compounds. The covalent radius of uranium is 142 pm and that of fluorine is 72 pm. Use these values to estimate the bond lengths in uranium hexafluoride. Calculate the principal moments of inertia of a UF_6 molecule. Find the energy and the degeneracy of the first excited rotational level of a UF_6 molecule.

22.42 Give the symmetry number and the number of vibrational normal modes for each of the following molecules in its equilibrium conformation. Assign each to a point group.

a. N_2O

b. C_2N_2

c. IF_3

d. CH_2Cl_2

22.43 Using a software package such as Spartan or CAChe, the normal modes and their predicted frequencies for carbon dioxide, sulfur dioxide, and water, using both semiempirical and ab *initio* methods. Compare the predicted frequencies with the experimental frequencies. The frequencies for carbon dioxide and sulfur dioxide are in Figure 22.6, and the frequencies (divided by the speed of light) for water are 3657 cm^{-1}, 1595 cm^{-1}, and 3756 cm^{-1}.

22.44 Using a software package such as CACHe or Spartan, find the vibrational normal modes of a molecule of your choice that contains some C–H bonds, a C=O bond, an O–H bond, and so on. Try to identify normal modes that you could classify as a C–H stretch, a C–H bend, an O–H stretch, and so on. Determine whether these normal modes have calculated frequencies that lie in the regions usually assumed for such vibrations.

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[8] Davis, *op. cit.*, p. 316 (note 1).

[9] Davis, *op. cit.*, p. 315 (note 1).

22.5 The Equilibrium Populations of Molecular States

So far in this chapter we have studied the quantum-mechanical states of isolated atoms or molecules. In a dilute gas, the molecules do not significantly interfere with each other, and we can apply these states to the individual molecules. However, all molecular states will not be occupied by the same numbers of molecules in a dilute gas at equilibrium. The *Boltzmann probability distribution* gives the probability of a molecular state of energy ε in a system at thermal equilibrium:

$$\text{(Probability of a state of energy } E) \propto e^{-E/k_BT} \qquad (22.5\text{-}1)$$

where k_B is Boltzmann's constant, equal to 1.3807×10^{-23} J K^{-1}, and T is the absolute (Kelvin) temperature.

Each state in an energy level has the same energy so it will have the same population. If g is the degeneracy of the level,

$$\text{(Population of energy level of energy } E) \propto ge^{-E/k_BT} \qquad (22.5\text{-}2)$$

In Chapter 9 there is a derivation of the Boltzmann probability distribution for classical dilute gases. There is a derivation of this probability distribution for a quantum dilute gas in Part 4. For now, we introduce it without derivation. The important fact about the Boltzmann probability distribution is that states of energy much larger than k_BT are quite improbable.

To a good approximation, the energy of a molecule is a sum of four different energies

$$E_{\text{tot}} = E_{\text{tr}} + E_{\text{vib}} + E_{\text{rot}} + E_{\text{el}} \qquad (22.5\text{-}3)$$

The probabilities of each of these energies is independent of the others, so that the probability of an energy level is the product of four Boltzmann factors:

$$\text{(Probability)} \propto g_{\text{tr}}e^{-Etr/k_BT}g_{\text{vib}}e^{-Evib/k_BT}g_{\text{rot}}e^{-Erot/k_BT}g_{\text{el}}e^{-Eel/k_BT} \qquad (22.5\text{-}4)$$

The translational levels are very closely spaced. The electronic energy levels are typically very widely spaced compared with k_BT, and all energy levels except the ground level are typically almost completely unpopulated at room temperature.

EXAMPLE 22.10

Calculate the ratio of the population of one of the states of the first excited electronic level of the Cl_2 molecule to that of the ground state at 298 K. The energy of the first excited level is 2.128 eV above the ground state.

Solution

$$\text{Ratio} = \frac{e^{-E_1/k_BT}}{e^{-E_2/k_BT}} = e^{-(E_1-E_2)/k_BT}$$

$$= \exp\left(\frac{(2.128\,\text{eV})\left(1.602\times10^{-19}\,\text{J(eV)}^{-1}\right)}{\left(1.3807\times10^{-23}\,\text{J K}^{-1}\right)(298\,\text{K})}\right) = e^{-82.87} = 1.03\times10^{-36}$$

The result of this example is typical for most atoms and molecules except for a few molecules such as NO that have one low-lying excited level.

Exercise 22.9

Calculate the ratio of the population of the $2s$ hydrogen state to that of the $1s$ state at 298 K.

The Population of Rotational States of Diatomic Molecules

To the rigid-rotor approximation, the rotational energy of a diatomic molecule is

$$E_v = hB_eJ(J+1) = hc\widetilde{B}_eJ(J+1) \tag{22.5-5}$$

The rotational levels have a degeneracy

$$g_J = 2J+1 \tag{22.5-6}$$

Therefore,

$$\begin{pmatrix}\text{population of rotational}\\ \text{energy level } J\end{pmatrix} \propto (2J+1)e^{-E_J/k_BT} \tag{22.5-7}$$

EXAMPLE 22.11

a. Using the value of $\widetilde{B}_e$ for CO in Table A.22, find the ratio of the population of one of the $J=2$ states to that of the $J=0$ state at 298 K.

b. Find the ratio of the population of the $J=2$ level to that of the $J=0$ state at 298 K.

Solution

a. Let $N(J, M)$ be the number of molecules with quantum numbers J and M.

$$\frac{N(2,0)}{N(0,0)} = e^{-(E_2-E_0)/k_BT} = e^{-6hc\widetilde{B}_e/k_BT}$$

$$= \exp\left(\frac{-6\left(6.6261\times10^{-34}\,\text{J s}\right)\left(2.9979\times10^{10}\,\text{cm s}^{-1}\right)\left(1.931\,\text{cm}^{-1}\right)}{\left(1.3807\times10^{-23}\,\text{J K}^{-1}\right)(298\,\text{K})}\right)$$

$$= e^{-0.05594} = 0.9456$$

b. Let $N(J)$ be the population of level J:

$$N(J) = (2J+1)N(J,M)$$

$$\frac{N(2)}{N(0)} = \frac{5N(2,0)}{N(0,0)} = 5(0.9456) = 4.728$$

The level of maximum population is the level with the maximum value of $(2J+1)\exp(-E_J/k_BT)$. The quickest way to find this is to treat J as a continuously variable quantity, differentiating the function to be maximized with respect to J, setting this derivative equal to zero, and solving for J. A nonintegral value of J can result, but rounding to the nearest integer gives the desired value.

$$\frac{d}{dJ}(2J+1)\exp\left(\frac{-hc\widetilde{B}_e J(J+1)}{k_BT}\right) = \exp\left(\frac{-hc\widetilde{B}_e J(J+1)}{k_BT}\right)\left(2 - \frac{hc\widetilde{B}_e}{k_BT}(2J+1)^2\right)$$

The exponential factor does not vanish except for $J \to \infty$, so we seek the value of J for which the second factor vanishes, which occurs when

$$(2J_{\mathrm{mp}}+1)^2 = \frac{2k_BT}{hc\widetilde{B}_e} \qquad (22.5\text{-}8)$$

EXAMPLE 22.12

Find the rotational level of the CO molecule with the largest population at 298 K.

Solution

$$\begin{aligned}(2J_{\mathrm{mp}}+1)^2 &= \frac{2(1.3807\times10^{-23}\ \mathrm{J\,K^{-1}})(298\ \mathrm{K})}{(6.6261\times10^{-34}\ \mathrm{J\,s})(2.9979\times10^{10}\ \mathrm{cm\,s^{-1}})(1.931\ \mathrm{cm^{-1}})}\\ &= 214.5\\ 2J_{\mathrm{mp}}+1 &= \sqrt{214.5} = 14.65\\ J_{\mathrm{mp}} &= 6.82 \approx 7\end{aligned}$$

For a typical molecule at room temperature, several of the rotational energy levels are significantly populated and the levels of maximum population correspond to a value of J larger than 1. Molecules with smaller reduced masses have fewer occupied rotational levels, and molecules with larger reduced masses have more occupied rotational levels.

Exercise 22.10

a. Find the rotational level with the largest population for HF molecules at 500.0 K.
b. Find the rotational level with the largest population for Br_2 molecules at 500.0 K.

The Population of Vibrational States of Diatomic Molecules

Since the vibrational levels of a diatomic molecule are nondegenerate, we have for the population of a vibrational energy level with quantum number v

$$(\text{Population of vibrational level } v) \propto e^{-E_v/k_BT} \qquad (22.5\text{-}9)$$

EXAMPLE 22.13

Find the ratio of the population of the $v=1,\ J=0$ state to the $v=0,\ J=0$ state for the CO molecule at 298 K. Neglect the anharmonicity correction $\nu_e x_e$.

Solution

From Example 22.5, $\nu_e = 6.5049 \times 10^{13}\ \mathrm{s}^{-1}$:

$$\frac{E_{10} - E_{00}}{k_B T} = \frac{h\nu_e}{k_B T}$$

$$= \frac{\left(6.6261 \times 10^{-34}\ \mathrm{J\,s}\right)\left(6.5049 \times 10^{13}\ \mathrm{s}^{-1}\right)}{(1.3807 \times 10^{-23}\ \mathrm{J\,K}^{-1})(298.15\ \mathrm{K})} = 10.47$$

$$\frac{N(1,0)}{N(0,0)} = e^{-10.47} = 2.84 \times 10^{-5}$$

The populations of excited vibrational states are very small at room temperature for typical diatomic molecules. However, the difference is smaller with molecules that have smaller vibrational frequencies.

Exercise 22.11

Find the ratio of the population of the $v = 1$ vibrational level to that of the $v = 0$ vibrational level for the I_2 molecule at 500.0 K.

The rotational and vibrational energies are independent of each other. It is a fact of probability theory that the probability of the occurrence of two independent events is the product of the probabilities of the two events. If we denote the probability of a vibrational level v by $p_{\mathrm{vib}}(v)$ and the probability of a rotational level by $p_{\mathrm{rot}}(J)$, the probability that these two levels are simultaneously occupied is

$$p_{\mathrm{vib,rot}}(v, J) = p_{\mathrm{vib}}(v)\, p_{\mathrm{rot}}(J) \tag{22.5-10}$$

The same result can be obtained by combining the two contributions to the energy.

EXAMPLE 22.14

For CO at 298.15 K, find the ratio of the population of the level with $v = 1$, $J = 2$ to the $v = 0$, $J = 0$ level.

Solution

From the previous two examples,

$$\text{Probability} = (4.728)(2.84 \times 10^{-5}) = 1.34 \times 10^{-4}$$

The Rotation and Vibration of Polyatomic Molecules

The states of polyatomic molecules are governed by the same Boltzmann probability distribution as those of atoms and diatomic molecules. The rotational levels of polyatomic molecules are generally large enough that many rotational states are occupied. The rotation of a linear polyatomic molecule such as acetylene or cyanogen is just like that of a diatomic molecule. The rotational energies of the rotational states of a spherical top molecule are given in Eq. (22.4-10) and the degeneracies are given in Eq. (22.4-12). The degeneracies of the rotational levels of symmetric top and asymmetric top molecules are more complicated, and we do not discuss them.

EXAMPLE 22.15

If we assume that the bond lengths in SF_6 are equal to 1.80×10^{-10} m, the three principal moments of inertia are equal to $4.18 \times 10^{-45}\ \mathrm{kg\,m^2}$.

a. Find the ratio of the population of one of the state of the $J = 2$ level to the population of the $J = 0$ level at 298 K.

b. Find the ratio of the population of the $J = 2$ level to the population of the $J = 0$ level at 298 K.

Solution

a.

$$\text{Ratio} = \frac{e^{-E_2/k_\mathrm{B}T}}{e^{-E_0/k_\mathrm{B}T}} = e^{-(E_2-E_0)/k_\mathrm{B}T}$$

$$E_2 - E_0 = \frac{\hbar^2}{2I_A}2(2+1) = \frac{3\hbar^2}{I_A} = \frac{3h^2}{4\pi^2 I_A} = \frac{3\left(6.6261 \times 10^{-34}\ \mathrm{J\,s}\right)^2}{4\pi^2\left(4.18 \times 10^{-45}\ \mathrm{kg\,m^2}\right)}$$

$$= 7.98 \times 10^{-24}\ \mathrm{J}$$

$$\text{Ratio} = \exp\left(\frac{-7.98 \times 10^{-24}\ \mathrm{J}}{(1.3807 \times 10^{-23}\ \mathrm{J\,K^{-1}})(298\ \mathrm{K})}\right) = e^{-0.00194}$$

$$= 0.9981$$

b.

$$\text{Ratio} = \frac{g_2 e^{-E_2/k_\mathrm{B}T}}{g_0 e^{-E_0/k_\mathrm{B}T}} = (25)e^{-0.00194} = 24.95$$

The vibrational energy levels of polyatomic molecules are the sum of harmonic oscillator energy level expressions, as in Eq. (22.4-19).

EXAMPLE 22.16

Find the ratio of the population of the vibrational state of SO_2 with $v_1 = 1$, $v_2 = 2$, and $v_3 = 1$ to the population of the ground vibrational state. The frequencies divided by the speed of light are given in Figure 22.6.

Solution

$$E_\mathrm{vib} = (6.6261 \times 10^{-34}\ \mathrm{J\,s})(2.9979 \times 10^{10}\ \mathrm{cm\,s^{-1}})$$

$$\times\ [1151.2\ \mathrm{cm^{-1}} + 2(519\ \mathrm{cm^{-1}}) + 1361\ \mathrm{cm^{-1}}]$$

$$= 7.052 \times 10^{-20}\ \mathrm{J}$$

$$\text{Ratio} = \exp\left(\frac{-7.052 \times 10^{-20}\ \text{J}}{(1.3807 \times 10^{-23}\ \text{J K}^{-1})(298\ \text{K})}\right) = 3.60 \times 10^{-8}$$

This value is typical of the fact that excited vibrational levels are not significantly populated at room temperature.

PROBLEMS

Section 22.5: The Equilibrium Populations of Molecular States

22.45 Find the ratio of the populations of the $v = 1, J = 2$ level and the $v = 0, J = 0$ level at 298.15 K in the rigid-rotor-harmonic oscillator approximation for:

a. H_2

b. HD, where D is deuterium, ^2H

c. D_2

22.46 Find the ratio of the population of the $v = 1, J = 0$ level of CO to the population of the $v = 0, J = 0$ level at 298.15 K.

22.47 Find the ratio of the populations of the $v = 1, J = 1$ level and the $v = 0, J = 0$ state at 298 K for:

a. $^1H^{35}Cl$

b. $^1H^{37}Cl$

c. $^2H^{35}Cl$

d. $^2H^{37}Cl$

The parameters for $^1H^{35}Cl$ are in Table A.22 of Appendix A. Assume that isotopic substitution does not change the bond length or the force constant.

22.48 **a.** For a temperature of 298 K, find the ratio of the population of the $v = 1$ vibrational state to the population of the $v = 0$ vibrational state of H_2.

b. For a temperature of 298 K, find the ratio of the population of the $v = 1$ vibrational state to the population of the $v = 0$ vibrational state of I_2.

c. Explain why the values in parts a and b are so different.

22.49 Find the rotational level of maximum population for H_2 at 298 K. Do it separately for *ortho*- and *para*-hydrogen.

22.50 Find the rotational level of maximum population for I_2 at 298 K.

Summary of the Chapter

In addition to electronic motion, atoms can have translational motion, and molecules can have translational, rotational, and vibrational motions. To a good approximation the translational energy of a molecule confined in a box is the same as that of a point-mass particle in the same box. To a first approximation, the vibrational energy of a diatomic molecule is that of a harmonic oscillator, and the rotation is that of a rigid rotor. Correction terms can be included if high accuracy is necessary. The rotational energy of a polyatomic molecule is taken to be that of a rigid rotating body. The vibrational energy of a polyatomic molecule is taken to be that of normal modes, each one of which oscillates like a harmonic oscillator. Only a fraction of the conceivable set of rotational quantum numbers is possible. This fraction is equal to $1/\sigma$, where σ is the symmetry number of the molecule, equal to the number of equivalent orientations of the molecule.

ADDITIONAL PROBLEMS

22.51 If a molecule is confined in a very small box, its energy levels can be spaced widely enough that the spacing can be observed with light absorbed or emitted by transitions between translational levels. Assume that a CO molecule is confined in a matrix of solid argon at 75 K, and that the center of the CO molecule can move in a cubical region that is 3.5×10^{-10} m on a side.

a. Find the energies and degeneracies of the first three translational energy levels.

b. Find the wavelength and frequency of the light absorbed if a molecule makes a transition from the lowest energy level to the next energy level.

22.52 **a.** From information in Table A.22, find the value of the force constant for each of the molecules: N_2, O_2, and F_2. From the LCAOMO treatment in Chapter 20, find the bond order for each molecule. Comment on the relative sizes of these force constants.

b. From information in Table A.22, find the value of the internuclear distance in each of the molecules: N_2, O_2, and F_2. Comment on the relative sizes of these internuclear distances.

22.53 **a.** From information in Table A.22, find the value of the force constant for HF and HI. Comment on the relative sizes of these force constants.

b. From information in Table A.22. find the value of the internuclear distance for HF and HI. Comment on the relative sizes of these distances.

22.54 For the NO molecule, find the following:

a. The difference in energy between the $v = 1$, $J = 2$ level and the $v = 0$, $J = 1$ level, without corrections for anharmonicity, centrifugal stretching, and rotation-vibration interaction.

b. The degeneracies of these two levels.

c. The ratio of the populations of these two levels at 298.15 K and at 1000.0 K.

22.55 Identify each of the following statements as either true or false. If a statement is true only under specific circumstances, label it as false.

a. The behavior of a molecule confined in a container will be noticeably different from the behavior of a free molecule.

b. Although part of the electronic energy in the Born–Oppenheimer approximation is kinetic energy, this energy acts as a potential energy for nuclear motion.

c. Principal axes can be chosen for any object.

d. A linear triatomic molecule will exhibit more distinct frequencies of vibration than a bent triatomic molecule.

e. A methane molecule has nine vibrational normal modes.

f. An SeO_2 molecule has four vibrational normal modes.

g. A normal oxygen molecule $^{16}O_2$ will have rotational levels that are qualitatively different from those of the isotopically substituted oxygen molecule $^{16}O^{18}O$.

h. The corrections for anharmonicity in the vibrational energy levels of a diatomic molecule cause the energy levels to be farther apart than the uncorrected energy levels.

i. The corrections for centrifugal stretching in the rotational energy levels of a diatomic molecule cause the energy levels to be closer together than the uncorrected energy levels.

j. The corrections for the interaction of rotation and vibration cause the energy levels to be closer together than the uncorrected energy levels.

k. Every diatomic molecule can exhibit only even values of J or odd values of J.

22.56 Repeat Problem 22.54 with the corrections for anharmonicity, centrifugal stretching, and rotation-vibration interaction.

23

Optical Spectroscopy and Photochemistry

PRINCIPAL FACTS AND IDEAS

1. Spectroscopy is the study of the interactions of matter with electromagnetic radiation and the extraction of information about molecular structure from this study.
2. Emission and absorption of photons are governed by the Bohr frequency rule:

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda} = E_{\text{upper}} - E_{\text{lower}}$$

   where the E's are energy eigenvalues of two energy levels.
3. Selection rules predict which transitions between pairs of levels will occur with absorption or emission of radiation.
4. Concentrations can be determined spectroscopically using the Beer–Lambert law.
5. Transitions between electronic energy levels produce spectra that are generally in the visible and ultraviolet regions.
6. Transitions between rotational states of molecules produce spectra in the microwave region.
7. Transitions between vibrational states of molecules produce spectra in the infrared region.
8. Photochemistry is closely related to spectroscopy and involves chemical reactions that are initiated by absorption of radiation.
9. Other types of optical spectroscopy such as Raman spectroscopy can supplement emission/absorption spectroscopy.

23.1 Emission/Absorption Spectroscopy and Energy Levels

The energy levels of atoms and molecules can be studied experimentally by measuring the wavelengths of the light that is emitted, absorbed, or scattered in transitions between energy levels. According to the Planck–Einstein relation of Eq. (14.4-8), the energy of a photon is

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda} \tag{23.1-1}$$

where h is Planck's constant, c is the speed of light, ν is the frequency of the radiation, and λ is the wavelength of the radiation. The basic idea of optical spectroscopy is that if a photon is emitted or absorbed by an atom or molecule the atom or molecule makes a transition between energy levels whose difference in energy is equal to the energy of the photon. This is an expression of the conservation of energy and is expressed by the *Bohr frequency rule*:

$$\boxed{E_{\text{photon}} = h\nu = \frac{hc}{\lambda} = E_{\text{upper}} - E_{\text{lower}}} \tag{23.1-2}$$

where E_{upper} and E_{lower} are the energy eigenvalues for the upper and lower energy levels of the atom or molecule. If a photon is absorbed the atom or molecule makes a transition from a lower to a higher energy level. If a photon is emitted the atom or molecule makes a transition from a higher to a lower energy level. The Bohr frequency rule is based on the assumption that only one photon is absorbed or emitted at a time. Multiphoton transitions can also occur.[1]

The spectrum of electromagnetic radiation is divided into several regions, as shown in Table 23.1. Typical spacings between electronic energy levels correspond to photon energies in the visible and ultraviolet regions. Spacings between vibrational energy

Table 23.1 Regions of the Electromagnetic Spectrum

Name of Region	Wavelength	Photon Energy/eV
Gamma radiation	<10 pm	>124000
X-radiation	10 pm−10 nm	124000−124
Ultraviolet radiation	10 nm−400 nm	124−3.1
Visible radiation(light)	400 nm−750 nm	3.1−1.65
Infrared radiation	750 nm−1 mm	1.65−0.00124
Microwave radiation (including radar)	1 mm−10 cm	0.00124−0.00124
Radio-frequency radiation (including AM, FM, TV)	10 cm−10 km	<0.00124

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[1] See for example C. H. Lin, A. A. Villaeys, and Y. Fujimora, eds., *Advances in Multiphoton Processes and Spectroscopy*, Vol. 17, World Scientific Publishing Co., 2006.

levels correspond to photon energies in the infrared region, and spacings between rotational energy levels correspond to photon energies in the microwave region. Spacings between translational energy levels are too small to observe spectroscopically.

Photochemistry involves absorption of photons that can break chemical bonds or cause transitions to reactive excited states. Typical chemical bond energies are roughly 400 to 1000 kJ mol^{-1}. Photons with energies large enough to break chemical bonds lie in the ultraviolet region.

EXAMPLE 23.1

Find the frequency and wavelength of a photon with enough energy to break a chemical bond with bond energy of 4.31 eV (corresponding to 416 kJ mol^{-1}), which is the average bond energy of a C–H bond.

Solution

$$\nu = \frac{E}{h} = \frac{(4.31\,\text{eV})(1.602\times10^{-19}\,\text{J}\,(\text{eV})^{-1})}{6.6261\times10^{-34}\,\text{J s}} = 1.04\times10^{15}\,\text{s}^{-1}$$

$$\lambda = \frac{2.9979\times10^{8}\,\text{m s}^{-1}}{1.04\times10^{15}\,\text{s}^{-1}} = 2.88\times10^{-7}\,\text{m} = 288\,\text{nm}$$

Exercise 23.1

An *einstein* is a mole of photons. Find the energy per photon and per einstein for

a. Microwave radiation with $\lambda = 1.00$ cm
b. Infrared radiation with $\lambda = 3.00\ \mu$m
c. Ultraviolet radiation with $\lambda = 200.0$ nm
d. X-radiation with $\lambda = 100.0$ pm

The Quantum Mechanics of Spectroscopic Transitions

Our discussion of quantum mechanics in previous chapters has focused on stationary states of atomic and molecular systems as described by the time-independent Schrödinger equation. Spectroscopy involves a time-dependent process, the evolution of the state of a system containing atoms or molecules plus electromagnetic radiation. Electromagnetic radiation consists of an oscillating electric field and an oscillating magnetic field as depicted in Figure 14.9. Because an electric field puts a force on any charged particle and a magnetic field puts a force on a moving charged particle, both of these fields interact with the nuclei and electrons of an atom or molecule, and both can cause absorption or emission of energy. A transition produced by the electric field is called an *electric dipole transition*, and a transition due to the magnetic field is called a *magnetic dipole transition*. The electric dipole transitions dominate in optical spectroscopy. Magnetic dipole transitions are involved in nuclear magnetic resonance (NMR) spectroscopy and electron spin resonance (ESR) spectroscopy, which we discuss in the next chapter.

Time-dependent perturbation theory is applied to study electric dipole transitions. We give a brief introduction and quote some of the results. The Hamiltonian operator of the molecule in the presence of radiation is written in a way similar to Eq. (19.3-1):[2]

$$\widehat{H} = \widehat{H}^{(0)} + \widehat{H}' \tag{23.1-3}$$

The zero-order Hamiltonian $\widehat{H}^{(0)}$ is not the same as the zero-order Hamilton in Section 19.3. It is the complete time-independent Hamiltonian operator of the molecule in the absence of radiation. The perturbation term $\widehat{H}'$ describes the interaction between the molecule and the electric field of the radiation, and is time-dependent because of the oscillation of the radiation.

We assume that the zero-order time-independent Schrödinger equation has been solved to a usable approximation:

$$\widehat{H}^{(0)}\psi_j^{(0)} = E_j^{(0)}\psi_j^{(0)} \tag{23.1-4}$$

The wave function $\psi_j^{(0)}$ is one of the energy eigenfunction of the molecule in the absence of radiation. Inclusion of the perturbation produces a time-dependent wave function, which is written as a linear combination of the zero-order wave functions:

$$\Psi(q,t) = \sum_j a_j(t)\psi_j^{(0)}(q) \tag{23.1-5}$$

where q stands for all of the coordinates of the particles in the molecule. Since the zero-order wave functions are time-independent, the a_j coefficients must depend on time. They contain all of the time dependence of the wave function.

In order to observe transitions we specify that at time $t = 0$ the wave function is equal to one of the zero-order functions, $\psi_n^{(0)}$,

$$\Psi(q,0) = \psi_n^{(0)}(q) \tag{23.1-6}$$

so that at $t = 0$ only a_n is nonzero:

$$a_j(0) = \delta_{jn} = \begin{cases} 1 & \text{if } j = n \\ 0 & \text{if } j \neq n \end{cases} \tag{23.1-7}$$

where δ_{jn} is the *Kronecker delta*, introduced in Eq. (16.4-43). If at later times another coefficient, a_j, becomes nonzero, this corresponds to a nonzero probability of a transition from the state $\psi_n^{(0)}$ to the state $\psi_j^{(0)}$.

Time-dependent perturbation theory provides an approximate formula that gives the coefficients as functions of time. If the radiation is polarized with its electric field in the z direction, $|a_j(t)|^2$ is proportional to the intensity of the radiation of the wavelength that satisfies the Bohr frequency rule and is also proportional to the square of the following integral:[3]

$$(\mu_z)_{jn} = \int \psi_j^{(0)*}\widehat{\mu}_z\psi_n^{(0)}\,dq = \int \widehat{\mu}_z\psi_j^{(0)*}\psi_n^{(0)}dq \tag{23.1-8}$$

where $\widehat{\mu}_z$ is operator for the z component of the operator for the electric dipole of the atom or molecule, as in Eq. (20.4-9). The operator $\widehat{\mu}_z$ is a multiplication operator,

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[2] J. C. Davis, *Advanced Physical Chemistry*, The Ronald Press, New York, 1965, p. 243ff.

[3] J. C. Davis, *loc. cit.* (note 2).

which allows the second version of this equation to be written. The integration is over all values of all of the coordinates of the system, abbreviated by the symbol q. The integral in Eq. (23.1-8) is the z component of the *transition dipole moment* for states n and j.

For two states that have a nonzero transition dipole moment, a transition between them is predicted to occur with the absorption or emission of a photon. Such a transition is called an *allowed transition*. A transition between two states that have a zero transition dipole moment is predicted not to occur, and is called a *forbidden transition*. A rule that tells which transitions are allowed is called a *selection rule*. The selection rules that we give in this chapter are generally obtained with approximate wave functions using first-order perturbation theory. Most of the selection rules are therefore not exactly obeyed. Forbidden transitions frequently do occur, but generally with lower probabilities than allowed transitions.

Inspection of Eq. (23.1-8) shows that the transition dipole moment is replaced by its complex conjugate if the wave functions for the initial and final states are switched. This means that incident radiation will induce transitions in either direction with the same probability. A transition that raises the energy of the atom or molecule corresponds to *absorption* of radiation, whereas one that lowers the energy corresponds to *stimulated emission* of radiation.

We observe the emission or absorption from a system of many atoms or molecules. Absorption and stimulated emission occur simultaneously if both the upper and lower states are populated. Absorption is observed if the lower-energy state has a greater population than the higher-energy state, and stimulated emission is observed if the higher-energy state has a greater population. Stimulated emission has the same wavelength as the incident radiation, moves in the same direction, and is in phase with the incident radiation. That is, the crests and troughs of its waves coincide with those of the waves of the incident radiation. With many atoms or molecules emitting radiation stimulated by the same wave, a strong beam of unidirectional radiation can result with all of its waves in phase. Such radiation is said to be *coherent*. This kind of radiation is emitted by lasers, which amplify electromagnetic radiation by adding radiation to an incident beam by stimulated emission. "*Laser*" is an acronym for "*light amplification by stimulated emission of radiation*." In a laser, some means must provide a nonequilibrium excess population in the upper energy state.

Transitions resulting in the emission of photons can also occur in the absence of stimulating radiation. This is called *spontaneous emission*. The probability of such transitions is also proportional to the square of the transition dipole moment, but is independent of the intensity of any radiation. Because there is no inducing radiation to specify a direction and phase, radiation that is spontaneously emitted by a system of many molecules is emitted in all directions and is not coherent. In *emission spectroscopy* spontaneously emitted radiation from excited atoms or molecules is observed.

In *absorption spectroscopy* the attenuation of an incident beam is observed. The amount of absorption of radiation depends on three things: the intensity of the radiation, the inherent probability that the transition will take place, and the numbers of molecules in the initial state and in the final state. In a system of many atoms or molecules at thermal equilibrium, the number of atoms or molecules occupying a state of energy E is proportional to the Boltzmann factor of Eq. (22.5-1):

$$(\text{Number of molecules in a state with energy } E) \propto e^{-E/k_{\mathrm{B}}T} \tag{23.1-9}$$

where k_{B} is Boltzmann's constant (equal to 1.3807×10^{-23} J K^{-1}) and T is the absolute temperature. The symbol $\propto$ stands for "is proportional to."

Exercise 23.2

For hydrogen atoms at thermal equilibrium at 298 K, find the ratio of the number of hydrogen atoms in one of the $n = 2$ states to the number in one of the $n = 1$ states. Take $E_1 = 0$ (for the ground level), so that $E_2 = 10.2$ eV.

The classical way to observe emission or absorption spectra is to *disperse* the radiation, which means separating the different wavelengths from each other. A triangular prism of transparent material was first used for this purpose, because the speed of light in a transparent material depends on wavelength. Light that strikes a boundary between two materials is refracted (its path is bent) if it strikes the boundary at an angle other than a right angle. Different wavelengths are refracted by different amounts, so that the radiation is dispersed when it passes through a triangular prism. Figure 23.1a shows schematically how radiation is dispersed by a prism. The different directions correspond to different wavelengths.

Figure 23.1b shows how radiation is dispersed by a transmission grating, which passes radiation through a set of equally spaced parallel slits that diffract the radiation. The diffracted radiation moves away from the slits in various directions. Radiation from different slits that is in constructive interference produces a beam in a direction determined by the wavelength of the radiation and the slit spacing. A reflection grating functions in a similar way, except that the diffracted radiation moves from right to left if the incident radiation moves from left to right.

In a simple spectroscope, the wavelengths of emitted light are observed by viewing the dispersed radiation. Bright images of the slit are seen at angles that depend on the wavelengths of emitted light. If only narrow bands of wavelengths are emitted, the slit images look like line segments and are called *spectral lines*. In a spectrograph the dispersed light falls on a photographic film or plate and a permanent record of the spectral lines is obtained, which allows accurate measurement of the line positions. Figure 23.2 shows a simulation of the visible portion of the emission spectrum of atomic hydrogen at low pressure.

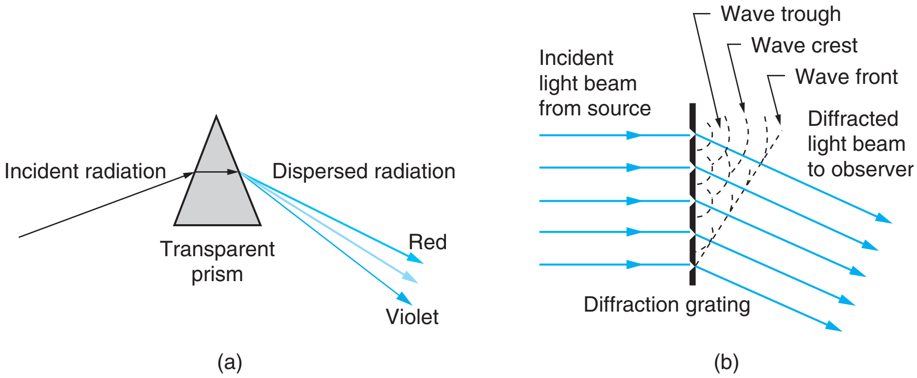

Figure 23.1 The Dispersion of Electromagnetic Radiation. (a) Prism. Since the refractive index depends on wavelength, different wavelengths are refracted through different angles. (b) Transmission grating. Since constructive interference is necessary to give the diffracted beam, different wavelengths are diffracted through different angles.

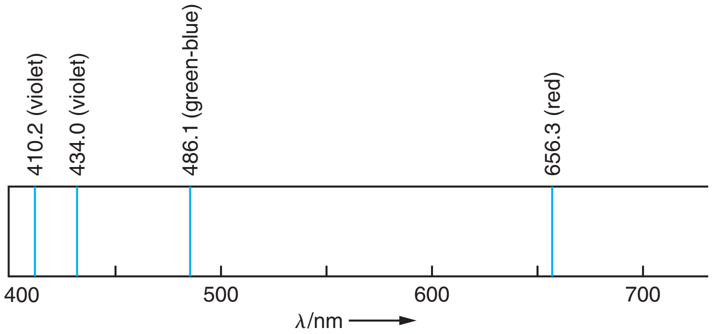

Figure 23.2 The Visible Portion of the Hydrogen Atom Emission Spectrum (Simulated). Each wavelength represented produces an image of the slit of the spectrograph. If only discrete wavelengths are present, as in this case, the spectrum is called a line spectrum.

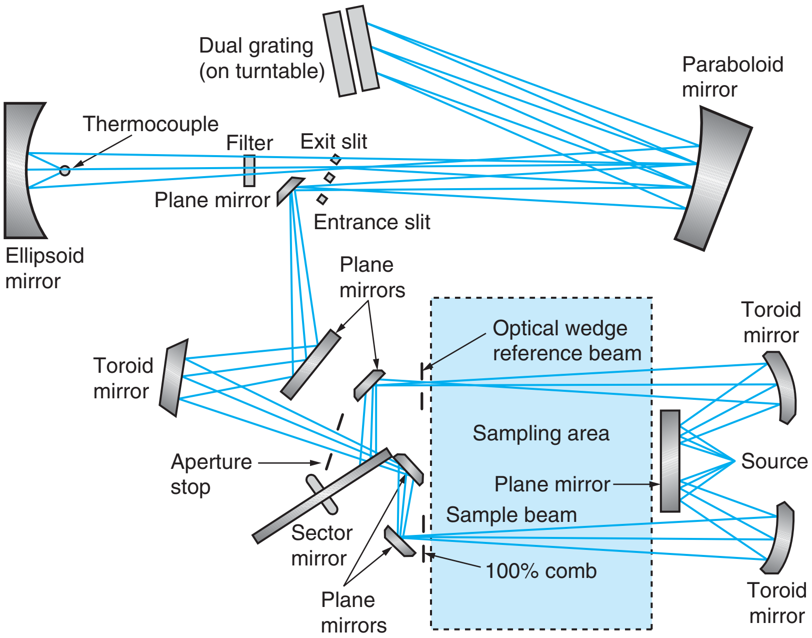

Figure 23.3 Schematic Diagram of a Filter-Grating, Double-Beam Infrared Spectrophotometer. This diagram shows a scanning instrument. The wavelength passed is determined by the angular position of the grating, which is mounted on a turntable, and is rotated automatically by a motor. Courtesy of Perkin-Elmer Corporation.

Absorption Spectroscopy

Absorption spectroscopy has traditionally been carried out in a *spectrophotometer*, such as the one shown schematically in Figure 23.3. The light is dispersed by a prism or grating, collimated into a beam of nearly parallel rays, and passed through a cell containing the sample. Only a narrow band of wavelengths passes at one time and the bandwidth determines the resolution of the instrument. The wavelength can be chosen by turning the prism or grating, and this is done automatically in a scanning instrument.

A photocell or other detector determines the intensity of transmitted radiation. In a single-beam instrument, the cell containing the sample substance and a "blank" cell not containing this substance are placed alternately in the beam. In a double-beam instrument, the beam is divided and passed simultaneously through the sample cell and the blank cell. In a diode-array instrument, a number of detectors in different locations are used, and the entire spectrum is taken at one time.

The intensity of a collimated beam of radiation is defined as the energy passing unit area per unit time. We define a total intensity, I_{tot}, which is the energy of all wavelengths per unit area per unit time, and an intensity per unit wavelength interval, $I(\lambda)$. The energy carried by radiation with wavelengths in the infinitesimal wavelength range between λ and $\lambda + d\lambda$ is

$$\text{(Energy in range } d\lambda \text{ per unit time per unit area)} = I(\lambda)d\lambda \qquad (23.1\text{-}10)$$

A variable that is commonly plotted to represent an absorption spectrum is the *transmittance*, $T(\lambda)$, usually expressed in percent:

$$T(\lambda) = \left(\frac{I(\lambda)_{\text{out}}}{I(\lambda)_{\text{in}}}\right) \times 100\% \quad \text{(definition of transmittance)} \qquad (23.1\text{-}11)$$

where $I(\lambda)_{\text{out}}$ is the intensity after the light beam passes through the cell and $I(\lambda)_{\text{in}}$ is the incident intensity.

The Beer–Lambert Law

Figure 23.4 depicts a cell of length b containing an absorbing substance with concentration c and a beam of light passing through it in the x direction. Consider a thin slab of unit area within the cell, lying between x and $x + dx$. The volume of the slab is dx times unit area, so the amount of absorbing substance in this portion of the slab equals cdx times unit area. Let the intensity of light in the small range of wavelengths $d\lambda$ be denoted by $I(\lambda, x)d\lambda$. This intensity depends on x because the light becomes less intense as it travels into the cell. The amount of light absorbed in the slab per unit

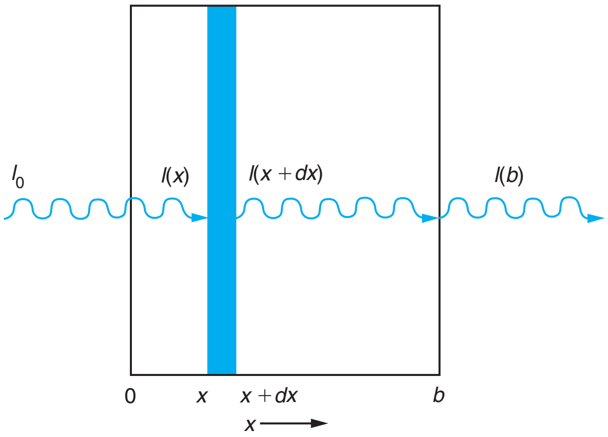

Figure 23.4 Absorption of Light in a Thin Slab. The attenuation of the light due to the absorbing substance in the thin slab is assumed to be proportional to the concentration of the substance and to the thickness of the slab.

time is proportional to the intensity of light and to the concentration of the absorbing substance, so the change in I from one side of the thin slab to the other is

$$-dI = k(\lambda)Icdx \tag{23.1-12}$$

where c is the concentration of the absorbing substance. The proportionality factor $k(\lambda)$ depends on the identity of the absorbing substance and on the identity of the solvent. It is a function of wavelength, but if the Beer–Lambert law is obeyed, it does not depend on the concentration.

Equation (23.1-12) is a differential equation that can be solved by separation of variables. Division by I gives

$$-\frac{dI}{I} = k(\lambda)cdx \tag{23.1-13}$$

We carry out a definite integration, letting $x = 0$ be the front of the cell and $x = b$ be the back of the cell. Assuming that the concentration is uniform,

$$-\int_{I(0)}^{I(b)} \frac{dI}{I} = k(\lambda)c\int_{0}^{b} dx \tag{23.1-14a}$$

$$-\ln\left(\frac{I(\lambda, b)}{I(\lambda, 0)}\right) = \ln\left(\frac{I(\lambda, 0)}{I(\lambda, b)}\right) = k(\lambda)cb \tag{23.1-14b}$$

The *absorbance* $A(\lambda)$ (formerly called the *optical density*) is defined as the common logarithm of the same ratio as in the second natural logarithm in Eq. (23.1-14b):

$$\boxed{A(\lambda) = \log_{10}\left(\frac{I(\lambda, 0)}{I(\lambda, b)}\right) = \log_{10}\left(\frac{100\%}{T}\right) \quad \left(\begin{array}{c}\text{definition}\\ \text{of absorbance}\end{array}\right)} \tag{23.1-14c}$$

The Beer–Lambert law is

$$A(\lambda) = a(\lambda)bc \tag{23.1-15}$$

where $a(\lambda)$ is the *absorptivity* (formerly called the *extinction coefficient*):

$$a(\lambda) = \frac{k(\lambda)}{\ln(10)} = \frac{k(\lambda)}{2.302585} \tag{23.1-16}$$

The absorptivity depends on the wavelength of light as well as on the identity of the absorbing substance and the identity of the solvent. If the concentration is measured in mol L^{-1}, the absorptivity is called the *molar absorptivity*. The Beer–Lambert law is well obeyed by many substances at low to moderate concentrations. Deviations occur at higher concentrations, corresponding to an absorptivity that depends on concentration. These deviations can be caused by specific chemical effects such as association of the molecules of the substance.

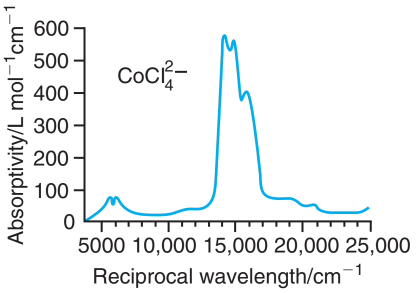

Figure 23.5 The Absorption Spectrum of 0.001 mol L^{-1} $CoCl_4^{2-}$ in 10 mol L^{-1} HCl Solution. This continuous spectrum arises because of the broadening of the spectral lines due to solvent interaction. From Russell S. Drago, *Physical Methods in Chemistry*, W. B. Saunders Co., Philadelphia, 1977, p. 392.

Figure 23.5 shows an absorption spectrum for a sample in liquid solution, with the absorptivity plotted as a function $1/\lambda$, measured in cm^{-1}. This spectrum shows absorption over broad ranges of wavelength, not just at a few wavelengths. This is common for absorbing substances dissolved in liquid solvents. The spectral lines are broadened by several effects, including the coupling of vibrational and electronic transitions, Doppler shifts from the translation of molecules and the uncertainty broadening due to the finite life time of the states, introduced in Eq. (16.5-11).[4] If the absorption spectrum of the same substance were taken in the gas phase instead of in a solvent, the regions of absorption would be much narrower. However, every spectral line has an inherent nonzero range of wavelengths that are absorbed (a nonzero *linewidth*). In addition, no spectrograph or spectrophotometer can disperse radiation so completely that a single wavelength is separately detected. The difference in wavelength of the most closely spaced narrow spectral lines that an instrument can distinguish is called the *resolution* of the instrument.

EXAMPLE 23.2

A solution of a certain dye has a molar absorptivity of 1.8×10^5 L mol^{-1} cm^{-1} at a wavelength of 606 nm. Find the concentration of a solution of this dye that has an absorbance at this wavelength equal to 1.65 in a cell 1.000 cm in length.

Solution

$$c = \frac{A}{ab} = \frac{1.65}{(1.8 \times 10^5\ \mathrm{L\,mol^{-1}\,cm^{-1}})(1.000\ \mathrm{cm})} = 9.2 \times 10^{-6}\ \mathrm{mol\,L^{-1}}$$

PROBLEMS

Section 23.1: Emission/Absorption Spectroscopy and Energy Levels

23.1 A solution of phenylalanine in neutral water with concentration equal to 0.110×10^{-3} mol L^{-1} has an absorbance at $\lambda = 206.0$ nm of 1.027 in a 1.000-cm cell. Find the molar absorptivity.

23.2 A cell of path length 1.50 cm is filled with gaseous bromine at a pressure of 100.0 torr and a temperature of 298.15 K. It is found that 10.76% of light of wavelength 400 nm is transmitted through the cell. Find the molar absorptivity of gaseous bromine at this wavelength.

23.3 The molar absorptivity of *para*-xylene at 212 nm is equal to 6.31×10^3 L mol^{-1} cm^{-1}. What is the concentration of *para*-xylene in a nonabsorbing solvent if the solution has a percentage transmission of 11.35% at 212 nm in a cell of length 1.000 cm?

23.4 Two solutions of the same dye in the same cell give transmittances of 63.52% and 87.32%. Find the concentration of the second solution if the concentration of the first solution is 1.000 m mol L^{-1}.

23.5 If more than one absorbing substance is present, the contributions to the absorbance are additive if the Beer–Lambert law holds. A solution of azomethane in ethanol with concentration of 1.0×10^{-3} mol L^{-1} has an absorbance of 0.1285 at a wavelength of 357 nm in a cell with path-length 2.00 cm. The absorbance of pure ethanol in the same cell at the same wavelength is 0.0500. Find the absorptivity of azomethane at this wavelength.

23.6 The absorptivity of hemoglobin at 430 nm is found to be 532 L mol^{-1} cm^{-1}. The molar mass of hemoglobin is 68000 g mol^{-1}.

a. The concentration of hemoglobin inside red blood cells is approximately 17% by mass. Estimate the absorbance of such a solution in a cell of length 1.000 cm.

b. Find the concentration in mol L^{-1} and in percent by mass for a solution that would have an absorbance of 1.00 at 430 nm.

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[4] V. B. E. Thomsen, *J. Chem. Educ.*, **72**, 616 (1995).

23.7 **a.** Calculate the wavelength of the light absorbed when an electron in a box of length 1.000 nm makes the transition from $n = 1$ to $n = 2$. In what region of the electromagnetic spectrum (X-ray, ultraviolet, visible, infrared, microwave) does this light lie?

b. The contribution of this electron to the dipole moment is $-\mathscr{e}(x - a/2)$, where $-\mathscr{e}$ is the charge on the electron, x is its coordinate, and a is the length of the box. Argue that the transition dipole moment for this transition is nonzero for all transitions. *Hint:* Consider graphs of the factors in the integrand function in the integral used to calculate the transition dipole moment.

23.8 **a.** A solution of a certain dye in ethanol has a concentration of 0.0001000 mol L^{-1} and gives an absorbance of 1.034 at a wavelength of 480 nm in a cell of length 1.000 cm. Find the molar absorptivity of this dye in this solvent at this wavelength. If this is the wavelength of maximum absorbance, what is the color of the solution?

b. A solution of a different dye in methanol gives an absorbance of 0.987 at a wavelength of 680 nm. If the molar absorptivity of this dye in this solvent at this wavelength is equal to $1.80 \times 10^4\ \mathrm{L\ mol^{-1}\ cm^{-1}}$, what is its molar concentration?

23.2 The Spectra of Atoms

The Hydrogen Atom

The spectra of atoms are due to electronic transitions. The following selection rules are derived when the hydrogen atom orbitals are substituted in the integral of Eq. (23.1-8):[5]

Hydrogen Atom Selection Rules

$$\Delta m = m_{\text{final}} - m_{\text{initial}} = 0, \pm 1 \qquad \text{(23.2-1a)}$$

$$\Delta l = l_{\text{final}} - l_{\text{initial}} = \pm 1 \qquad \text{(23.2-1b)}$$

$$\Delta n: \text{no restrictions} \qquad \text{(23.2-1c)}$$

These selection rules correspond to conservation of angular momentum in the atom–radiation system, because the angular momentum component of a photon is $\pm\hbar$. Because $\Delta l = \pm 1$, a hydrogen atom in an s subshell can make a transition only to a p subshell, whereas an atom in a p subshell state can make a transition to an s subshell or to a d subshell, and so on. All states in the same shell have the same energy in hydrogen atoms, and a simple spectrum is obtained as was shown in Figure 23.2. Figure 23.6 shows schematically some of the transitions that take place, with line segments connecting each pair of states between which transitions can occur. This type of diagram is called a *Grotrian diagram*.

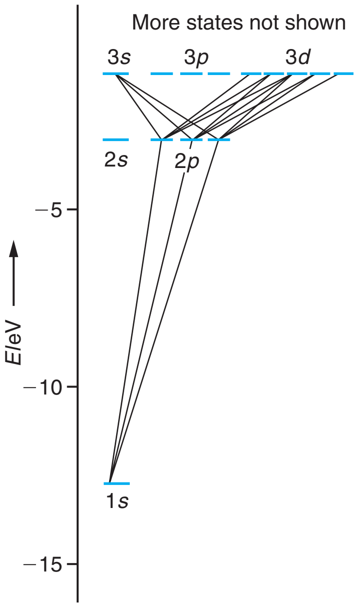

Figure 23.6 The Energy Levels of the Hydrogen Atom and the Allowed Transitions between Them. This type of diagram is known as a Grotrian diagram.

EXAMPLE 23.3

From Rydberg's formula in Eq. (14.4-10), find the wavelength and frequency of the photons emitted by a hydrogen atom undergoing the $n = 2 \rightarrow n = 1$ transition.

Solution

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1} - \frac{1}{n_2}\right) = (109678\ \mathrm{cm})^{-1}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

---

[5] J. C. Davis, *op. cit.*, pp. 256–257 (note 2).

For the $n = 2$ to $n = 1$ transition

$$\frac{1}{\lambda} = (109678\ \text{cm}^{-1})\left(\frac{1}{1} - \frac{1}{4}\right) = 82258\ \text{cm}^{-1}$$

$$\lambda = \frac{1}{82258\ \text{cm}^{-1}} = 1.2157 \times 10^{-5}\ \text{cm} = 121.568\ \text{nm, in the ultraviolet}$$

Exercise 23.3

From Rydberg's formula in Eq. (14.4-10), find the wavelength and frequency of the photons emitted by a hydrogen atom undergoing the $n = 3 \to n = 2$ transition and the $n = 4 \to n = 3$ transition. In what spectral range (visible, ultraviolet, or infrared) does each lie?

Multielectron Atoms

If orbital wave functions are used to calculate transition dipole moments, the following selection rules are obtained for multielectron atoms:[6]

Selection Rules for Multielectron Atoms

$$\Delta L = \pm 1 \tag{23.2-2a}$$

$$\Delta S = 0 \tag{23.2-2b}$$

$$\Delta J = 0, \pm 1 \quad (0 \to 0 \text{ not allowed}) \tag{23.2-2c}$$

$$\Delta M_J = 0, \pm 1 \quad (0 \to 0 \text{ not allowed for } \Delta J = 0) \tag{23.2-2d}$$

where J is the quantum number for the total electronic angular momentum and M_J is the quantum number for its z component. Because approximate wave functions were used to derive these selection rules, forbidden transitions do occur. The most important selection rule is that $\Delta S = 0$. For example, transitions between singlet and triplet states are forbidden.

PROBLEMS

Section 23.2: The Spectra of Atoms

23.9 A positronium atom[7] consists of a positron, which is an antiparticle with the same mass as an electron and the same charge as a proton, and one electron. Find the wavelengths of the photons emitted in the following "electronic" transitions:

a. $n = 3$ to $n = 2$

b. $n = 4$ to $n = 2$

c. $n = 5$ to $n = 2$

d. $n = 6$ to $n = 2$

Compare these wavelengths with those of a normal hydrogen atom.

23.10 A tritium atom has a nucleus that contains a proton and two neutrons. Its atomic mass is approximately 3.0 amu. Find the wavelengths of the photons emitted in the following electronic transitions:

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[6] J. C. Davis, *op. cit.*, pp. 256–257 (note 2).

[7] The dipositronium molecule has been synthesized. It persisted for less than a nanosecond before the positrons and electrons annihilated each other. See D. B. Cassidy and A. P. Mills, Jr., *Nature*, 449, **195** (2007).

a. $n = 3$ to $n = 2$

b. $n = 4$ to $n = 2$

c. $n = 5$ to $n = 2$

d. $n = 6$ to $n = 2$

Compare these wavelengths with those of a normal hydrogen atom.

23.11 Calculate the frequency and the wavelength of the light emitted in the following electronic transitions of a He^+ ion. For each transition specify whether the radiation is in the ultraviolet, visible, or infrared parts of the spectrum.

a. $n = 3$ to $n = 2$

b. $n = 2$ to $n = 1$

c. $n = 5$ to $n = 4$

23.12 Crudely approximate the electronic motion in a hydrogen atom by assuming that the electron moves in a cubical three-dimensional hard box of dimension 1.00 Å on a side. Calculate the wavelength of the light emitted if the electron makes a transition from the first excited level to the ground state, and compare this with the wavelength of the light emitted in the $n = 2$ to $n = 1$ transition using the correct energy levels. What would the dimension of the hard box be to make the transition have the same wavelength as the correct $n = 2$ to $n = 1$ transition?

23.13 Tell whether each of the following transitions in a hydrogen atom is allowed or forbidden:

a. $n = 2, l = 1, m = 1$ to $n = 1, l = 0, m = 0$

b. $n = 4, l = 2, m = 1$ to $n = 2, l = 1, m = 1$

c. $n = 3, l = 2, m = 1$ to $n = 2, l = 2, m = 1$

d. $n = 6, l = 4, m = 1$ to $n = 2, l = 2, m = 1$

23.14 Tell whether each of the following transitions in a carbon atom is allowed or forbidden:

a. ${}^1D_2$ to ${}^1S_0$

b. ${}^3P_2$ to ${}^3P_1$

23.15 Tell whether each of the following transitions in a selenium atom is allowed or forbidden:

a. ${}^1D_2$ to ${}^3P_1$

b. ${}^3P_0$ to ${}^1S_0$

23.16 **a.** Consider the excited states of the helium atom that arise from the $(1s)(2s)$ and $(1s)(2p)$ configurations. These states were discussed in Chapters 18 and 19. Draw a Grotrian diagram for these states and the ground state of the He atom.

b. Using energies from Figure 19.3, estimate the wavelengths at which spectral lines would be found from the transitions of part a.

23.3 Rotational and Vibrational Spectra of Diatomic Molecules

Rotational Spectra of Diatomic Molecules

If a diatomic molecule is represented as a rigid rotor, the transition dipole moment integral for a rotational transition is

$$(\mu)_{J_{M''},J'M'} = \int Y^*_{J''M''}\mu Y_{J'M'}\sin(\theta)d\theta d\phi \tag{23.3-1}$$

The Y functions are the rotational wave functions (spherical harmonic functions) and $\mu = \mu(r, \theta, \phi)$ is the dipole moment operator of the molecule in the Born–Oppenheimer approximation. The selection rules that result are[8]

$$\Delta J = \pm 1 \text{ for a molecule with nonzero permanent dipole moment} \tag{23.3-2a}$$

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[8] I. N. Levine, *Molecular Spectroscopy*, Wiley, New York, 1975, p. 162ff.

$$\text{All } \Delta J \text{ values forbidden for a molecule with zero permanent dipole moment} \tag{23.3-2b}$$

where J is the quantum number for the rotational angular momentum. The rotational selection rules are well obeyed by diatomic molecules with $^1\Sigma$ electronic states.

The selection rule of Eq. (23.3-2b) can be understood classically. In order for a molecule to interact with the electric field of the radiation, it must exhibit a periodically varying electric dipole moment of the correct frequency. A rotating diatomic molecule with a permanent dipole moment does present a periodically varying dipole to the radiation, so it should absorb or emit radiation if it is rotating with the correct frequency. If a molecule has no permanent dipole moment it does not exhibit any periodic variation in the dipole moment.

Rotational transitions correspond to photon wavelengths in the microwave region. The radiation sources in microwave spectrometers are klystron tubes, which were originally developed for radar apparatuses in World War II. Hollow metal wave guides carry the radiation to the sample cell, which is a hollow metal cavity, and the resonant radiation in the cavity is sampled to detect absorption. Microwave spectroscopy has played an important role in identifying molecules in interstellar space, but it is not a common tool in many chemical laboratories.

From the selection rule, the photon energy for an allowed transition is

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda} = E_{v,J+1} - E_{vJ} \tag{23.3-3}$$

where J is the value of the rotational quantum number for the lower-energy state and the vibrational quantum number v has the same value for both states. Since the vibrational quantum number v does not change, the reciprocal of the wavelength is

$$\widetilde{\nu} = \frac{1}{\lambda} = \frac{1}{hc}(E_{v,J+1} - E_{vJ}) \tag{23.3-4}$$

The reciprocal wavelength is usually expressed in cm^{-1}, sometimes called "wave numbers."

Equation (22.2-40) gives the energy levels for rotation in the rigid rotor approximation. The reciprocal wavelength corresponding to absorption is

$$\begin{aligned} \widetilde{\nu} = \frac{1}{\lambda} &= \widetilde{B}_e[(J+1)(J+2) - J(J+1)] \\ &= \widetilde{B}_e[J^2 + 3J + 2 - J^2 - J] = 2\widetilde{B}(J+1) \end{aligned} \tag{23.3-5}$$

where J is the quantum number for the initial state. Since J can take on values $0, 1, 2, \ldots,$ this corresponds to a set of equally spaced spectral lines with reciprocal wavelengths equal to $2\widetilde{B}_e, 4\widetilde{B}_e$, and so on. Figure 23.7a shows the energy levels with the allowed transitions and Figure 23.7b shows a simulated spectrum for carbon monoxide. The intensities of the lines are related to the populations of the rotational levels.

EXAMPLE 23.4

The splitting between the spectral lines in the CO spectrum is $3.8626\ \text{cm}^{-1}$. Find the value of r_e, the equilibrium internuclear distance.

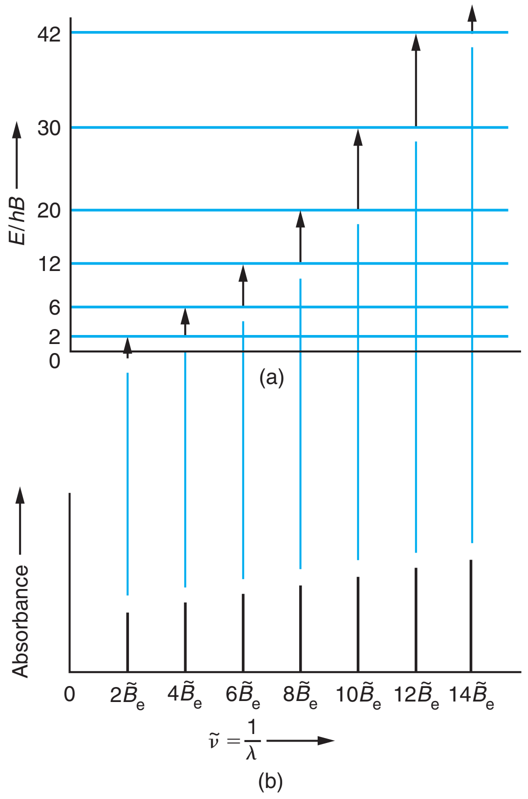

Figure 23.7 A Microwave Spectrum. (a) The allowed transitions. (b) The simulated spectrum. The positions of the spectral lines are correlated with the transitions that produce the lines.

Solution

The splitting is equal to $2\tilde{B}_e$, so the value of $\tilde{B}_e = 1.9313\ \text{cm}^{-1}$, in agreement with the value in Table A.22 of Appendix A. We assume that the molecule contains the isotopes ^{12}C and ^{16}O, with masses 12.0000 amu and 15.994915 amu.

$$\mu = \left(\frac{(12.0000\ \text{amu})(15.994915\ \text{amu})}{12.0000\ \text{amu} + 15.994915\ \text{amu}}\right)\left(\frac{0.001\ \text{kg}}{6.02214 \times 10^{23}\ \text{amu}}\right)$$

$$= 1.1385 \times 10^{-26}\ \text{kg}$$

$$r_e^2 = \frac{h}{8\pi^2 \mu \tilde{B}_e c}$$

$$= \frac{6.6261 \times 10^{-34}\ \text{J s}}{8\pi^2(1.1385 \times 10^{-26}\ \text{kg})(1.9313\ \text{cm}^{-1})(2.9979 \times 10^{10}\ \text{cm s}^{-1})}$$

$$= 1.2731 \times 10^{-20}\ \text{m}^2$$

$$r_e = \sqrt{1.1283 \times 10^{-20}\ \text{m}^2} = 112.83\ \times 10^{-10}\ \text{m} = 1.1283\ \text{PM} = 1.1283\ \text{Å}$$

The expression in Eq. (23.3-5) can be improved on by including the correction terms in the energy level expression of Eq. (22.2-45).

Exercise 23.4

The equilibrium internuclear distance of HCl is 1.275×10^{-10} m. Find the spacing between the lines in the microwave spectrum for both $^{1}H^{35}Cl$ and $^{1}H^{37}Cl$. The chlorine atomic masses are 34.96885 amu and 36.96590 amu and the ^{1}H atomic mass is 1.007825 amu.

The intensity of a given line in a spectrum is determined by the magnitude of the transition dipole moment for the transition that produces the spectral line and by the number of molecules occupying the initial state and the final state. At thermal equilibrium the population of a level is given by the Boltzmann distribution of Eq. (22.5-1):

$$\begin{aligned}(\text{Population of energy level } J) &\propto gje^{-E_J/k_\mathrm{B}T}\\ &\propto (2J+1)_{\mathrm{e}}^{-hB_\mathrm{e}J(J+1)/k_\mathrm{B}T} \qquad (23.3\text{-}6)\end{aligned}$$

The degeneracy increases and the Boltzmann factor $e^{-E_J/k_\mathrm{B}T}$ decreases as J increases, so the population rises to a maximum and then decreases as J increases. If the transition dipole moments for different rotational transitions in the same molecule are roughly equal, the level with the largest population is the one with the largest absorption intensity.

Exercise 23.5

a. Find the rotational level with the largest population for HCl molecules at 298 K. The internuclear distance equals 1.275×10^{-10} m.
b. Find the rotational level with the largest population for Br_2 molecules at 298 K. The internuclear distance equals 2.281×10^{-10} m.

Vibration–Rotation Spectra of Diatomic Molecules

When transitions are observed between vibrational energy levels, infrared radiation is emitted or absorbed. The vibrational selection rules are derived in the Born–Oppenheimer approximation by evaluating the transition dipole moment integral

$$(\mu_x)_{v'v''} = \int \psi_{v'}^{*}\,\widehat{\mu}(x)\psi_{v''}dx \qquad (23.3\text{-}7)$$

where $\psi_{v'}$ and $\psi_{v''}$ are two vibrational wave functions, expressed in terms of $x = r - r_\mathrm{e}$, and where $\widehat{mu}(x)$ is the operator for the molecular dipole moment. Since the vibrational wave functions approach zero rapidly for large magnitudes of x, taking the limits of the integral as infinite produces no significant numerical error, but does contribute to the fact that vibrational selection rules are only approximately correct.

We assume that the dipole moment can be represented by the truncated Taylor series

$$\mu(x) = \mu(0) + \left(\frac{d\mu}{dx}\right)_0 x + \cdots \qquad (23.3\text{-}8)$$

where $\mu(0)$ is the value of the dipole moment at $x = 0$ and where the subscript 0 on the derivative means that it is evaluated at $x = 0$. Using harmonic oscillator wave functions and the two terms included explicitly in Eq. (23.3-8), the selection rule is

$$\Delta v = 0, \pm 1 \text{ for nonzero dipole moment} \tag{23.3-9a}$$

$$\text{All } \Delta v \text{ forbidden for zero dipole moment} \tag{23.3-9b}$$

Since $\Delta v = 0$ is allowed, transitions in which only the rotational quantum number changes are allowed, giving the pure rotational spectrum in the microwave region that we have discussed. Transitions for which $\Delta v = \pm 1$ give spectra in the infrared region in which both rotational and vibrational quantum numbers change.

It is possible to interpret the selection rule of Eq. (23.3-9b) classically. In order for a vibrating diatomic molecule to interact with electromagnetic radiation, the molecule must present a fluctuating dipole to the radiation as the molecule vibrates with the correct frequency. The molecule must have a permanent dipole moment to do this.

EXAMPLE 23.5

A permanent dipole moment corresponds to a constant nonzero value of $\mu(0)$ in Eq. (23.3-8). Using the $v = 0$ harmonic oscillator function of Eq. (15.4-10), show that a nonzero value of $\mu(0)$ leads to a nonzero value of the transition dipole moment for the $v = 0$ to $v = 0$ transition.

Solution

From Eqs. (15.4-10) and (23.3-8):

$$\begin{aligned}(\mu_x)_{00} &= \int_{-\infty}^{\infty} \psi 0^* \widehat{\mu}(x) \psi 0 dx = \left(\frac{a}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} e^{-ax^2/2} [\mu(0) + \left(\frac{d\mu}{dx}\right)_0 x] e^{-ax^2/2} dx \\ &= \left(\frac{a}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} e^{-ax^2/2} \mu(0) e^{-ax^2/2} dx + \left(\frac{a}{\pi}\right)^{1/2} \int_{-\infty}^{\infty} e^{-ax^2/2} \left(\frac{d\mu}{dx}\right)_0 x e^{-ax^2/2} dx \\ &= \left(\frac{a}{\pi}\right)^{1/2} \mu(0) \int_{-\infty}^{\infty} e^{-ax^2} dx + \left(\frac{a}{\pi}\right)^{1/2} \left(\frac{d\mu}{dx}\right)_0 \int_{-\infty}^{\infty} x e^{-ax^2} dx \\ &= \mu(0) + 0 = \mu(0) \neq 0\end{aligned}$$

Exercise 23.6

Use the $v = 0$ function and the $v = 1$ function from Eq. (15.4-11) to show that a nonzero value of the second term on the right-hand side of the equation leads to a nonzero value of the transition dipole moment for the $v = 0$ to $v = 1$ transition.

Vibrational transitions do not occur without rotational transitions, because $\Delta J = 0$ is forbidden for diatomic molecules. Figure 23.8 shows the allowed transitions that occur between the ground vibrational state ($v = 0$) and the first excited vibrational state ($v = 1$) of a diatomic molecule. The resulting set of spectral lines is called the *fundamental band*. Those spectral lines for which the value of J in the upper state is larger than the value of J in the lower state constitute the *R branch* of the band, and the spectral lines for which the value of J in the upper state is smaller than that in the lower state constitute the *P branch*. If lines occurred for which the values of J in both states were the same, they would constitute the *Q branch*. The rotational selection rules are well obeyed, and they forbid the Q branch, which is not observed. The location that the Q branch would have if it were present is the *band center*. The vibrational selection rules are less well obeyed than are the rotational selection rules, and forbidden vibrational transitions are frequently observed. A spectral band corresponding to $\Delta v = \pm 2$ is called a *first overtone*, one corresponding to $\Delta v = \pm 3$ is called a *second overtone*, and so on. Bands for which the lower value of v is larger than zero are called *hot bands*. Hot bands are generally not seen in absorption spectra near room temperature because of the small population of excited vibrational states.

If we neglect the x_e, α, and $\mathscr{D}$ terms in the energy level expression of Eq. (22.2-45) the reciprocal wavelength of a line of the R branch of the fundamental band is given by

$$\tilde{\nu}_R = \frac{1}{\lambda_R} = (E_{1,J+1} - E_{0,J})/hc = \tilde{\nu}_e + 2\tilde{B}_e(J+1) \quad (J = 0, 1, 2, \ldots) \quad (23.3\text{-}10)$$

where J is the value of the rotational quantum number in the lower ($v = 0$) state. In this approximation the R branch consists of a set of equally spaced lines with spacing $2\tilde{B}_e$.

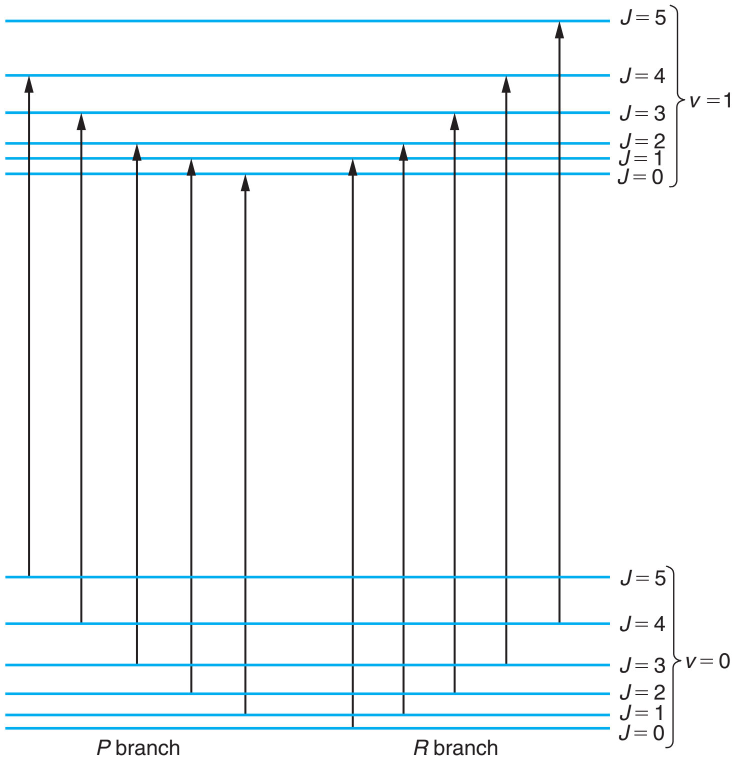

Figure 23.8 Allowed Transitions Leading to a Vibration–Rotation Spectral Band of a Diatomic Substance. In the R branch, the value of J in the upper level is greater than that in the lower level, and in the P branch, the opposite is the case. There is no Q branch, which would correspond to the same value of J in the upper and lower energy levels.

It looks like the rotational spectrum except that these lines start from the band center instead of from zero reciprocal wavelength. In the same approximation the reciprocal wavelengths of the lines of the P branch are given by

$$\widetilde{\nu}_P = \frac{1}{\lambda_P} = (E_{1,J-1} - E_{0,J})/hc = \widetilde{\nu}_e - 2\widetilde{B}_e J \quad (J = 1, 2, 3, \ldots) \tag{23.3-11}$$

where J is the value of J in the lower ($v = 0$) state, which must be at least as large as unity since the transition is to the next lower value of J. The P branch consists of a set of equally spaced lines with spacing $2\widetilde{B}_e$ as does the R branch, but the lines are on the other side of the band center. The splitting between the first line of the P branch and the first line of the R branch is $4\widetilde{B}_e$.

EXAMPLE 23.6

a. Using the values of the parameters for CO in Table A.22 in Appendix A, find the reciprocal wavelength at the band center and the splitting between the lines of the fundamental band in the rigid rotor–harmonic oscillator approximation.

b. Find the value of the force constant k for the CO molecule.

c. Assuming that all transition dipole moments are equal and that the temperature is 298 K, find the most intense line in the P branch and in the R branch of the fundamental band.

Solution

a. The reciprocal wavelength of the band center is

$$\widetilde{\nu}_{\mathrm{BC}} = \frac{1}{\lambda_{\mathrm{BC}}} = \widetilde{\nu}_e = 2169.81\ \mathrm{cm}^{-1}$$

The splitting is

$$\Delta\widetilde{\nu} = \Delta(1/\lambda) = 2\widetilde{B}_e = 2(1.93127\ \mathrm{cm}^{-1}) = 3.86254\ \mathrm{cm}^{-1}$$

b. From Example 23.4 the reduced mass of CO equals 1.1385×10^{-26} kg. From Eq. (22.2-30):

$$\nu = \widetilde{\nu}_e c = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad \text{or} \quad k = 4\pi^2 \mu \widetilde{\nu}_e^2 c^2$$

$$k = 4\pi^2 (1.1385 \times 10^{-26}\ \mathrm{kg})(2169.81\ \mathrm{cm}^{-1})^2 (2.9979 \times 10^{10}\ \mathrm{cm\ s}^{-1})^2$$

$$= 1901.8\ \mathrm{kg\ s}^{-2} = 1901.8\ \mathrm{N\ m}^{-1} = 1901.8\ \mathrm{J\ m}^{-2}$$

The value of the force constant of the CO molecule is fairly large, because CO has a triple bond, which is quite stiff compared to most single and double bonds.

c. From Example 22.12, the most populated level is that for $J = 7$. This corresponds to the eighth line from the band center in the R branch and the seventh line from the band center in the P branch.

Figure 23.9 shows the fundamental band of the HCl molecule. The double lines are due to the presence of two isotopes of chlorine. The lines are not equally spaced, mostly due to the effect of the α term in the energy level expression of Eq. (22.2-45).

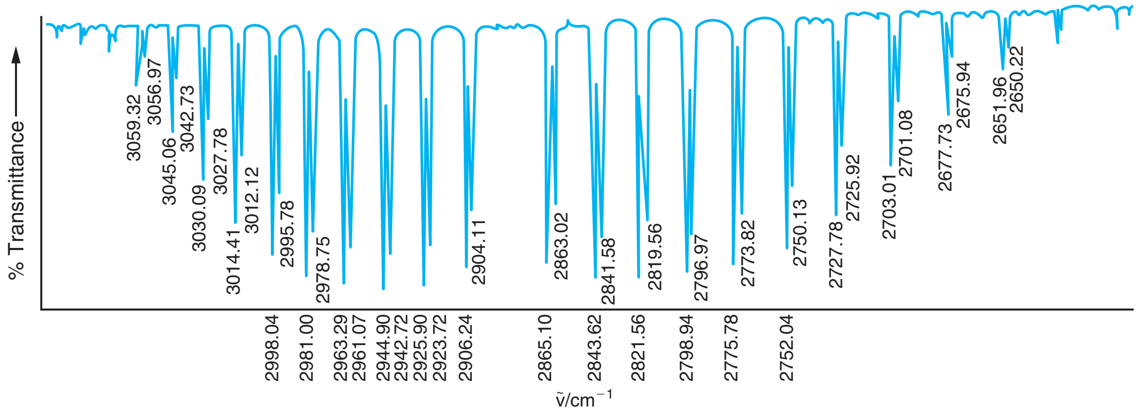

Figure 23.9 The Fundamental Band of the Vibration–Rotation Spectrum of HCl. The resolution of the spectrum is sufficient to show the lines for $H^{35}Cl$ and $H^{37}Cl$. The ^{35}Cl is the more abundant isotope of chlorine, and produces the more intense lines. From N. L. Alpert, W. E. Keiser, and H. A. Szymanski, *IR Theory and Practice of Infrared Spectroscopy*, 2nd ed., Plenum Press, New York, 1970.

As in most molecules, the $\mathscr{D}$ term is small and its effect is negligible. The $\nu_e x_e$ term does not affect this spectrum because all lines in this spectrum correspond to the same vibrational transition, from $v = 0$ to $v = 1$.

With the full energy level expression of Eq. (22.2-45), the reciprocal wavelength of the band center of the fundamental band is

$$\begin{aligned}\tilde{\nu}_{BC} &= \frac{1}{\lambda_{BC}} = \tilde{\nu}_e - \tilde{\nu}_e x_e[(3/2)^2 - (1/2)^2] \\ &= \tilde{\nu}_e - 2\tilde{\nu}_e x_e \quad \text{(center of the fundamental band)} \qquad (23.3\text{-}12)\end{aligned}$$

The reciprocal wavelength of the band center of the first overtone band is

$$\tilde{\nu}_{BC} = \frac{1}{\lambda_{BC}} = 2\tilde{\nu}_e - 6\tilde{\nu}_e x_e \quad \text{(center of the first overtone band)} \qquad (23.3\text{-}13)$$

If the overtone band can be observed it is possible to evaluate the anharmonicity parameter $\tilde{\nu}_e x_e$ from it.

EXAMPLE 23.7

Find the reciprocal wavelength for the band centers of the fundamental and the first overtone of the CO molecule, including the $\tilde{\nu}_e x_e$ correction.

Solution

For the fundamental, the reciprocal wavelength of the band center is

$$\tilde{\nu}_{BC} = \frac{1}{\lambda_{BC}} = 2169.81\ \text{cm}^{-1} - 2(13.29\ \text{cm}^{-1}) = 2167.22\ \text{cm}^{-1}$$

For the first overtone,

$$\tilde{\nu}_{BC} = \frac{1}{\lambda_{BC}} = 2(2169.81\ \text{cm}^{-1}) - 6(13.29\ \text{cm}^{-1}) = 4259.86\ \text{cm}^{-1}$$

Fourier Transform Infrared Spectroscopy

Most modern infrared spectrometers use Fourier transform techniques rather than dispersion techniques. In a Fourier transform infrared spectrometer a pulse of infrared radiation is passed through an *interferometer*, as depicted in Figure 23.10.[9] The beam splitter divides the beam into two beams of equal intensity, which are recombined after being reflected by separate mirrors, one of which is movable. As this mirror moves, the detector responds to changes in the intensity as the two beams interfere constructively or destructively. The intensity of the pulse as a function of time is called an *interferogram*. As depicted in the figure, a single frequency produces a sinusoidal interferogram. A pulse can be thought of as containing many frequencies, and an interferogram can have a complicated appearance depending on the intensities of the various frequencies.

An interferogram is taken without a sample in position and another is taken with the sample in position. The difference between the interferograms is a function of time and can be represented by a *Fourier transform*:

$$I(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} c(\omega) e^{i\omega t} d\omega \tag{23.3-14}$$

Appendix B contains a brief introduction to Fourier series and transforms. Equation (23.3-14) is analogous to a linear combination of basis functions, but with an integration instead of a sum. The variable ω is sometimes called the "circular frequency" of the

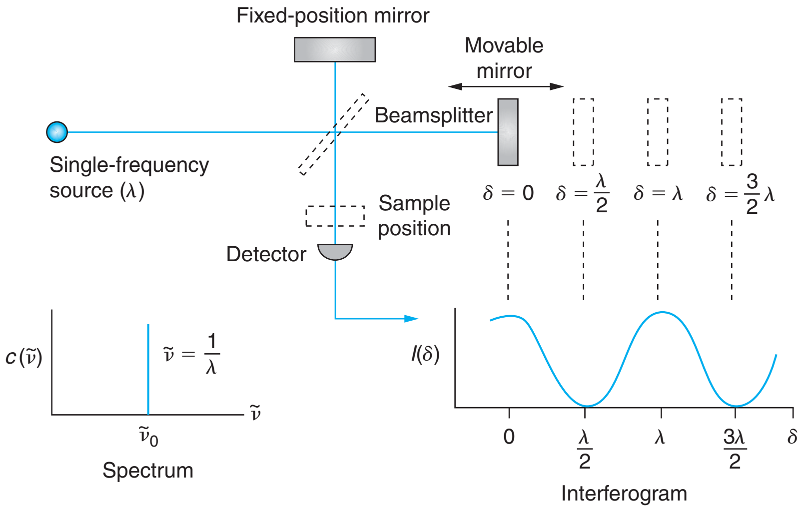

Figure 23.10 The Radiation Path in a Fourier Transform Infrared Spectrophotometer (Schematic). If only one wavelength is present, the sinusoidal interferogram at the lower right is observed as the movable mirror in the Michelson–Morley interferometer changes its position. The Fourier transform of this signal is a single sharp line, as shown at the lower left. From W. D. Perkins, *J. Chem. Educ.*, **63**, A5 (1986).

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[9] W. D. Perkins, *J. Chem. Educ.*, **63**, A5 (1986); and **64**, A296 (1987).

basis function $e^{i\omega t}$. The frequency of oscillation is

$$\nu = \frac{\omega}{2\pi} \tag{23.3-15}$$

The function $c(\omega)$ plays the same role as the expansion coefficients in a linear combination and expresses the intensities of the different frequencies. It is called the *Fourier transform* of $I(t)$.[10] It contains the same information as $I(t)$, encoded as a function of frequency instead of time. It is the infrared spectrum of the sample.

To find the spectrum $c(\omega)$, one must invert the Fourier transform, which is done by calculating the integral

$$c(\omega) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} I(t) e^{-i\omega t} dt \tag{23.3-16}$$

Since Eq. (23.3-14) and Eq. (23.3-16) differ only in the sign of the exponent, $I(t)$ is also called the Fourier transform of $c(\omega)$.

EXAMPLE 23.8

Find the Fourier transform of the function $f(\omega) = 1/a^2 + \omega^2$, where a is a positive constant.

Solution

$$I(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{e^{i\omega t}}{a^2 + \omega^2} d\omega = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{\cos(\omega t) + i\sin(\omega t)}{a^2 + \omega^2} d\omega$$

The real part of the integrand is an even function, and the imaginary part is an odd function. The imaginary part will vanish upon integration, and the even part will give twice the value of the integrand from 0 to ∞:

$$I(t) = \frac{2}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \frac{\cos(\omega t)}{a^2 + \omega^2} d\omega = \frac{2}{\sqrt{2\pi}} \frac{\pi}{2a} e^{-a|t|} = \sqrt{\frac{\pi}{2}} \frac{1}{a} e^{-a|t|}$$

where we have looked the integral up in a table.[11]

The Fourier transform of the interferogram must be carried out numerically. Fourier transform infrared (FTIR) instruments have a dedicated computer to do this. A numerical procedure known as the *fast Fourier transform* (FFT) is generally used.[12] The procedure is carried out repeatedly for different frequencies. Depending on the instrument, the intensity might be obtained for values of the reciprocal wavelength differing by 1 cm^{-1} or 2 cm^{-1}. With 1 cm^{-1} resolution (spacing), a spectrum from 500 cm^{-1} to 4000 cm^{-1} would consist of 3501 separate points representing the percent transmittance or the absorbance at each reciprocal wavelength. A graph of the spectrum

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[10] See L. Glasser, *J. Chem. Educ.*, **64**, A261 (1987); and *J. Chem. Educ.*, **64**, A306 (1987) for an introduction to Fourier series and transforms.

[11] H. B. Dwight, *Tables of Integrals and Other Mathematical Data*, 4th ed., Macmillan, New York, 1961.

[12] J. R. Barrante, *Applied Mathematics for Physical Chemistry*, 3rd ed., Prentice Hall, Upper Saddle River, NJ, 2004, p. 182ff.

as a function of reciprocal wavelength is produced by connecting these points. The spectrum is obtained rapidly and it is possible to take the spectrum repeatedly and to add the separate spectra, allowing weak spectral lines to be seen and allowing random "noise" to be reduced by the averaging procedure. An interferogram can be taken in less than one second using a deuterated triglycine sulfate (DTGS) detector, and as many as 20 or 30 interferograms can be taken in a second with a mercury–cadmium–telluride detector.

PROBLEMS

Section 23.3: Rotational and Vibrational Spectra of Diatomic Molecules

23.17 Using an identity from Appendix F, derive the selection rule for a harmonic oscillator, $\Delta v = 0, \pm 1$.

23.18 From the spectroscopic constants of the CO molecule, find the value of the force constant of the CO bond. Typical force constants are near 500 N m^{-1}. Comment on the size of your answer.

23.19 **a.** Find an expression for the reciprocal wavelengths of the microwave spectrum of a diatomic molecule including all of the terms in Eq. (22.2-50). Assume that $v = 0$.

b. Find the reciprocal wavelengths and the wavelengths for the first four lines in the microwave spectrum of CO using your expression of part a. Assume that $v = 0$. The values of the parameters are in Table A.22 of Appendix A. Compare your values with those obtained with the approximation of Eq. (23.3-5).

23.20 **a.** Find the wavelength of the first line of the R branch of the IR spectrum of HBr, using the harmonic oscillator–rigid rotor approximation.

b. Repeat the calculation of part a including the corrections for anharmonicity, centrifugal stretching, and rotation–vibration interaction.

23.21 **a.** Find the wavelength of the band center of the first overtone vibrational band of the HF molecule. $\widetilde{\nu}_e = 4138.5\ \text{cm}^{-1}$, and $\widetilde{B}_e = 20.956\ \text{cm}^{-1}$. Neglect the correction terms in the energy level expression.

b. Find the splitting in cm^{-1} between the individual lines in the R branch of this band.

c. Find the wavelengths of the first line in the P branch and the first line in the R branch of this band.

23.22 Find a formula for the rotational frequency (number of revolutions per second) of a rigid diatomic molecule assuming that classical mechanics holds, but that the angular momentum happens to have the magnitude $\hbar\sqrt{J(J+1)}$. Compare this formula with that for the frequency of a photon absorbed when a quantum-mechanical molecule makes a transition from J to $J + 1$. Show that the two frequencies are nearly equal for large values of J.

23.23 Using information on the normal HF molecule from Table A.22 of Appendix A, predict the reciprocal wavelengths of the absorptions in the microwave spectrum of DF, where D is deuterium, ^{2}H. Assuming equal oscillator strengths, find the line of maximum intensity at 298 K.

23.24 Which of the following substances will have a microwave spectrum?

a. CO_2

b. N_2O

c. CCl_4

d. $CHCl_3$

e. CH_2Cl_2

23.25 Which of the following substances will have a microwave spectrum?

a. CH_3Cl

b. BH_3

c. NH_3

d. C_2H_4

e. SO_3

23.26 Using the $\widetilde{\nu}_e$ and $\widetilde{\nu}_e x_e$ values from Table A.22 of Appendix A, find the reciprocal wavelength of the band center of the fundamental band, the first overtone band, and the second overtone band of $^1H^{19}F$. Find the reciprocal wavelength of the center of the (high-temperature) band corresponding to the transition from $v = 1$ to $v = 2$.

23.27 Using the $\widetilde{\nu}_e$ and $\widetilde{\nu}_e x_e$ values from Table A.22 of Appendix A, find the reciprocal wavelength of the band center of the fundamental band, the first overtone band, and the second overtone band of $^1H^{81}Br$. Find the reciprocal wavelength of the center of the "hot band" (high-temperature band) corresponding to the transition from $v = 1$ to $v = 2$.

23.28 Using values of parameters in Table A.22 of Appendix A, find the reciprocal wavelength of the radiation absorbed in the transition from the $v = 0$, $J = 6$ state to the $v = 1$, $J = 7$ state of $^1H^{81}Br$. To which branch does this line belong, and how many lines lie between it and the band center?

23.29 Assuming that the transition dipole moments are roughly equal, estimate the temperature at which the spectrum of Figure 23.9 was taken.

23.30 **a.** Using the full expression for the energy levels in Eq. (22.2-50) obtain the expression for the reciprocal wavelengths of the lines in the P and R branches of the fundamental band of a diatomic molecule.

b. Use the expression derived in part a to find the reciprocal wavelength of the first line of the P branch and the first line of the R branch of the fundamental band of CO.

c. Obtain the expression for the reciprocal wavelength of the band center of the $(n + 1)$th harmonic (nth overtone) and find the reciprocal wavelength of the band center of the third and fourth overtones for the CO molecule.

23.31 If the energy level expression of Eq. (22.2-50) is used, the reciprocal wavelengths of the lines in the R branch of the first overtone band are given by

$$\widetilde{\nu}_R = \frac{1}{\lambda_R} = 2\widetilde{\nu}_e - 6\widetilde{\nu}_e x_e + 2\widetilde{B}_e(J+1) - 4\widetilde{D}(J+1)^3 - \widetilde{\alpha}(2J^2 + 7J + 4)$$

a. Verify this equation.

b. Obtain the analogue of this equation for the P branch of the first overtone band.

c. Find the reciprocal wavelength of each of the first three lines in the R branch of the first overtone of the CO molecule.

23.32 **a.** Find the Fourier transform $c(\omega)$ of the function

$$I(t) = Ae^{-(t-t_0)^2/D}$$

where A, t_0, and D are constants.

b. Sketch graphs of $I(t)$ and $c(\omega)$.

c. Explain in physical terms what $c(\omega)$ represents if $I(t)$ represents the intensity of a pulse of radiation as a function of time. Explain why $c(\omega)$ depends on t_0 as it does and describe what happens if $t_0 = 0$.

23.4 Electronic Spectra of Diatomic Molecules

The electronic spectra for most diatomic molecules are found in the ultraviolet and visible regions. The electronic transitions are usually accompanied by rotational and vibrational transitions. The following selection rules are obtained for electronic transitions in diatomic molecules:[13]

$$\Delta\Lambda = 0, \pm 1 \tag{23.4-1a}$$

$$\Delta S = 0 \tag{23.4-1b}$$

$$\text{Parity of electronic state changes: } (u \to g \text{ or } g \to u) \tag{23.4-1c}$$

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[13] I. N. Levine, *op. cit.*, p. 298ff (note 8).

where Λ is the quantum number for the projection of the total electronic orbital angular momentum on the internuclear axis and S is the total electron spin quantum number. The selection rules for the rotational and vibrational transitions that accompany electronic transitions are:

$$\Delta J = \pm 1 \tag{23.4-1d}$$

$$\Delta v\text{: not restricted} \tag{23.4-1e}$$

where J is the rotational quantum number (not the quantum number for the total electronic angular momentum, which does not apply to diatomic molecules) and v is the vibrational quantum number.

The selection rule of Eq. (23.4-1b) forbids transitions that change the value of S. Since our selections rules are approximate, forbidden transitions between triplet ($S = 1$) states and singlet ($S = 0$) states do occur, but with low probabilities compared with allowed transitions.

EXAMPLE 23.9

The lowest-lying excited singlet electronic energy level of the CO molecule lies 8.0278 eV above the ground state. Find the wavelength of the light absorbed in the transition to this level from the ground state, neglecting changes in rotational and vibrational energy.

Solution

$$\lambda = \frac{hc}{\Delta E} = \frac{(6.6261 \times 10^{-34}\ \text{J s})(2.9979 \times 10^{8}\ \text{m s}^{-1})}{(8.0278\ \text{eV})(1.6022 \times 10^{-19}\ \text{J eV}^{-1})}$$

$$= 1.544 \times 10^{-7}\ \text{m} = 154.4\ \text{nm}$$

Exercise 23.7

Find the wavelength of the light absorbed in the transition of the previous example if J changes from 0 to 1 and v changes from 0 to 2.

Each electronic transition produces a number of bands, with one band for each vibrational transition and with the lines of each band corresponding to different rotational transitions. Measurement and interpretation of such an electronic band spectrum can yield not only the energy differences between electronic levels but also between vibrational and rotational levels. Figure 23.11 depicts an electronic transition for a typical diatomic molecule. The two curves are the Born–Oppenheimer electronic energies of two different electronic states. The vibrational energy levels are superimposed on the graph in the appropriate positions, and a graph of the square of each vibrational wave function (probability density for internuclear distance) is drawn on the line segment representing its energy level. The vertical scales of these wave function graphs are separate from the energy scale. The rotational levels are too closely spaced to be shown.

We apply the *Franck–Condon principle*, which states that the nuclei do not move appreciably during an electronic transition. This principle is closely related to the Born–Oppenheimer approximation. In Figure 23.11 a line segment is drawn to represent a

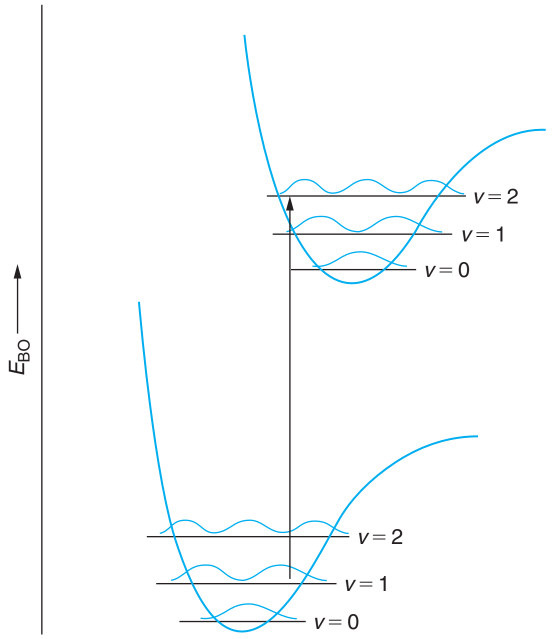

Figure 23.11 An Electronic Transition According to the Franck–Condon Principle. In the case of this figure, a transition from the $v = 1$ state of the lower electronic state most likely will lead to the $v = 2$ state of the upper electronic state.

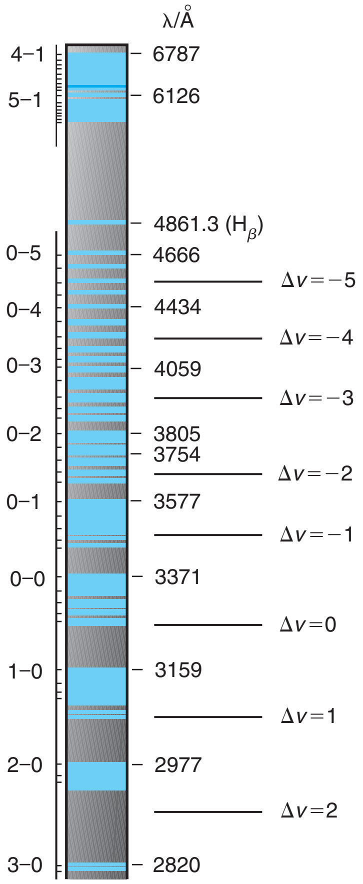

Figure 23.12 The Electronic Band Spectrum of Diatomic Nitrogen.

typical electronic transition. The line segment is vertical, corresponding to the Franck–Condon principle. One factor in the integrand of the transition dipole moment is the product of the vibrational wave functions in the initial and final states. Integration over the vibrational coordinate gives an overlap integral for the two vibrational states that is called the *Franck–Condon factor*. The value of the Franck–Condon factor will be small unless there is a range of internuclear distance over which both vibrational wave functions are appreciably different from zero. For a highly probable transition the vertical line segment in Figure 23.11 must connect one of the regions of relatively large value of one vibrational wave function to a region of relatively large value of the other vibrational wave function. Since the equilibrium internuclear distance of the upper electronic state in Figure 23.11 is somewhat larger than that of the lower state, the most probable transitions will take place from the ground vibrational state of the lower electronic state to excited vibrational states of the upper electronic state. Figure 23.12 shows the electronic band spectrum of nitrogen, which exhibits bands corresponding to various vibrational transitions occurring with the electronic transition and sets of lines within each band corresponding to different initial and final rotational states.

If the electronic wave functions are represented by orbital approximations, an electronic transition corresponding to the transition of a single electron from one orbital to another can be characterized by specifying the initial orbital and the final orbital. For example, if an electron makes a transition from a pi bonding orbital to a pi antibonding orbital, the transition is called a $\pi \rightarrow \pi^*$ (pi to pi-star) transition. If an electron goes from a nonbonding orbital to a pi antibonding orbital, the transition is said to be an $n \rightarrow \pi^*$ (n to pi-star) transition.

PROBLEMS

Section 23.4: Electronic Spectra of Diatomic Molecules

23.33 $H^{35}Cl$ has an important excited electronic state that lies above the ground state by 77575 cm^{-1}. Describe the bands in the ultraviolet spectrum arising from the transition from the ground state to this excited electronic state, including only the values 0 and 1 for the vibrational quantum numbers and $J = 0$, 1, and 2 for the rotational quantum numbers. Give numerical values for the band origin (corresponding to the forbidden transition $J = 0$ to $J = 0$) and the splittings between lines. The selection rules allow Δv to have any value, but ΔJ follows the same selection rules as for the microwave and infrared spectra. Assume the harmonic oscillator–rigid rotor energy levels. For the excited state[14]

$$\tilde{\nu}_e = 2684.0\ \text{cm}^{-1} \text{ and } \tilde{B}_e = 9.33\ \text{cm}^{-1}$$

23.34 Look up the necessary data and repeat the calculation of Problem 23.33 for HBr. The data can be found in the book by Huber and Herzberg.[15]

23.5 Spectra of Polyatomic Molecules

The spectra of polyatomic molecules are more complicated than those of atoms or diatomic molecules. As with diatomic molecules, rotational transitions can occur without vibrational or electronic transitions, vibrational transitions can occur without electronic transitions but are generally accompanied by rotational transitions, and electronic transitions are accompanied by both vibrational and rotational transitions.

Microwave Spectra of Polyatomic Molecules

Transitions between the rotational states of a polyatomic molecules can produce a microwave spectrum. We will not discuss the details of the microwave spectra of polyatomic molecules, but make some elementary comments.[16] As with diatomic molecules, we apply the rigid-rotor approximation, assuming that a rotating polyatomic molecule is locked in its equilibrium conformation. Any molecule in its equilibrium conformation must belong to one of four classes: linear molecules, spherical top molecules, symmetric top molecules, and asymmetric top molecules.

As with diatomic molecules, the principal selection rule is that a permanent dipole moment is required for a molecule to produce a microwave spectrum. Linear polyatomic molecules have rotational wave functions exactly like those of diatomic molecules, so their rotational selection rules and spectra are the same as those of diatomic molecules. A symmetric linear molecule such as acetylene (ethyne) has no permanent dipole moment, and does not have a microwave spectrum. The fact that N_2O has a microwave spectrum establishes the fact that it is NNO, not NON. Spherical top molecules such as CCl_4 and SF_6 are so symmetrical that they cannot have a nonzero permanent dipole moment, and they have no microwave spectrum. A symmetric top molecule with a permanent dipole moment will have a microwave spectrum. A microwave spectrum is always observed for an asymmetric top molecule, because it has so little symmetry that it must have a nonzero permanent dipole moment.

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[14] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. IV, Constants of Diatomic Molecules*, Van Nostrand Reinhold, New York, 1979, p. 284ff.

[15] K. P. Huber and G. Herzberg, *op. cit.*, p. 280ff (note 14).

[16] J. C. Davis, *op. cit.*, p. 322ff (note 2).

Vibrational Spectra of Polyatomic Molecules

In the harmonic oscillator approximation the vibration of polyatomic molecules is that of normal modes, each acting like an independent harmonic oscillator. We number the normal modes with an index i, ranging from 1 to $3n-5$ for linear molecules and ranging from 1 to $3n-6$ for nonlinear molecules. The selection rules for vibrational transitions are:

$$\Delta v = 0 \text{ or } \pm 1 \text{ for one normal mode, } \Delta v = 0 \text{ for all other normal modes} \quad (23.5\text{-}1a)$$

The classical motion of the normal mode must modulate the molecule's dipole moment (23.5-1b)

The case in which all Δv's vanish corresponds to a microwave spectrum. According to Eq. (23.5-1a), $\Delta v = \pm 1$ for only one normal mode at a time. Transitions obeying this selection rule produce *fundamental bands*. There is a fundamental band in the infrared region for each normal mode that modulates the molecule's dipole moment. The vibrational selection rules are less well obeyed than the rotational selection rules. There are *overtone bands* in which $\Delta v = 2$ (and sometimes 3), and *combination bands*, in which two (or more) normal modes change their quantum numbers at once. These forbidden bands are usually less intense than the fundamental bands.

The selection rule of Eq. (23.5-1b) means that the classically pictured motion must cause the dipole moment to oscillate in value. It is generally a well-obeyed rule. If a polyatomic molecule possesses a permanent dipole moment, all of its normal modes modulate the dipole and give rise to vibrational bands. For example, in nonlinear triatomic molecules such as H_2O or SO_2, all three of the normal modes shown in Figure 22.6 will produce fundamental bands.

EXAMPLE 23.10

The infrared spectrum of hydrogen sulfide, H_2S, shows three strong bands at 1290 cm^{-1}, 2610.8 cm^{-1}, and 2684 cm^{-1}. There are weaker bands at 2422 cm^{-1}, 3789 cm^{-1}, and 5154 cm^{-1}. Interpret the spectrum.

Solution

The three strong bands are fundamentals. The lowest frequency generally belongs to the bend, so that 1290 cm^{-1} belongs to the bend, denoted by ν_2.The symmetric stretch is generally intermediate in frequency, so that the 2610.8 cm^{-1} frequency is that of the symmetric stretch, denoted by ν_1. The 2684 cm^{-1} frequency belongs to the asymmetric stretch, ν_3. It is customary to number the modes of a triatomic molecule in this way. The weak bands are identified by trial and error, seeing whether their frequencies approximate a multiple of a fundamental frequency or a sum of two fundamental frequencies. (The addition is never exact.) The 2422 cm^{-1} frequency is roughly twice that of the bend, so it is the first overtone of the bend. The 3789 cm^{-1} frequency is roughly the sum of 1290 cm^{-1} and 2684 cm^{-1}, and is a combination band of the bend and the asymmetric stretch. The 5154 cm^{-1} frequency is roughly twice as large as ν_1 and is also roughly equal to $\nu_1 + \nu_3$. It has been assigned both ways but is more likely to be the combination band, by analogy with the H_2O spectrum.[17]

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[17] G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. II, Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand Reinhold, New York, 1945, p. 283.

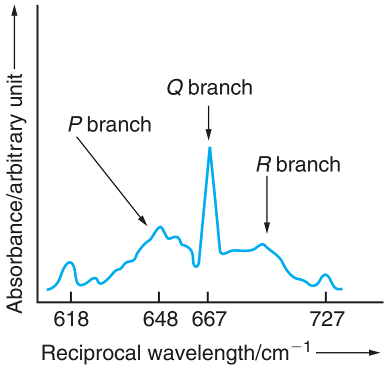

Figure 23.13 The Perpendicular Band of Carbon Dioxide. From G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. II, Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand Reinhold, New York, 1945, p. 273.

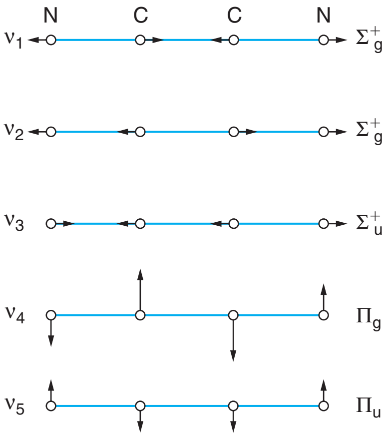

Figure 23.14 The Vibrational Normal Modes of Cyanogen, C_2N_2. The arrows show the directions of motion of the nuclei during half of the period of vibration, and the lengths are proportional to the amplitudes of the nuclear oscillations. From G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. II, Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand Reinhold Co., New York, 1945, p. 181.

In molecules without a permanent dipole, some of the normal modes can produce a fluctuating dipole that oscillates about zero magnitude, and thus produce infrared absorption. For example, the CO_2 molecule is linear and has no permanent dipole moment, although each C=O bond is polar. The normal modes of CO_2 were shown in Figure 22.6. The two bending modes, which have the same frequency, produce temporary dipoles that are perpendicular to the molecule axis and fluctuate about zero magnitude. They produce a vibrational band that is called a *perpendicular band*. The asymmetric stretch produces an oscillating dipole parallel to the molecule axis, because it stretches one bond as it compresses the other. The spectral band that it produces is called a *parallel band*. The symmetric stretch increases and then decreases both bond dipoles simultaneously, not modulating the dipole moment and not giving rise to a spectral line. The infrared spectrum of carbon dioxide contains only two fundamental bands, the parallel band at 1340 cm^{-1} and the perpendicular band at 667 cm^{-1}.

The perpendicular band of a linear molecule like carbon dioxide exhibits a Q branch corresponding to $\Delta J = 0$ in addition to P and R branches. The two bending modes together can produce a motion in which the center atom moves around in a circle perpendicular to the axis of the molecule. This motion is similar to a rotation of a bent molecule, which turns out to permit $\Delta J = 0$ as well as $\Delta J = \pm 1$.[18] Figure 23.13 shows the carbon dioxide perpendicular band at 667 cm^{-1}, containing P, Q, and R branches. The line widths are such that the lines are not completely resolved from each other, even with a high-resolution instrument.

The situation with nonlinear triatomic molecules is similar. Vibrational motions in which the dipole oscillates perpendicular to a single symmetry axis produce a band with a Q branch as well as P and R branches. For example, the asymmetric stretch in a nonlinear triatomic molecule such as H_2O or H_2S produces a band with a Q branch.

In order for a given normal mode of a polyatomic molecule to give rise to a vibrational band (be "infrared active"), the transition dipole moment integral for the two vibrational wave functions of the normal modes must be nonzero. This integral can be studied by group theory.[19] However, it is often possible by inspection of the normal modes to identify those that modulate the dipole moment of the molecule.

EXAMPLE 23.11

The normal modes of cyanogen, C_2N_2, are shown in Figure 23.14. (The last two diagrams represent two modes each, of equal frequency.) Determine which modes are infrared active.

Solution

The molecule is symmetrical, and has a zero dipole moment in its equilibrium configuration. The motions of modes 1 and 2 are symmetrical about the center of the molecule so that any changes in the bond dipole moments cancel. These modes are not infrared active. Mode 3 corresponds to one end of the molecule moving in as the other end moves out. It produces an oscillating dipole and is infrared active. Mode 4 corresponds to rotation of the polar C–N bonds such that they remain parallel while the nonpolar C–C bond rotates. All changes in the dipole moment cancel and the mode is not infrared active. Mode 5 corresponds to the relatively negative nitrogen atoms moving in one direction while the relatively positive carbon atoms move in the other direction, producing an oscillating dipole moment. It is infrared active.

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[18] I. N. Levine, *op. cit.*, p. 255ff (note 7).

[19] P. W. Atkins, *Molecular Quantum Mechanics*, 2nd ed., Oxford University Press, Oxford, 1983, p. 303ff; N. C. Craig and N. N. Lacuesta, *J. Chem. Educ.*, **81**, 1199 (2004).

Exercise 23.8

One of the normal modes of the benzene molecule is the "breathing mode," in which the entire molecule alternately expands and contracts. Will this mode be infrared active?

Electronic Spectra of Polyatomic Molecules

As with diatomic molecules, vibrational and rotational transitions in polyatomic molecules take place along with electronic transitions. The Franck–Condon principle applies, so that the final state will usually be an excited vibrational state as well as an excited electronic state. Since there are several normal modes in any polyatomic molecule the simultaneous electronic, vibrational, and rotational transitions can give very complicated spectra. The most important selection rule is the same for all molecules and atoms: The total spin quantum number is the same for the final as for the initial state:

$$\Delta S = 0 \tag{23.5-2}$$

The selection rules for the space part of the electronic wave function can be derived using group theory to investigate the effects of wave function symmetry.[20] We state only the most important rule:

The symmetry of the electronic wave function must change

For example, a transition from a u state to a g state is ordinarily allowed (and vice versa), whereas a transition from a g state to another g state or from a u state to another u state is not allowed. The other selection rules are more complicated, and we will not discuss them.

The molecular electronic selection rules are not exact because they are derived with approximate wave functions. "Forbidden" transitions are often observed but usually have smaller probabilities. For example, a transition from an excited singlet state to a singlet ground state with emission of a photon is allowed and will generally occur with a mean lifetime of the excited state of a microsecond to a millisecond. Such a transition is called *fluorescence*. A transition from an excited triplet state to a singlet ground state with emission of a photon is forbidden, and if it occurs it will have a smaller intensity and a longer mean lifetime of the excited state (sometimes as long as 10 seconds). Such a transition is called *phosphorescence*.

If orbital wave functions are used for a polyatomic molecule the electronic transitions can be classified by specifying the initial and final orbitals. If an absorption corresponds to a transition from a nonbonding orbital to an antibonding π orbital, we call it an n to π^* ($n \rightarrow \pi^*$) transition, and similarly for a π to π^* ($\pi \rightarrow \pi^*$) transition. In many cases a whole class of compounds will exhibit similar spectral lines that can be attributed to a functional group or other group of atoms within a molecule. Such a group that exhibits a characteristic absorption is called a *chromophore*. For example, most organic compounds containing a carbonyl group have an absorption near 200 nm corresponding to a $\pi \rightarrow \pi^*$ transition and another absorption near 300 nm corresponding to an $n \rightarrow \pi^*$ transition.

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[20] B. S. Tsukerblat, *Group Theory in Chemistry and Spectroscopy*, Academic Press, San Diego, 1994, p. 223ff.

PROBLEMS

Section 23.5: Spectra of Polyatomic Molecules

23.35 The infrared spectrum of HCN shows strong bands at 712.1 cm^{-1} and at 3312.0 cm^{-1}. There is a strong Raman band at 2089.0 cm^{-1}. There are weaker infrared bands at 1412.0 cm^{-1}, at 2116.7 cm^{-1}, at 2800.3 cm^{-1}, at 4004.5 cm^{-1}, at 5394 cm^{-1}, and at 6521.7 cm^{-1}. Identify these bands as fundamental, overtone, or combination bands, and give the shape of the molecule.

23.36 The N_2O molecule has three strong bands in its IR spectrum, at 588.8 cm^{-1}, at 1285.0 cm^{-1}, and at 2223.5 cm^{-1}. The band at 588.8 cm^{-1} has a Q branch. All three bands are fundamentals, and the molecule has been shown to be linear. Explain why CO_2, which is also linear, has only two fundamental IR bands whereas N_2O has three.

23.37 Using the frequencies in Problem 23.36, tell where to look for overtone and combination bands in the spectrum of N_2O.

23.38 The H_2S molecule has strong infrared bands at 1290 cm^{-1}, 2610.8 cm^{-1}, and 2684 cm^{-1}. There are weaker bands at 2422 cm^{-1}, 3789 cm^{-1}, and 5154 cm^{-1}. Assign these bands as fundamentals, overtones, or combination bands, and specify which normal mode corresponds to each fundamental.

23.39 The NO_2 molecule has strong infrared bands at 648 cm^{-1}, 1320 cm^{-1}, and 1621 cm^{-1}. There are weaker bands at 1373 cm^{-1}, 2220 cm^{-1}, and 2910 cm^{-1}. Assign these bands as fundamentals, overtones, or combination bands, and specify which normal mode corresponds to each fundamental.

23.40 **a.** Predict the shape of the CS_2 molecule.

b. Draw sketches depicting the vibrational modes of this molecule. Tell which will be seen in the Raman spectrum and which will be seen in the infrared spectrum.

c. Describe the microwave and rotational Raman spectra of this substance.

23.6 Fluorescence, Phosphorescence, and Photochemistry

In this section we discuss various processes that involve emission or absorption of photons. The material in this section is somewhat separate from spectroscopy, and the entire section can be skipped without loss of continuity.

Fluorescence and Phosphorescence

We discuss an example substance, benzophenone ($Ph_2C{=}O$, where Ph stands for the phenyl group, C_6H_5). Figure 23.15 shows schematically some low-lying electronic energy levels of benzophenone. The excited levels that are shown correspond to excitation of electrons in the carbonyl group. An excited level that is reached from the ground level by an $n \rightarrow \pi^*$ transition is labeled (n, π^*) and an excited level that is reached by a $\pi \rightarrow \pi^*$ transition is labeled (π, π^*).

There are two levels labeled (n, π^*), a singlet level ($S = 0$) and a triplet level ($S = 1$). There are two levels labeled (π, π^*), also a singlet and a triplet. The ground level is a singlet level. The singlet levels are labeled as S_0, S_1, S_2, and so on, in order of increasing energy. We reserve the subscript 0 for the ground level, so the triplet levels are labeled T_1, T_2, and so on. The selection rules allow absorption of a photon

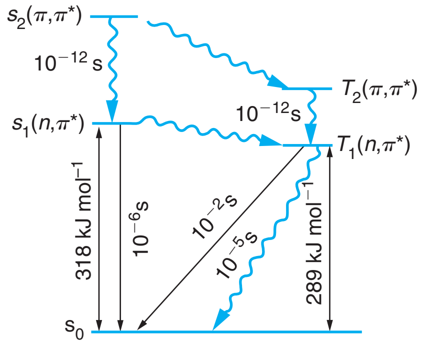


Figure 23.15 Some Energy Levels of the Benzophenone Molecule. The wavy arrows represent radiationless transitions, and the straight arrows represent emissions of photons. The times shown are relaxation times for the transitions. Data from D. L. Pavia, G. M. Lampman, and G. S. Kriz, Jr., *Introduction to Organic Laboratory Techniques*, 2nd ed., Saunders College Publishing, Philadelphia, 1982, p. 364.

to produce transitions only to excited singlet levels from the ground level. Transitions from the ground level to the two excited singlet levels give rise to two absorptions, one near 330 nm ($n \to \pi^*$) and one near 260 nm ($\pi \to \pi^*$).

If a molecule absorbs a photon to make a transition to an excited singlet level, the molecule can make the reverse transition and emit a photon of the same wavelength as the absorbed photon, but this is not the only thing that can happen. Because of the Franck–Condon principle, the molecule will probably be in an excited vibrational state after the upward transition so that the molecule can make a transition to a lower-energy vibrational level, losing some vibrational energy without changing the electronic state. This energy can be emitted as an infrared photon, or a *radiationless transition* can occur, in which case the vibrational energy lost by the molecule is transferred to other vibrational modes in the molecule or to rotation or translation of the molecule or to other molecules.

Once the molecule is in a lower vibrational level of the excited singlet level, it can emit a photon and return to the ground electronic level. Such a radiative transition to the ground level from an excited level with the same value of S is called *fluorescence*. Since vibrational energy was lost, the emitted light will have a longer wavelength than the absorbed light. Many common objects, including human teeth, certain minerals, and blacklight posters, can fluoresce, emitting visible light after absorbing ultraviolet light.

Another possibility is that the molecule might make a radiationless transition to the ground level or to a lower-energy electronic level with the same value of S. Such a radiationless transition is called an *internal conversion*. In our example of a carbonyl compound, an internal conversion could occur from the singlet (π, π^*) level to the singlet (n, π^*) level, followed by fluorescence to the ground level. Still another possibility is a radiationless transition to an electronic level with a different value of S, called an *intersystem crossing*. To each of the excited singlet levels in Figure 23.15, there corresponds a triplet level with the same electron configuration that can be reached by an intersystem crossing. After an intersystem crossing, the molecule might make a radiative transition to the ground state. This process is called *phosphorescence*. Since this process is forbidden by our approximate selection rules, a typical mean time for phosphorescence is longer than for fluorescence (typically 1 ms to 10 s). In Figure 23.15, the approximate values of mean transition times are indicated near each arrow.

Photochemistry

A molecule in an excited electronic state can possibly undergo a chemical reaction that is inaccessible in the ground level. If the excited state was reached directly or indirectly by absorption of radiation, the reaction is a *photochemical reaction*. Most photochemical reactions are governed by the *Stark–Einstein law of photochemistry*, which states that absorption of one photon causes the reaction of one molecule. However, the number of molecules that react is not necessarily equal to the number of photons absorbed. Some of the excited molecules might undergo internal conversion, intersystem crossing, fluorescence, or phosphorescence processes leading to unreactive states and therefore not react chemically. A *chain reaction* might occur in which the reaction of one molecule can lead to the reaction of other molecules without absorption of additional radiation.

The *quantum yield* of a photochemical reaction, Φ, is defined by

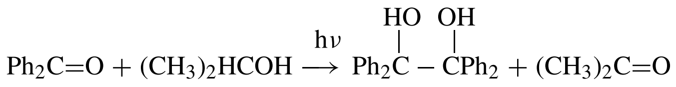
$$\Phi = \frac{\text{number of molecules reacted}}{\text{number of photons absorbed}} \tag{23.6-1}$$

Equation (23.6-1) can also be stated in terms of moles of reactant and moles of photons. One mole of photons is called an *einstein*, so that

$$\Phi = \frac{\text{amount reacted in moles}}{\text{amount of photons absorbed in einsteins}} \tag{23.6-2}$$

In a chain reaction, Φ can exceed unity, but in a nonchain reaction, $\Phi \leq 1$.

Upon radiation with ultraviolet light of 300 nm to 350 nm wavelength, benzophenone undergoes a reaction with 2-propanol to form benzpinacol and acetone.[21]



$$\mathrm{Ph_2C{=}O + (CH_3)_2HCOH \xrightarrow{h\nu} Ph_2\overset{\displaystyle HO}{\overset{|}{C}} - \overset{\displaystyle OH}{\overset{|}{C}}Ph_2 + (CH_3)_2C{=}O} \tag{23.6-3}$$

Because radiation of 300 nm wavelength has photons of insufficient energy to reach the $S_2(\pi, \pi^*)$ level, and because the radiative transition to a triplet level is forbidden, the first step in the mechanism for this reaction must be absorption of radiation to excite the benzophenone to the $S_1(n, \pi^*)$ level:

$$\mathrm{Ph_2C{=}O} + h\nu \longrightarrow \mathrm{Ph_2C}\overset{\bullet}{=}\dot{\mathrm{O}}\,(\mathrm{S_1}) \tag{23.6-4}$$

where the electron remaining in the nonbonding orbital is represented by a dot over the oxygen atom and the electron that has made the transition to the antibonding π orbital is represented by a dot over the double bond (which is now a bond with order 3/2).

The next step in the mechanism is an intersystem crossing to the T_1 level:

$$\mathrm{Ph_2C}\overset{\bullet}{=}\dot{\mathrm{O}}(\mathrm{S_1}) \xrightarrow{\text{isc}} \mathrm{Ph_2C}\overset{\bullet}{=}\dot{\mathrm{O}}(\mathrm{T_1}) \tag{23.6-5}$$

This step is followed by the abstraction of a hydrogen atom (complete with one electron) from a 2-propanol molecule by a benzophenone molecule in the T_1 level, forming a

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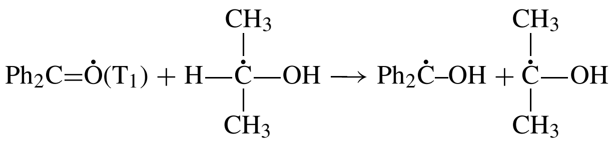
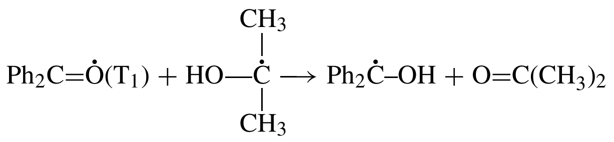
[21] D. L. Pavia, G. M. Lampman, and G. S. Kriz, Jr., *Introduction to Organic Laboratory Techniques*, 2nd ed., Saunders, Philadelphia, 1982, p. 362ff.

free radical:



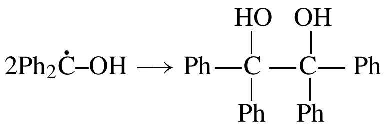
$$\mathrm{Ph_2C{=}\dot{O}(T_1) + H{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\dot{C}}}{-}OH \longrightarrow Ph_2\dot{C}{-}OH + \overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\dot{C}}}{-}OH} \tag{23.6-6}$$

The next step is the abstraction of a second hydrogen atom from the 2-propanol molecule by another excited benzophenone molecule, forming another radical and an acetone molecule (one of the final products):



$$\mathrm{Ph_2C{=}\dot{O}(T_1) + HO{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\dot{C}}} \longrightarrow Ph_2\dot{C}{-}OH + O{=}C(CH_3)_2} \tag{23.6-7}$$

The final step is combination of two radicals:



$$\mathrm{2Ph_2\dot{C}{-}OH \longrightarrow Ph{-}\overset{\displaystyle HO}{\underset{\displaystyle Ph}{C}}{-}\overset{\displaystyle OH}{\underset{\displaystyle Ph}{C}}{-}Ph} \tag{23.6-8}$$

The photochemical reaction can be carried out by use of an ultraviolet lamp, but sunlight contains enough ultraviolet light to produce a significant amount of product in a few days. The reaction will proceed in a borosilicate glass flask. Borosilicate glass blocks almost all radiation of wavelength shorter than 300 nm, so the radiation that causes the reaction to proceed must have wavelengths longer than 300 nm.

Exercise 23.9

Calculate the energy per photon and per einstein for radiation of wavelength equal to 300 nm.

If naphthalene is placed in the reaction mixture, no reaction takes place. We say that the reaction is *quenched*. The explanation is that a rapid intermolecular energy transfer from an excited benzophenone molecule to a naphthalene molecule returns the benzophenone molecule to its ground level, before it can react chemically. Naphthalene has a singlet ground level a singlet (π, π^*) level 4.1 eV above the ground level, and a triplet (π, π^*) level 2.7 eV above the ground level. A well-obeyed selection rule requires that in an intermolecular energy transfer the sum of the two electron spin quantum numbers remains constant. This means that if the benzophenone molecule makes a transition from a triplet excited level to a singlet ground level, the naphthalene molecule must make a transition from its singlet ground level to a triplet excited level. If the benzophenone molecule makes a transition from a singlet excited level the naphthalene molecule must make a transition to a singlet excited level.

Since the (π, π^*) singlet excited level of naphthalene lies higher than the (n, π^*) singlet excited level of benzophenone by 0.8 eV, this level cannot be reached by energy transfer from a benzophenone molecule in its (n, π^*) level. However, the (π, π^*) triplet excited level of the naphthalene molecule lies lower than the (n, π^*) triplet level of benzophenone, so that this level can be reached by energy transfer from a benzophenone molecule. The fact that the naphthalene quenches the reaction shows that the triplet (n, π^*) level of benzophenone must be the reactive level.

Vision

Photochemical reactions are involved in vision in vertebrates.[22] There are two kinds of light-sensitive cells in the retina, called *rods* and *cones*. The rods provide for vision in dim light but do not provide color vision. Color vision is provided by three varieties of cone cells that are sensitive to red, green, and blue light respectively, and these require greater illumination than do the rod cells.

In the rod cells there is a protein called *rhodopsin*, which consists of a protein called *opsin* bonded to a polyene called *retinal*. Retinal is related to retinol, which is known as vitamin A and which is depicted in Figure 23.16a. Retinal occurs in the eye as the all-*trans* isomer and as the 11-*cis* isomer. The structural formulas of these isomers are shown in Figures 23.16b and 23.16c. The 11-*cis* isomer attaches to the free NH_2 group of a lysine residue in opsin, forming a Schiff base, as shown in Figure 23.16d. The all-*trans* isomer does not bond to the opsin. Rhodopsin has a broad absorption ranging from 400 nm to 600 nm, with maximum absorption around 500 nm. The corresponding absorption band of 11-*cis*-retinal is centered at 380 nm, in the ultraviolet. Each variety of cone cell has one of three proteins that are similar to rhodopsin, but which absorbs light only in either the red, green, or blue wavelength region.

Exercise 23.10

a. Using the structural formulas in Figure 23.16 and the free-electron molecular orbital (particle-in-a-box) model for a conjugated polyene, explain why the absorption maximum of the Schiff base form of rhodopsin is at longer wavelength than that of 11-*cis*-retinal.

b. Using the free-electron model, calculate the wavelength of maximum absorbance for 11-*cis*-retinal and for rhodopsin, taking an average bond length of 1.39×10^{-10} m and adding one bond length to each end of the conjugated system of bonds. Remember to count the pi electrons and assign two to each space orbital according to the Aufbau principle.

The accepted mechanism of the photochemical process in rod cells is as follows. First, the rhodopsin absorbs a photon, raising it to an excited state in which a 90° rotation has occurred about the double bond between carbons 11 and 12 of the retinal, making the molecule intermediate in shape between the all-*trans* isomer and the 11-*cis* isomer. Some of these molecules (about two-thirds) convert into the all-*trans* form, called bathorhodopsin. The retinal is still attached to the opsin, and this protein now undergoes a sequence of transformations, producing a series of identifiable proteins called lumirhodopsin, metarhodopsin I, and metarhodopsin II. A signal is apparently sent into a fiber of the optic nerve when metarhodopsin II undergoes a conformational change. Over a period of several minutes, the metarhodopsin II dissociates into opsin and free all-*trans*-retinal, which can be converted to the 11-*cis* form and attached again to opsin. The length of time required for this process is related to the time required for the eye to become dark adapted, but is much too slow to be involved in the actual process of vision.

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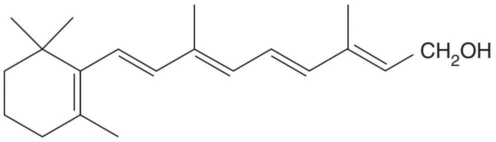
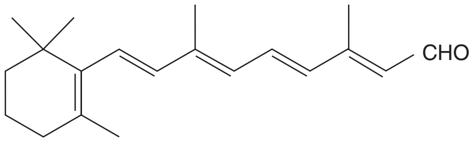
[22] G. L. Zubay, *Biochemistry*, Addison-Wesley, Reading, MA, 1983, p. 409ff.



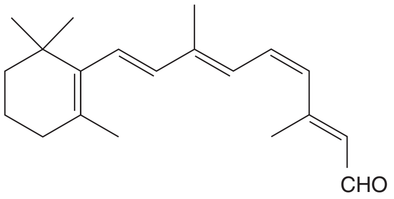
all-*trans*-Retinol (vitamin A_1)

(a)



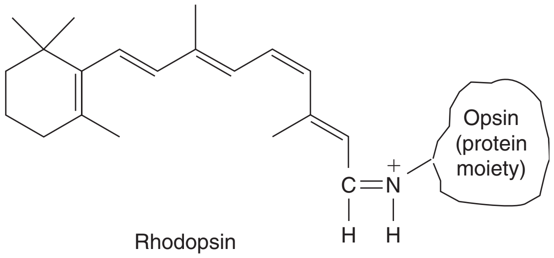
all-*trans*-Retinal

(b)



11-*cis*-Retinal

(c)



Rhodopsin

(d)

Figure 23.16 The Structures of Retinal and Rhodopsin. (a) All-*trans*-retinol (vitamin A) (b) All-*trans*-retinal. (c) 11-*cis*-retinal. (d) Rhodopsin.

PROBLEMS

Section 23.6: Fluorescence, Phosphorescence, and Photochemistry

23.41 Find the frequency and wavelength of light given off by the benzophenone molecule in (a) fluorescence from the S_1 state, and in (b), phosphorescence from the T_1 state.

23.42 In a photochemical reaction, 0.00100 watt of radiant energy of wavelength 254 nm is incident on the reaction vessel, and 61.2% of this energy is absorbed.
If 2.45 mole of the absorbing reactant reacts to form products in 30.0 seconds, find the quantum yield.

23.43 Which of the following substances could quench the photochemical reaction of benzophenone discussed in Section 23.6?

Substance	Energy of First Triplet State/eV
Biphenyl	2.9
Toluene	3.6
Benzene	3.7
9,10-Diphenylanthracene	1.8
trans-1,3-Pentadiene	2.6

23.7 Raman Spectroscopy

Raman spectroscopy was invented by Chandrasekhara Venkata Raman, 1888–1970, an Indian physicist who received the 1930 Nobel Prize in physics for this work.

In Raman spectroscopy, radiation is inelastically scattered by the sample substance, either giving energy to or accepting energy from the substance. You can think of the process as consisting of absorption of photons of one frequency accompanied by emission of photons of a different frequency, with the difference in photon energy being absorbed or given off by the molecule. Figure 23.17 shows a schematic diagram of a Raman spectrometer. The scattered radiation is observed at right angles to the incident beam. It is generally much weaker than the incident beam, and lasers are now used to provide intense incident beams.

The difference in the photon energies of the incident and scattered radiation must equal the energy difference between two energy levels of the sample molecules. We denote the frequency of the incident radiation by ν and the frequency of the scattered radiation by ν'. If the radiation loses energy to the molecules,

$$h\nu - h\nu' = E_{\text{upper}} - E_{\text{lower}} \tag{23.7-1}$$

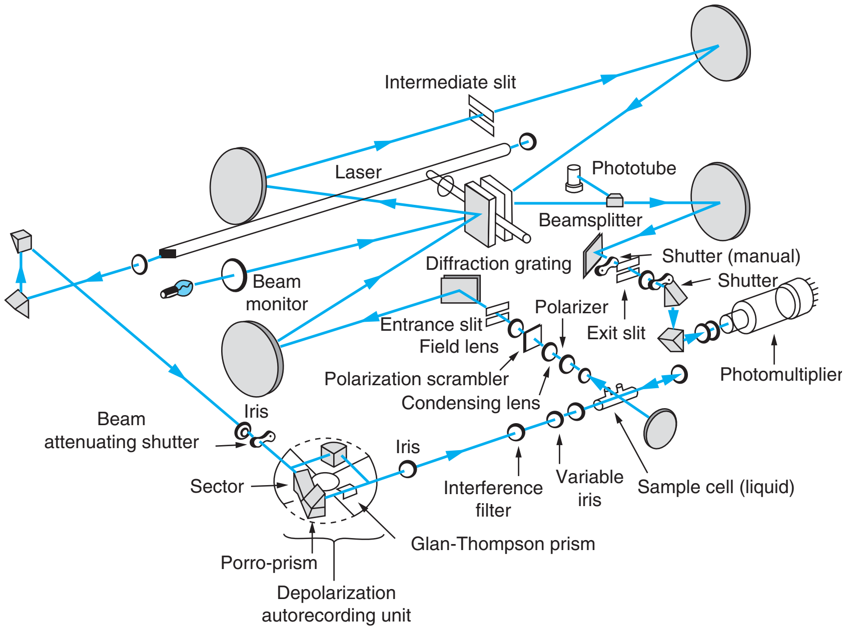


Figure 23.17 Schematic Diagram of a Laser Raman Spectrophotometer. In the diagram, there are two distinct beams: the incident beam, and the scattered beam at right angles to the incident beam. Courtesy of Jeol, Ltd.

and if the molecules lose energy to the radiation,

$$h\nu' - h\nu = E_{\text{upper}} - E_{\text{lower}} \tag{23.7-2}$$

The difference between the scattered and incident frequencies or reciprocal wavelengths is called the *Raman shift*. Spectral lines corresponding to transitions from a lower to a higher molecular energy as in Eq. (23.7-1) are called *Stokes lines*, and those corresponding to Eq. (23.7-2) are called *anti-Stokes lines*.

The selection rules for Raman transitions are different from those of absorption or emission, and this makes it possible to observe transitions that are forbidden in emission or absorption spectroscopy. The Raman selection rules for rotational and vibrational transitions are:

$$\Delta J = 0, \pm 2 \quad \text{(linear molecules)} \tag{23.7-3a}$$

$$\Delta J = 0, \pm 1, \pm 2 \quad \text{(nonlinear molecules)} \tag{23.7-3b}$$

$$\Delta v = 0, \pm 1 \tag{23.7-3c}$$

The nuclear motion must modulate the polarizability of the molecule. (23.7-3d)

The *polarizability* is a measure of the tendency of a molecule to acquire an electric dipole in the presence of an electric field (see Problem 19.44). For a molecule with the same properties in all directions (an isotropic molecule), the induced moment μ_{ind} is proportional to the electric field $\mathscr{E}$ and in the same direction as the electric field:

$$\mu_{\text{ind}} = \alpha\mathscr{E} \quad \text{(isotropic molecule)} \tag{23.7-4}$$

where α is the polarizability (a scalar quantity), and where $\mathscr{E}$ is the electric field (a vector). A symmetric top molecule such as methane or sulfur hexafluoride obeys Eq. (23.7-4). For an anisotropic molecule (with different properties in different directions) the x component of the induced moment is given by

$$\mu_{x,\text{ind}} = \alpha_{xx}\mathscr{E}_x + \alpha_{xy}\mathscr{E}_y + \alpha_{xz}\mathscr{E}_z \tag{23.7-5}$$

with similar equations for the y and z components. The polarizability is now a matrix with nine components (a *tensor*) with components that have two subscripts. Equation (23.7-5) and its analogues become the same as Eq. (23.7-4) if

$$\alpha_{xx} = \alpha_{yy} = \alpha_{zz} \tag{23.7-6}$$

and if the other components vanish.

Just as principal axes for rotation of a molecule could be found, principal axes for the polarizability of a molecule can be found such that the polarizability "cross-terms" with unequal indexes vanish. The components of the induced dipole are then given by

$$\mu_{x',\text{ind}} = \alpha_{x'x'}\mathscr{E}_{x'} \tag{23.7-7a}$$

$$\mu_{y',\text{ind}} = \alpha_{y'y'}\mathscr{E}_{y'} \tag{23.7-7b}$$

$$\mu_{z',\text{ind}} = \alpha_{z'z'}\mathscr{E}_{z'} \tag{23.7-7c}$$

where we label the principal axes by x', y', and z'. The principal axes will generally lie in the symmetry elements of the molecule.

The polarizability can be described by an *ellipsoid of polarizability*.[23] This ellipsoid is a surface such that the distance to the surface from the origin in any direction is proportional to $\alpha^{-1/2}$ in that direction. The ellipsoid of polarizability will generally possess all of the symmetry elements of the molecule. If a rotational or vibrational motion modulates the polarizability the value of the polarizability in some direction varies periodically as the motion occurs. This corresponds to changes in the shape or orientation of the ellipsoid of polarizability.

Rotational Raman Spectra

There are two contributions to the polarizability of a molecule: the distortion of the electronic wave function and the distortion of the nuclear framework. The major contribution is from the electrons, and can be considered to be the sum of contributions from the individual electrons. The contributions of the inner-shell electrons are nearly independent of orientation and these contributions can be ignored. The polarizability of electrons in a bond parallel to the bond direction is different from the polarizability perpendicular to that bond. As a diatomic molecule or linear polyatomic molecule rotates, the components of the polarizability in fixed directions are modulated (fluctuate periodically) as the ellipsoid of polarizability rotates. The rotation of a diatomic or linear polyatomic molecule will be *Raman active* (produce a Raman spectrum). In a nonlinear polyatomic molecule, the polarizabilities of the individual bonds add vectorially to make up the total polarizability. If the molecule is a symmetric top, the total polarizability is the same in all directions and the ellipsoid of polarizability is a sphere. A spherical top molecule has no rotational Raman spectrum. Symmetric tops and asymmetric tops have anisotropic polarizabilities and produce rotational Raman spectra.

EXAMPLE 23.12

Which of the following will have a rotational Raman spectrum?

a. $CHCl_3$
b. IF_3
c. CS_2

Solution

a. $CHCl_3$ is a symmetric top, and will have a rotational Raman spectrum.
b. IF_3 is predicted by the VSEPR theory to be T-shaped, and will have a rotational Raman spectrum.
c. CS_2 is linear, like CO_2, and will not have a rotational Raman spectrum.

Vibrational Raman Spectra

The stretching or compression of a bond changes the electronic wave function and therefore changes the polarizability. The vibration of a diatomic molecule is Raman active, whether the molecule is homonuclear or heteronuclear. A vibrational normal

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[23] N. B. Colthup, L. H. Daly, and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, 3rd ed., Academic Press, San Diego, 1990, p. 65ff.

mode in a polyatomic molecule will be Raman active if it produces a periodic change in the shape or the orientation of the ellipsoid of polarizability. The normal modes of carbon dioxide are shown in Figure 22.6. The asymmetric stretch, which is seen in the infrared, is not seen in the Raman spectrum. The stretching of one bond is accompanied by the compression of the other bond so that the effects cancel, and the ellipsoid of polarizability is not changed. The symmetric stretch alternately compresses and stretches the ellipsoid of polarizability since both bonds stretch and compress simultaneously. It is Raman active. The bending modes, which are seen in the infrared, are not seen in the Raman spectrum, because the bonds do not stretch appreciably as the bond angle bends and because the variations in the bond directions cancel.

There is a *rule of mutual exclusion*, which states: In a molecule with a center of symmetry, a normal mode that is seen in the infrared spectrum will not be seen in the Raman spectrum, and vice versa.[24] The normal modes of carbon dioxide illustrate this rule. In molecules with more than three atoms, it is sometimes possible to determine whether a normal mode will be Raman active or IR active by inspection of the normal mode motions. Group theory is often used to simplify the analysis.[25]

EXAMPLE 23.13

Identify the normal modes of cyanogen shown in Figure 23.14 that will give rise to Raman lines.

Solution

In modes 1 and 2, the C–C bond oscillates in length and the two C–N bonds oscillate in unison, so that the polarizability is modulated. Both of these modes will be Raman active. In mode 3, the C–C bond length does not oscillate, and the C–N bonds oscillate out of phase, so this mode is not seen. Mode 5 is similar to the bend in carbon dioxide and this mode will not be seen in the Raman spectrum. Mode 4 must be Raman active because there is a rocking motion of the molecule. The ellipsoid of polarizability follows this rocking motion. Note that these conclusions could all have been reached by use of the rule of mutual exclusion.

Exercise 23.11

Figure 23.18 shows sketches representing some of the vibrational normal modes of ethylene. The direction of motion of each atom is shown for one-half of the period. For motions perpendicular to the plane, a positive sign (+) indicates upward motion and a negative sign (−) indicates downward motion. Tell which modes are infrared active and which are Raman active. There is a center of symmetry, so the rule of mutual exclusion applies.

It is possible to deduce the same kinds of structural information from Raman spectra as from infrared and microwave spectra. From the selection rule for rotation, Eq. (23.7-3a), the Raman shift of the Stokes rotational lines of a diatomic molecule is given in the rigid-rotor approximation by

$$\widetilde{\nu} - \widetilde{\nu}' = (E_{J+2} - E_J)/hc = \widetilde{B}_\mathrm{e}(4J + 6) \qquad (23.7\text{-}8)$$

where terms in α and $\mathscr{D}$ have been neglected.

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[24] I. N. Levine, *op. cit.*, p. 268 (note 7).

[25] N. B. Colthup, L. H. Daly, and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, 3rd ed., Academic Press, San Diego, 1990, p. 109ff.

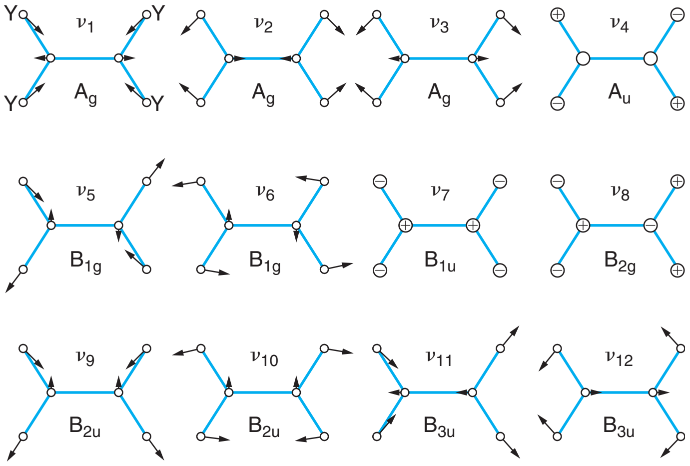

Figure 23.18 The Vibrational Normal Modes of Ethylene, C_2H_4. The arrows show the direction of motion of each nuclei in one-half of the period. The length of each arrow is proportional to the amplitude of motion of the nucleus. From G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. II, Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand Reinhold, New York, 1945, p. 107.

A linear polyatomic molecule has two equal moments of inertia, I_B and I_C. In the rigid rotor approximation, the energy levels are given by Eq. (22.4-7)

$$E_J = \frac{\hbar^2}{2I_B}J(J+1) \tag{23.7-9}$$

Equation (23.7-8) can be used for a linear polyatomic molecule if $\widetilde{B}_e$ is replaced by

$$\widetilde{B} = \frac{h}{8\pi^2 I_B c} \tag{23.7-10}$$

EXAMPLE 23.14

Figure 23.19 shows the rotational Raman spectrum of carbon dioxide. From the splitting between the lines, 3.09 cm^{-1}, calculate the equilibrium bond lengths.

Solution

Since the carbon nucleus at the center of mass and since the two bond lengths are equal to each other the two equal moments of inertia are

$$I_B = I_C = 2m_O r_e^2$$

where r_e is the bond length and m_O is the oxygen nuclear mass, 2.656×10^{-26} kg. The parameter $\widetilde{B}$ is given by

$$\widetilde{B} = \frac{h}{8\pi^2 I_B c} = \frac{h}{8\pi^2 2m_O r_e^2 c}$$

Since the selection rule requires that $\Delta J = \pm 2$, the Raman shift for the Stokes lines is given by

$$\Delta\widetilde{\nu} = \widetilde{\nu} - \widetilde{\nu}' = \widetilde{B}[(J+2)(J+3) - J(J+1)] = \widetilde{B}[J^2 + 5J + 6) - J^2 + J)]$$
$$= \widetilde{B}[4J + 6]$$

The ^{16}O nuclei are bosons ($I = 0$) and the electronic ground state is a sigma state, so only even values of J can occur. The first spectral line should occur at $6\widetilde{B}$, and the splitting between lines should equal $8\widetilde{B}$. The first full line that is visible in the figure is the second line, corresponding to the transition from $J = 2$ to $J = 4$. The splitting is found to be 3.09 cm^{-1} by measurement in the figure. Using the symbol $\Delta\widetilde{\nu}$ for the splitting, we obtain

$$r_e^2 = \frac{h}{2\pi^2 m_O c \Delta\widetilde{\nu}}$$
$$= \frac{6.6261 \times 10^{-34}\ \mathrm{J\,s}}{2\pi^2(2.656 \times 10^{-26}\ \mathrm{kg})(3.09\ \mathrm{cm^{-1}})(2.9979 \times 10^{10}\ \mathrm{cm\,s^{-1}})}$$
$$= 1.364 \times 10^{-20}\ \mathrm{m^2}$$
$$r_e = 1.17 \times 10^{-10}\ \mathrm{m} = 117\ \mathrm{pm} = 1.17\ \text{Å}$$

This result agrees fairly well with the accepted value, 116.15 pm.

The vibrational selection rule for a diatomic molecule is that $\Delta v = 0, \pm 1$ and the rotational selection rule is $\Delta J = 0, \pm 2$. A band in the vibrational Raman spectrum of a diatomic molecule has three branches corresponding to the different changes in the rotational quantum number. The Q branch corresponds to $\Delta J = 0$, the O branch

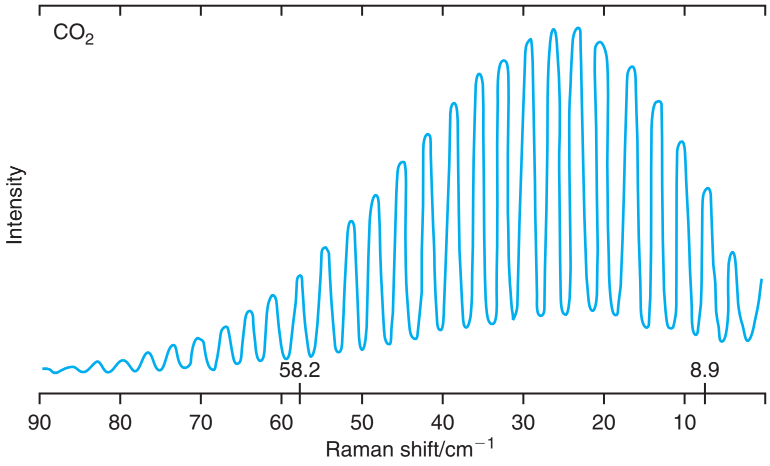

Figure 23.19 Rotational Raman Spectrum of Carbon Dioxide. The axis is the difference between the reciprocal wavelength of the incident and that of the scattered radiation. The peak at zero Raman shift is the scattered radiation with no change in energy of the molecules. From L. Claron Hoskins, *J. Chem. Educ.*, **54**, 642 (1977).

corresponds to $\Delta J = -2$, and the S branch corresponds to $\Delta J = +2$. These branches consist of sets of lines with the same spacings as the lines in the rotational Raman spectrum.

PROBLEMS

Section 23.7: Raman Spectroscopy

23.44 **a.** From data in Table A.22 of Appendix A, find the Raman shift for the band center of the Stokes vibrational fundamental band of diatomic oxygen. If the incident light has wavelength 253.7 nm, find the wavelength of this band center.

b. Find the splitting in cm^{-1} between the band center (the Q branch) and the first line of the S branch.

c. Find the splitting in cm^{-1} between adjacent lines in the S branch. How does this compare to the splittings between the lines of the O branch?

23.45 The rotational Raman spectrum of H_2 has lines at Raman shifts of 354 cm^{-1}, 586 cm^{-1}, 814 cm^{-1}, and 1034 cm^{-1}. At room temperature, the line of greatest intensity is at 586 cm^{-1}. Explain the relative intensities and calculate the internuclear distance for H_2.

23.46 From the frequency in Figure 22.6, find the Raman shift in reciprocal wavelength for the band center of the symmetric stretch of carbon dioxide. If the incident light has wavelength 253.7 nm, find the wavelength of this band center.

23.47 Which of the following substances will have a rotational Raman spectrum?

a. CCl_4

b. BF_3

c. CO_2

23.48 Which of the following substances will have a rotational Raman spectrum?

a. SF_6

b. PCl_5

c. NH_3

23.49 Which of the substances in Problem 23.25 will have a rotational Raman spectrum?

23.50 Using computer software such as CAChe or Spartan, find the normal modes of vibration of the following molecules, using both semiempirical and ab initio methods. Compare the calculated frequencies with the experimental frequencies.[26] Decide which modes will lead to an infrared band and which will lead to a Raman band.

a. Acetylene (ethyne) C_2H_2

b. CS_2

c. OF_2

23.8 Other Types of Spectroscopy

There are a number of types of spectroscopy in addition to those that we have discussed so far.

Photoelectron Spectroscopy

In this technique ultraviolet radiation is absorbed by a molecule, causing ejection of an electron:

$$M + \text{photon} \to M^{+} + e^{-} \tag{23.8-1}$$

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[26] G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. II, Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand Reinhold, New York, 1945.

where M represents a molecule of the sample substance. The kinetic energy of the ejected electron is measured, and the difference in energy between a photon of the incident radiation and the kinetic energy of the electron is taken to be the ionization energy of the ejected electron. Usually several different ionization energies are obtained. If the electronic wave function is approximated as an orbital wave function the ejected electron will come from a specific orbital. According to *Koopman's theorem* the ionization energy is equal to the magnitude of the orbital energy of the orbital from which the electron came.[27]

Figure 23.20 shows the photoelectron spectrum of N_2, using 58.4 nm ultraviolet radiation. The kinetic energy of the electrons increases from left to right so that the ionization energy increases from right to left. There are three sets of lines, each corresponding to ionization from a different orbital. The ground-level electron configuration of N_2 is

$$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)^2(\pi_u 2p)^4(\sigma_g 2p)^2$$

The rightmost set of lines arises from removal of an electron from the $\sigma_g 2p$ bonding orbital. The center set of lines arises from removal of an electron from a $\pi_u 2p$ bonding orbital, and the leftmost set of lines arises from removal of an electron from the $\sigma_u^* 2s$ antibonding orbital.

The lines within each set correspond to different vibrational states of the ion produced by the ionization. The absorption of a photon with removal of an electron is sufficiently rapid that the nuclei do not have time to move appreciably, as in the Franck–Condon principle. The ionization potential that is determined through photoelectron spectroscopy is referred to as the "vertical" ionization energy, as represented by a vertical line in a diagram such as that of Figure 23.11. In the nitrogen spectrum it appears that the ionization to the $v = 1$ vibrational state of the ion is the most probable process for the center set of lines, while in the other two sets the transition to the $v = 0$ vibrational state is the most probable transition.

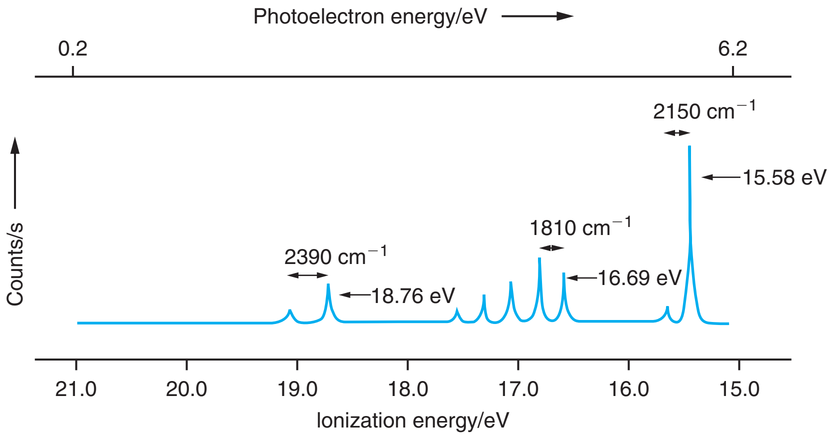

Figure 23.20 Photoelectron Spectrum of Nitrogen. From I. N. Levine, *Molecular Spectroscopy*, Wiley, New York, 1975, p. 316.

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[27] T. C. Koopman, *Physica*, **1**, 104 (1933).

EXAMPLE 23.15

The ground-state vibrational frequency for nitrogen is 2359 cm^{-1}. The spacing between the lines in the rightmost set of lines corresponds to 2150 cm^{-1}, and the line for the transition from $v = 0$ to $v = 0$ is at 15.58 eV. Find the ionization energy from the minimum of the ground-state potential curve to the minimum in the ion curve.

Solution

The ionization energy from the $v = 0$ vibrational state to the $v = 0$ vibrational state differs from the desired quantity by the difference of the zero-point vibrational energies, given by

$$\begin{aligned}\Delta E_{\text{zero-point}} &= \frac{h\nu_{\text{molecule}}}{2} - \frac{h\nu_{\text{ion}}}{2} = \frac{hc}{2}(\tilde{\nu}_{\text{molecule}} - \tilde{\nu}_{\text{ion}}) \\ &= \frac{(6.6261 \times 10^{-34}\ \text{J s})(2.9979 \times 10^{10}\ \text{cm s}^{-1})}{2}(209\ \text{cm}^{-1}) \\ &= 2.08 \times 10^{-21}\ \text{J} = 0.0130\ \text{eV} \\ \Delta E_{\text{e-e}} &= \Delta E_{0-0} + 0.013\ \text{eV} = 15.58\,\text{eV} + 0.013\,\text{eV} = 15.59\,\text{eV}\end{aligned}$$

Exercise 23.12

Explain why the spacing between the lines in the leftmost set in Figure 23.20 is greater than 2359 cm^{-1}, the vibrational spacing of the ground level, whereas the spacing between the lines in the other two sets is smaller than 2359 cm^{-1}.

Photoacoustic Spectroscopy

Photoacoustic spectroscopy was originated by Alexander Graham Bell, 1847–1922, the inventor of the telephone.

Photoacoustic spectroscopy is a type of absorption spectroscopy in which absorption of energy is detected by the generation of sound waves. A beam of monochromatic radiation is directed on the sample though a “chopper,” which is usually a rotating disk with several notches cut in the edge so that the beam is alternately passed and interrupted (chopped).

If the radiation is absorbed by the sample, it will heat the surface of the sample and the air next to it during the time that the beam is passed by the chopper. During the time that the beam is interrupted, the sample and the air will cool off. The air will thus alternately expand and contract with the frequency of the chopper, producing a sound wave that can be detected by a microphone. If the radiation is not absorbed, no sound wave is generated. The frequency of the chopper must be slow enough so that the air has time to cool off during the period of beam interruption, but fast enough to make a detectable sound wave. A chopper frequency of around 50 hertz is common. The intensity of the sound wave can be measured electronically as the wavelength of the light is varied, giving an absorption spectrum. The principal advantage of the method is that an opaque sample can be used.

Circular Dichroism and Optical Rotatory Dispersion

Circular dichroism and optical rotatory spectroscopy involve study of optically active substances. Plane-polarized light is described in Section 14.3 and in Appendix F as an electric field oscillating in one plane and a magnetic field oscillating in a plane perpendicular to the first plane. *Circularly polarized light* is equivalent to the sum of two plane-polarized rays of equal amplitude and wavelength that are polarized in perpendicular directions and out of phase by a fourth of a wavelength. Figure 23.21 shows the electric field. The sum of the two electric fields follows a helix at any one instant. If the wave shown in the figure propagates to the right of the figure, an observer facing the source of radiation sees an electric field that rotates clockwise. Such radiation is called *right-polarized* radiation, whereas radiation that gives a field rotating counterclockwise when looking into the source is called *left-polarized radiation*. Individual photons correspond to circularly polarized light rather than to plane polarized light. The projection of the spin angular momentum of a photon can equal either $\hbar$ (parallel to its direction of propagation) or $-\hbar$ (antiparallel to it), and these two possibilities correspond to the two directions of circular polarization.

It is also possible to depict plane polarized light as being made up of equal numbers of left circularly polarized photons and right circularly polarized photons. Figure 23.22a shows the rotation of the electric fields of a right-polarized ray and a left-polarized ray at a fixed location. As the two electric field contributions rotate in opposite directions their sum will remain in a plane if they are in phase and have the same frequency and the same amplitude.

As light passes through a transparent medium, its speed is less than the speed of light in a vacuum. This can be thought of as absorption of the light by the molecules or atoms of the medium followed by re-radiation in the same direction as before, slowing the propagation of the light. The *refractive index*, n, of a medium is defined as the ratio of the speed of light in a vacuum to the speed of light in the medium:

$$n = \frac{c(\text{vacuum})}{c(\text{medium})} \quad \text{(definition of refractive index)} \tag{23.8-2}$$

The refractive index depends on the wavelength of light as well as on the identity of the medium.

Molecules that have a plane of symmetry interact with photons of both circular polarizations in the same way. A molecule without a plane of symmetry appears different to the two kinds of photons, and the speed of light of the two kinds of photons can be different. The rotation of one circularly polarized electric field contribution lags behind the other, and the plane of polarization is rotated as shown in Figure 23.22b.

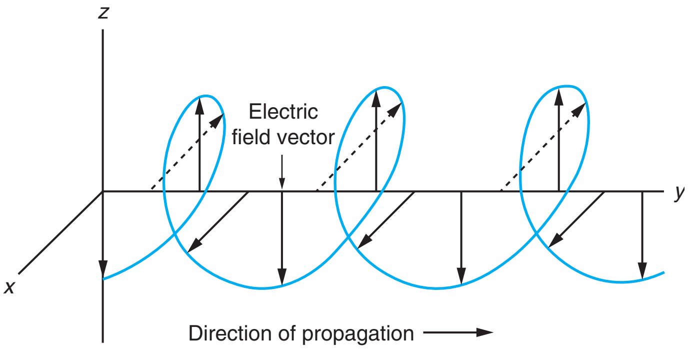

Figure 23.21 Circularly Polarized Light from Plane-Polarized Light. The circularly polarized light corresponds to the electric field vector moving in a helical pattern.

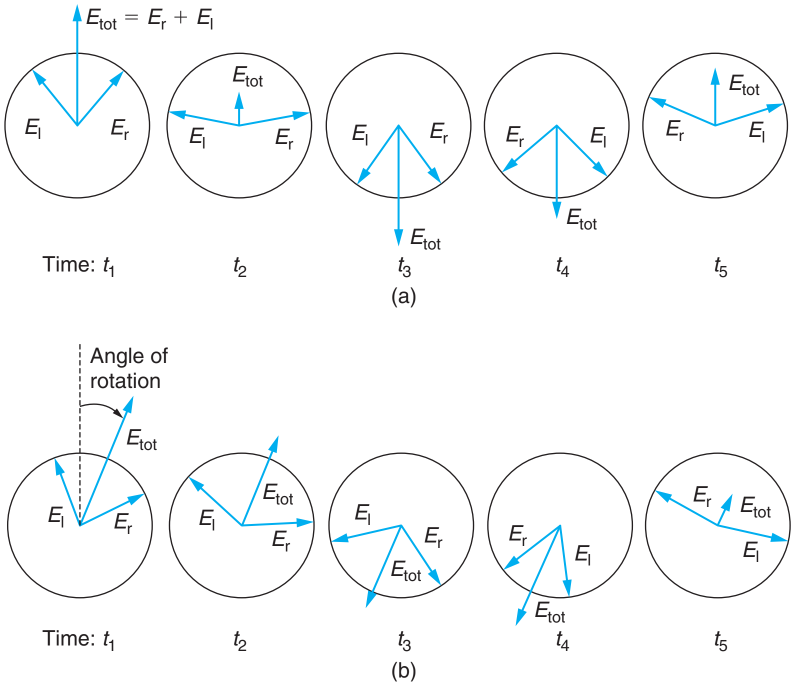

Figure 23.22 Plane-Polarized Light (E_{tot}) from Right-Polarized Light (E_r) and Left-Polarized Light (E_l). (a) Plane-polarized light in a vertical plane. This diagram shows how the two vectors from the right- and left-polarized light add to produce a sum vector that oscillates in one plane. (b) Plane-polarized light (E_{tot}) from right-polarized light (E_r) and left-polarized light (E_l) which is delayed relative to that in Figure 23.22a. This diagram shows how the two vectors from the right- and left-polarized light add to produce a sum vector that oscillates in one plane. Since one of the beams is delayed, the sum vector oscillates in a different plane from that of (a).

This phenomenon is called *circular birefringence*, and the substance is said to be optically active. The angle α through which the plane is rotated is proportional to the length of the sample and to the difference between the refractive indexes of right- and left-polarized light. It is given by

$$\alpha = \frac{\pi(n_R - n_L)L}{\lambda} \tag{23.8-3}$$

where n_R is the refractive index for right-polarized light and n_L is the refractive index for left-polarized light of the wavelength λ and where L is the length of the sample.

The rotating power of an optically active substance is commonly expressed as the *specific rotation* $[\alpha]$, defined by

$$[\alpha] = \alpha/\rho L \quad \text{(definition)} \tag{23.8-4}$$

where α is the angle of rotation, ρ is the density of the substance, and L is the length of the sample. If one has a solute in solution, the density is replaced by the concentration of the substance. The specific rotation depends on the identity of the substance, the identify of the solvent (if any), the temperature, and the wavelength of light.

The specific rotation often has different signs for two wavelengths between which a spectral line occurs. Specific rotations of many substances have often been tabulated for a single wavelength, usually the yellow sodium "D lines" at 589.0 and 589.6 nm, and the wavelength dependence has often been ignored. However, additional information about the stereochemical configuration of molecules can be obtained from the dependence of the specific rotation on wavelength, which is called *optical rotatory dispersion* (ORD).

The absorptivity of an optically active substance can also differ for right-polarized and left-polarized photons. This phenomenon is called *circular dichroism* (CD), and is also studied as a function of wavelength. Until the 1970s, only ultraviolet and visible light were used for ORD and CD. Since then techniques have been developed for infrared circular dichroism spectroscopy, which is usually called *vibrational circular dichroism* (VCD). In addition, techniques have been invented for determining the differences in scattering of left- and right-polarized light, and Raman optical activity (ROA) is now being studied.[28]

In addition to the types of spectroscopy that we have discussed, many other types and techniques of spectroscopy have been developed. A lot of work is being done in making rapid spectroscopic observations to study molecular species that have short lifetimes. Almost any issue of *The Journal of Chemical Physics* or the *Journal of Physical Chemistry* contains one or more articles reporting on spectroscopic techniques that we have not discussed.

PROBLEMS

Section 23.8: Other Types of Spectroscopy

23.51 By analogy with the photoelectron spectrum of N_2, predict what the photoelectron spectrum of O_2 would look like.

23.52 By analogy with the photoelectron spectrum of N_2, predict what the photoelectron spectrum of C_2 would look like.

Summary of the Chapter

Electromagnetic radiation that is absorbed or emitted by atoms or molecules gives information about energy level differences through the Bohr frequency rule

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda} = E_{\text{upper}} - E_{\text{lower}}$$

Each pair of energy levels does not necessarily lead to a spectral line for emission or absorption. Selection rules tell whether a transition with emission or absorption of radiation can occur between a given pair of energy levels.

Transitions between rotational states lead to emission or absorption in the microwave region. For diatomic and linear polyatomic molecules with permanent dipole moments, the selection rule is

$$\Delta J = \pm 1$$

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[28] S. C. Stinson, *Chem. Eng. News*, **63**(45), 21 (Nov. 11, 1985).

which leads to a spectrum of equally spaced lines with a spacing in terms of reciprocal wavelength equal to $2\widetilde{B}_e$. Molecules with no permanent dipole moment give no microwave spectrum. The microwave spectra of nonlinear polyatomic molecules are more complicated but the presence of a permanent dipole moment is required for a microwave spectrum to occur.

Transitions between vibrational levels lead to spectra in the infrared region. For diatomic molecules with permanent dipole moments, the selection rule is

$$\Delta v = \pm 1$$

leading to a "fundamental" band centered at a reciprocal wavelength equal to $\widetilde{\nu}_e$. Since the selection rule is only an approximation, "overtone" bands at multiples of this reciprocal wavelength also occur.

The infrared spectra of polyatomic molecules contain one fundamental band for each normal mode whose motion modulates the dipole moment of the molecule. Normal modes that do not modulate the dipole moment of the molecule are not seen in the infrared spectrum. Overtone bands occur as with diatomic molecules, along with combination bands, which are produced when two normal modes make simultaneous transitions.

Atomic and molecular spectra in the visible and ultraviolet regions arise from transitions from one electronic state to another. Vibrational and rotational transitions occur simultaneously with the electronic transitions, producing complicated band spectra. The electronic transitions take place rapidly compared with rotational and vibrational periods, and conform to the Franck–Condon principle: The nuclei remain stationary during the transition.

Raman spectroscopy involves inelastic scattering of light instead of absorption or emission. The selection rules for Raman transitions are different from those of absorption and emission spectroscopy, so that many transitions that are forbidden in absorption and emission occur in Raman scattering. Raman scattering requires that the motion modulate the polarizability of the molecule. For rotational Raman transitions in diatomic and linear polyatomic molecules

$$\Delta J = 0, \pm 2$$

which leads to a rotational Raman spectrum with lines whose reciprocal wavelengths have equal spacing of $4\widetilde{B}_e$ between them.

Almost every diatomic molecule has a vibrational Raman spectrum. The vibrational selection rule for diatomic molecules is

$$\Delta v = \pm 1$$

A nonlinear polyatomic molecule will exhibit a rotational Raman spectrum only if it has different values of polarizability in different directions. Most molecules exhibit a rotational Raman spectrum, except for highly symmetric molecules such as spherical tops.

A normal mode must modulate the polarizability to be seen in the vibrational Raman spectrum. The "rule of exclusion" states that in a molecule with a center of symmetry, those normal modes not seen in the infrared spectrum will be seen in the Raman spectrum, and those seen in the infrared spectrum will not be seen in the Raman spectrum.

ADDITIONAL PROBLEMS

23.53 **a.** Would H_2 have a microwave spectrum?

b. Would H_2 have an infrared spectrum?

c. Would H_2 have a rotational Raman spectrum?

d. Would H_2 have a vibrational Raman spectrum?

e. Describe all of the spectra that would occur, including band centers and splittings in reciprocal centimeters for optical spectra. For Raman spectra, specify the Raman shifts.

23.54 The nitronium ion, NO_2^+, has a single Raman band with a Raman shift of 1400 cm^{-1}. Strong IR bands are found at 540 cm^{-1} and at 2360 cm^{-1}, but not at 1400 cm^{-1}. What is the shape of NO_2^+? A weak IR band is found at 3735 cm^{-1}. What is it due to?

23.55 At room temperature, the most highly populated rotational level of HF corresponds to $J = 2$. Neglect the corrections to the energy levels and use the harmonic-oscillator, rigid-rotor approximation.

a. Sketch the room-temperature microwave spectrum of HF as a function of reciprocal wavelength. Specify the reciprocal wavelength of each of the first four spectral lines and indicate the approximate relative intensities of the lines.

b. Sketch the fundamental IR band of HF at room temperature as a function of reciprocal wavelength. Specify the reciprocal wavelength of the band center and the splitting between adjacent lines of the two branches. For each branch tell what transitions produce the lines.

c. At what reciprocal wavelength would you look for the center of the first overtone band of HF?

d. Sketch the Stokes branch of the rotational Raman spectrum of HF as a function of Raman shift in reciprocal wavelengths. Specify the Raman shift of each of the first four lines.

23.56 **a.** Would sulfur hexafluoride, SF_6, have a microwave spectrum?

b. Would sulfur hexafluoride have a rotational Raman spectrum?

c. How many vibrational normal modes would sulfur hexafluoride have?

d. Orient the sulfur hexafluoride molecule so that the fluorine atoms are on the coordinate axes. Consider a normal vibrational mode in which all fluorine atoms move perpendicular to the xz plane, with the fluorine atoms in the xz plane moving in one direction, whereas those on the y axis move in the opposite direction. Would this normal mode be seen in the infrared spectrum? Would it be seen in the Raman spectrum?

e. Consider the symmetric stretch normal mode, in which all fluorine atoms move away from the sulfur atom simultaneously. Would this normal mode be seen in the infrared spectrum? Would it be seen in the Raman spectrum?

23.57 For each of the following molecules, tell whether the specified motion will give rise to a Raman line or band, an emission/absorption line or band, both, or neither:

a. The symmetric stretch of CO_2.

b. The asymmetric stretch of CO_2.

c. The rotation of CH_4.

d. The vibration of N_2.

e. The rotation of N_2.

23.58 Carbon dioxide exhibits a strong infrared absorption band at 667.2 cm^{-1}. This band has a Q branch. There is another strong infrared band at 2349.3 cm^{-1}.

a. Identify the normal mode involved with each of these bands. Explain your answer. Would you expect to find a Q branch in the band at 2349.3 cm^{-1}?

b. How many additional strong infrared bands would you expect to find? If any, where would you expect to find them?

c. What would you expect to find in the vibrational Raman spectrum of CO_2?

23.59 Consider the two substances, N_2 and CO. Assume all nuclei are the most common isotopes.

a. Describe the microwave spectra of the two substances at room temperature, including reciprocal wavelength values.

b. Describe the fundamental band in the infrared spectra of the two substances, including the band center and the splittings between lines. Assume that the harmonic oscillator–rigid rotor energy level formula applies.

c. Describe the Stokes band of the rotational Raman spectra of the two substances, including the Raman shifts of the first four lines.

d. Describe the fundamental Stokes band of the vibrational Raman spectra of the two substances, including the Raman shifts of the first two lines in the *O* and *S* branches.

23.60 Consider the ozone molecule:

a. Draw the electron dot structure as you would in freshman chemistry. Is resonance necessary? If it is, include the principal resonance structures. Assign formal charges.

b. What is the shape of the molecule?

c. Is the molecule polar?

d. What vibrational normal modes would you expect to occur? List them in order of increasing frequency.

e. What normal modes will produce infrared absorption bands?

23.61 **a.** Calculate the reciprocal wavelength of the band center of the fundamental vibrational band of the CO molecule, using the expression for the corrected energy levels in Eq. (22.2-50) and information from Table A.22 of Appendix A. Compare your value with the value from the uncorrected energy level expression.

b. Calculate the reciprocal wavelength of the band center of the first overtone band of the CO molecule, using the expression for the corrected energy levels and information from Table A.22 of Appendix A. Compare this reciprocal wavelength with double the reciprocal wavelength from part a. Compare your value with the value from the uncorrected energy level expression.

c. Calculate the reciprocal wavelength of the first line of the microwave spectrum of the CO molecule using the corrected energy level expression. Compare your value with the value from the uncorrected energy level expression.

d. Calculate the reciprocal wavelength of the second line of the microwave spectrum of the CO molecule using the corrected energy level expression. Compare your value with the value from the uncorrected energy level expression.

23.62 Describe qualitatively the following spectra:

a. The microwave spectrum of CH_4.

b. The infrared spectrum of CO_2.

c. The emission spectrum of atomic hydrogen.

23.63 There is a vibrational normal mode of benzene in which all of the carbons rise above the plane of the molecule as all of the hydrogens move below the plane of the molecule. Will this normal mode be seen in the infrared spectrum of benzene? Will it be seen in the Raman spectrum of benzene? Explain your answer.

23.64 **a.** Write a computer program to calculate the reciprocal wavelength of the spectral lines in the fundamental band of the vibration–rotation spectrum of a diatomic molecule, using the corrected energy level expression of Eq. (23.2-50). Use the program to calculate the reciprocal wavelengths of the band center, of the first 15 lines in the *P* branch, and of the first 15 lines in the *R* branch of the HCl fundamental band, using information from Table A.22 of Appendix A.

b. Use the program to repeat the calculation of part a for the first overtone band of HCl.

c. Modify your program to calculate the reciprocal wavelengths of the lines in the microwave spectrum of a diatomic molecule. Use the program to calculate the reciprocal wavelengths of the first 15 lines of the microwave spectrum of HCl.

23.65 Write a computer program to calculate the relative intensities of the spectral lines in the fundamental band of the vibration–rotation spectrum of a diatomic molecule, assuming that the absorbance is displayed in the spectrum. Set the maximum absorbance of the first line of the *P* branch equal to 1. Assume the Boltzmann probability distribution and assume that the transition dipole moments for all transitions are equal. Use your program to calculate the relative intensities for the first 15 lines in each branch of the HCl spectrum at 298 K.

23.66 Using information from Table A.22 of Appendix A, consider the HF molecule.

a. Find the value of the moment of inertia.

b. Find the value of the force constant.

c. Draw a simulated microwave spectrum, assuming that the temperature is 298 K and using reciprocal centimeters as the independent variable. Use the uncorrected energy levels. Assume that the transition dipole moments are roughly equal, and show the line of maximum intensity.

d. Repeat part a, using the corrected energy levels. If you have done Problems 23.64 and 23.65, use your computer programs to calculate the reciprocal wavelengths and intensities.

e. Draw a simulated infrared spectrum of the fundamental band, assuming that the temperature is 298 K and using reciprocal centimeters as the independent variable. Use the uncorrected energy levels. Assume that the transition dipole moments are roughly equal, and show the lines of maximum intensity.

f. Repeat part c with corrected energy levels.

g. Draw a simulated rotational Raman spectrum of HF, showing the Stokes lines. Assume that the temperature is 298 K, and plot the Raman shift on the horizontal axis, using reciprocal centimeters as the independent variable. Use the uncorrected energy levels.

23.67 Label each statement as either true or false. If a statement is true only under special circumstances, label it as false.

a. A forbidden transition cannot occur.

b. A forbidden transition always produces a weaker spectral line than every allowed transition.

c. All forms of spectroscopy require that the radiation is dispersed.

d. All molecules exhibit an absorption spectrum in some part of the electromagnetic spectrum.

e. Any molecule that exhibits a rotational Raman spectrum does not exhibit a microwave absorption spectrum.

f. Any molecule that exhibits a vibrational Raman spectrum does not exhibit an infrared absorption spectrum.

g. Raman spectroscopy requires the use of a laser.

h. All infrared spectroscopy is absorption spectroscopy.

i. A nonpolar molecule cannot exhibit an infrared spectrum.

j. A molecule that is a spherical top exhibits $3n - 6$ vibrations that lead to infrared spectral lines.

k. A molecule that is a spherical top exhibits the same kind of infrared spectrum as a heteronuclear diatomic molecule.

l. Most organic substances are colorless in the visible region and also do not absorb in the ultraviolet region.

m. A linear polyatomic molecule exhibits the same type of infrared spectrum as a diatomic molecule.

n. A linear polyatomic molecule exhibits the same kind of microwave spectrum as a diatomic molecule.

23.68 Tell how you would distinguish between each pair of substances, using spectroscopic techniques. If possible specify two different techniques.

a. $^{1}H^{35}Cl$ and $^{2}H^{35}Cl$

b. $HC + CH$ and $HC + CCl$

c. $^{35}Cl_2$ and $^{35}Cl^{37}Cl$

24

Magnetic Resonance Spectroscopy

PRINCIPAL FACTS AND IDEAS

1. Magnetic fields can be produced by electric currents and moving charges.
2. Magnetic dipoles can be produced by currents flowing in loops and by rotating charges.
3. Electrons and nuclei with nonzero spins have magnetic dipoles.
4. Different spin states have different energies in a magnetic field.
6. Magnetic resonance spectroscopy involves transitions between spin states that have different energies in a magnetic field.
7. Electron spin resonance spectroscopy uses transitions between the two spin states of unpaired electrons in a magnetic field.
8. Nuclear magnetic resonance spectroscopy uses transitions between spin states of nuclei in a magnetic field.
9. Modern infrared and nuclear magnetic resonance (NMR) spectrometers use Fourier transform techniques.
10. Two-dimensional NMR spectra can provide additional information about molecular structure.

24.1 Magnetic Fields and Magnetic Dipoles

Any electric current produces a magnetic field, which is a vector quantity. The strength of a magnetic field is specified by the *magnetic induction* **B** or by the *magnetic field strength* H. These two vector quantities are proportional to each other. We will generally use the magnetic induction **B** and will follow the common terminology of chemists and call it the *magnetic field*. *Ampère's law* gives the magnitude of the magnetic field in a vacuum at a perpendicular distance r from a long straight wire carrying an electric current I:

Andre-Marie Ampère, 1775–1836, was a great French physicist who was largely responsible for the founding of the science of electromagnetism. He was a child prodigy who is said to have worked out complicated mathematical sums using pebbles before he knew the symbols for the numbers. The unit of electrical current is named for him.

$$B = |\mathbf{B}| = \frac{\mu_0 I}{2\pi r} \tag{24.1-1}$$

where μ_0 is the *permeability* of a vacuum, defined by

$$\mu_0 = 4\pi \times 10^{-7}\,\mathrm{T\,m\,A^{-1}} \quad \text{(exactly, by definition)} \tag{24.1-2}$$

The conventional direction of an electric current is the apparent direction of motion of positive charges. In a current of electrons, the electrons are moving in the opposite direction. If we construct a circle of radius r that is centered on the wire and is perpendicular to the wire, the magnetic field is tangent to the circle at any point on the circle, and its magnitude is given by Eq. (24.1-1). The direction can be obtained from a *right-hand rule*: If the thumb of the right hand points in the direction of the current, the curled fingers point in the direction of the magnetic field. If the current is measured in amperes (denoted by A and equal to coulombs per second) and the distance is measured in meters, then the magnetic field is measured in tesla (T). There is another unit of magnetic field called the *gauss*, defined by

The tesla is named for Nikola Tesla, 1856–1943, an eccentric Austrian-American electrical engineer and inventor who came to the United States in 1884 to work with Thomas Edison, but who soon parted with him and went to Westinghouse, because Edison favored direct current for municipal power grids but Tesla favored alternating current.

$$10000\,\text{gauss} = 1\,\mathrm{T} \quad \text{(exactly)} \tag{24.1-3}$$

The magnitude of the earth's magnetic field is somewhat less than 1 gauss at most locations on the earth's surface.

The direction of an electric current was defined by Benjamin Franklin, 1706–1790, American politician, printer, inventor, and self-taught physicist, who gained fame for many things, including showing that lightning is a transfer of electric charge and inventing the lightning rod. He also originated the designation of the two kinds of electric charge as positive and negative.

EXAMPLE 24.1

If a long straight wire is carrying a direct current of 15.0 A, find the magnitude of the magnetic field at a location 0.050 m from the wire. If the wire is vertical and the current is flowing upward (electrons flowing downward) and the location is due east of the wire, what is the direction of the magnetic field?

Solution

$$B = \frac{\mu_0 I}{2\pi r} = \frac{(4\pi \times 10^{-7}\,\mathrm{T\,m\,A^{-1}})(15.0\,\mathrm{A})}{2\pi(0.050\,\mathrm{m})} = 6.0 \times 10^{-5}\,\mathrm{T} = 0.60\,\text{gauss}$$

By the right-hand rule, the direction is due north. This magnetic field is roughly equal to the earth's magnetic field at the surface of the earth.

Exercise 24.1

a. What is the direction of the magnetic field in the previous example if the location is due south of the wire?

b. What is the direction and magnitude of the magnetic field at a location 0.100 m due west of the wire?

If a particle of charge Q is moving with velocity $\mathbf{v}$ through a magnetic field $\mathbf{B}$, there is a force on the particle given by

$$\mathbf{F} = Q\mathbf{v} \times \mathbf{B} \tag{24.1-4}$$

where × stands for the vector product (cross product) of the two vectors, which is discussed in Appendix B. There is a screw-thread rule for the cross product. If the vector on the left is rotated through an angle no greater than 180° to point in the direction of the second vector, the cross product points in the direction that a right-handed screw would move. The force on a positive charge is in this direction. The force on a negative charge is in the opposite direction.

EXAMPLE 24.2

If an electron ($Q = -\mathscr{e} = -1.602 \times 10^{-19}$ C) is located due east of the wire in Example 24.1 at a distance of 0.050 m from the wire and is moving east at a speed of 145 m s^{-1}, find the direction and the magnitude of the force on the electron direction.

Solution

From Eq. (B.3-38) in Appendix B and the fact that **v** and **B** are perpendicular to each other,

$$\begin{aligned} F = |\mathbf{F}| &= Q|\mathbf{v} \times \mathbf{B}| = Q|\mathbf{v}||\mathbf{B}|\sin(\alpha) = Q|\mathbf{v}||\mathbf{B}| \\ &= (-1.602 \times 10^{-19}\,\mathrm{C})(145\,\mathrm{m\,s^{-1}})(6.0 \times 10^{-5}\,\mathrm{T}) \\ &= (-1.602 \times 10^{-19}\,\mathrm{C})(145\,\mathrm{m\,s^{-1}})(6.0 \times 10^{-5}\,\mathrm{N\,s\,C^{-1}\,m^{-1}}) \\ &= 1.39\,\mathrm{N} \end{aligned}$$

where we have deduced the fact that the tesla unit must be equivalent to N s C^{-1} m^{-1}, or N A^{-1} m^{-1}, or kg s^{-1} C^{-1}. The direction of the force is downward by the screw-thread rule.

Exercise 24.2

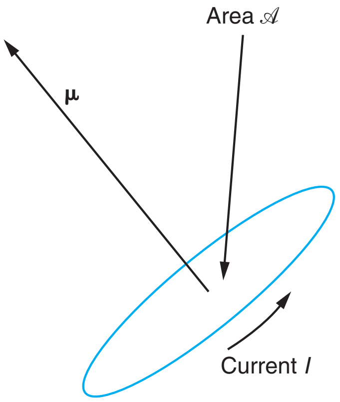
a. If an electron ($Q = -\mathscr{e} = -1.602 \times 10^{-19}$ C) is located due east of the wire in Exercise 24.1 at a distance of 0.050 m from the wire and is moving north at a speed of 145 m s^{-1}, find the direction and the magnitude of the force on the electron.

b. If the electron is in the position of part a but is moving directly toward the wire, find the direction and the magnitude of the force on the electron.

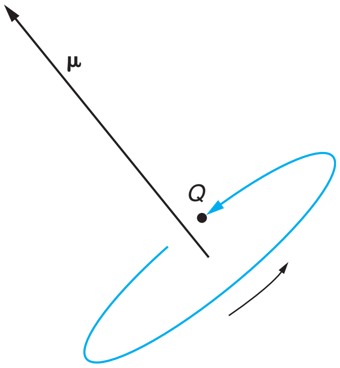
Magnetic Dipoles

Magnetic dipoles are like bar magnets or compass needles with a "north-seeking" pole at one end and a "south-seeking" pole at the other. A magnetic field applies a torque (turning force) on a magnetic dipole, much as an electric field applies a torque to an electric dipole. An electric dipole can be made up of a positive and a negative charge (two electric monopoles), but it is not yet certain whether magnetic monopoles can exist separately.[1] If they do exist, they are not commonly observed.

A magnetic dipole can be produced by an electric current flowing in a closed circular loop, as shown in Figure 24.1a. The magnetic dipole is denoted by $\boldsymbol{\mu}$ and is a vector with magnitude given by the product of the current, I, and the area of the loop, $\mathscr{A}$:



A current in a ring
(a)



An orbiting charge, *Q*
(b)

Figure 24.1 A Magnetic Dipole. (a) From a current. (b) From a moving charge. An orbiting charge is equivalent to a current, and produces a magnetic dipole just like any other current.

$$|\boldsymbol{\mu}| = \mu = I\mathscr{A} \tag{24.1-5}$$

Do not confuse the symbol μ for the magnitude of a magnetic dipole with the same letter used for the permeability. The magnetic dipole is perpendicular to the loop and its direction is given by a right-hand rule: If the curled fingers of the right hand point in the direction of the current around the loop, the thumb points in the direction of the magnetic dipole.

EXAMPLE 24.3

A current of 1.00 A is flowing counterclockwise in a horizontal circular loop 0.0500 m in radius. Find the magnitude and direction of the magnetic moment.

Solution

$$\mu = (1.00\ \text{A})\pi(0.0500\ \text{m})^2 = 0.0025\ \text{A m}^2$$

By the right-hand rule the direction is upward.

Exercise 24.3

A current of 145 mA (milliampere) is flowing in a circular loop 1.45 cm in radius. Find the magnitude of the magnetic moment.

The potential energy of a magnetic dipole in a magnetic field is given by

$$\boxed{E_{\text{mag}} = -\boldsymbol{\mu}\cdot\mathbf{B} = -|\boldsymbol{\mu}||\mathbf{B}|\cos(\alpha) = -\boldsymbol{\mu}B\cos(\alpha)} \tag{24.1-6}$$

where the dot (•) stands for the scalar product (dot product) of the two vectors. The scalar produce is discussed in Appendix B, and is defined by the second equality in Eq. (24.1-6), where α is the angle between the dipole and the field. The units of a magnetic dipole can be given as A m^2 or as J T^{-1} (joules per tesla). The energy is at a minimum if the dipole and the field are parallel, and is at a maximum if the dipole and the field are antiparallel. It vanishes if they are perpendicular to each other. A compass needle approximates a magnetic dipole and tends to orient itself in the direction of the magnetic field.

EXAMPLE 24.4

a. If the dipole of Example 24.3 points vertically upward and is located 0.200 m from the wire of Example 24.1, find the energy of the dipole.

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[1] J. E. Dodd, *The Ideas of Particle Physics*, Cambridge University Press, New York, 1984, p. 169ff; J. S. Song, *J. Undergrad. Sci.*, **3**, 47 (1996).

b. If the dipole is east of the wire and is rotated to point horizontally toward the north, find its energy.

Solution

a. Since the dipole and the magnetic field are perpendicular to each other, $E_{\text{mag}} = 0$.

b.

$$B = \frac{\mu_0 I}{2\pi r} = \frac{(4\pi \times 10^{-7}\,\text{T m A}^{-1})(15.0\,\text{A})}{2\pi(0.200\,\text{m})} = 1.5 \times 10^{-5}\,\text{T}$$

$$E_{\text{mag}} = -(0.0025\,\text{J T}^{-1})(1.5 \times 10^{-5}\,\text{T})\cos(0) = -3.75 \times 10^{-8}\,\text{J}$$

If a particle of charge Q is moving with a constant speed in a circular orbit as in Figure 24.1b, its motion is equivalent to an average electric current with magnitude

$$I = \frac{Q}{t_{\text{orbit}}} = \frac{Qv}{2\pi r} \tag{24.1-7}$$

where t_{orbit} is the time required to make one circuit of the orbit, where r is the radius of the particle's orbit, and where v is its speed. Equations (24.1-5) and (24.1-7) give

$$\mu = |\boldsymbol{\mu}| = \frac{\pi r^2 Qv}{2\pi r} = \frac{Qvr}{2} \tag{24.1-8}$$

This can be restated in terms of the angular momentum, which for a circular orbit is given by Eq. (E-19) of Appendix E:

$$L = |\mathbf{L}| = mvr \quad \text{(circular orbit)} \tag{24.1-9}$$

so that

$$\mu = |\boldsymbol{\mu}| = \frac{Q}{2m}|\mathbf{L}| \quad \text{(circular orbit)} \tag{24.1-10}$$

The same relation holds for the vector quantities as for their magnitudes, even for orbits that are not circular (although we do not prove this fact):

$$\boxed{\boldsymbol{\mu} = \frac{Q}{2m}\mathbf{L} \quad \text{(general relation)}} \tag{24.1-11}$$

If the orbiting particle is positively charged, the magnetic moment is in the same direction as the angular momentum, and if it is negatively charged, the magnetic moment is in the opposite direction.

EXAMPLE 24.5

An electron is moving in a circular orbit of radius 0.529 Å (52.9 pm) at a speed of $2.187 \times 10^6\,\text{m s}^{-1}$ (the average speed of an electron in a 1s state of a hydrogen atom). Find the magnitude of the magnetic dipole.

Solution

$$\mu = \frac{|Q|vr}{2} = \frac{(1.6022 \times 10^{-19}\,\mathrm{C})(2.187 \times 10^{6}\,\mathrm{m\,s^{-1}})(5.29 \times 10^{-11}\,\mathrm{m})}{2}$$

$$= 9.27 \times 10^{-24}\ \mathrm{A\,m^2} = 9.27 \times 10^{-24}\,\mathrm{J\,T^{-1}}$$

PROBLEMS

Section 24.1: Magnetic Fields and Magnetic Dipoles

24.1 Find the current in amperes necessary to give a magnetic field of 1.00 gauss (10^{-4} T) at a distance of 1.00 m from a long wire. Express this current in electrons per second.

24.2 Assume that a long straight wire carries a current of 1.00 A. Find the distance from the wire such that the magnetic field is equal to 0.50 gauss, the value of the earth's magnetic field in some parts of North America.

24.3 The magnetic field at the center of a circular loop carrying a current I is given by

$$B = \frac{\mu_0 I}{2r}$$

where r is the radius of the loop. If $B = 10.0$ gauss and $r = 0.500$ cm, find the value of I. If the current is counterclockwise, what is the direction of the magnetic field?

24.2 Electronic and Nuclear Magnetic Dipoles

Equation (24.1-11) can be used to construct the operator for a magnetic dipole due to an orbiting electron:

$$\widehat{\boldsymbol{\mu}} = -\frac{e}{2m_e}\widehat{\mathbf{L}} \tag{24.2-1}$$

where m_e is the mass of the electron, 9.10939×10^{-31} kg, $-e$ is the charge on the electron, and $\widehat{\mathbf{L}}$ is the operator for the orbital angular momentum.

EXAMPLE 24.6

Find the magnitude of the magnetic dipole due to the orbital angular momentum of a hydrogen atom in a $3d$ state.

Solution

$$\langle \boldsymbol{\mu}^2 \rangle = \left(\frac{e}{2m_e}\right)^2 \langle \mathbf{L}^2 \rangle = \left(\frac{e}{2m_e}\right)^2 \hbar^2(2)(3)$$

$$= \left(\frac{1.60218 \times 10^{-19}\,\mathrm{C}}{2(9.10939 \times 10^{-31}\,\mathrm{kg})}\right)^2 \left(\frac{6.62608 \times 10^{-34}\,\mathrm{J\,s}}{2\pi}\right)^2 (6)$$

$$= 5.16 \times 10^{-46}\,\mathrm{C^2\,kg^{-2}\,J^2\,s^2} = 5.16 \times 10^{-46}\,\mathrm{J^2\,T^{-2}}$$

$$|\boldsymbol{\mu}| = 2.27166 \times 10^{-23}\,\mathrm{C\,kg\,J\,s} = 2.27166 \times 10^{-23}\,\mathrm{J\,T^{-1}}$$

Electron Spin Magnetic Dipole

The electron spin angular momentum also produces a magnetic dipole. This magnetic dipole is found experimentally to be slightly more than twice as large as predicted by Eq. (24.2-1). The correct operator for this magnetic dipole is

$$\widehat{\boldsymbol{\mu}} = -g\frac{e}{2m_e}\widehat{\mathbf{S}} = -g\frac{e}{2m_e}(\mathbf{i}\widehat{S}_x + \mathbf{j}\widehat{S}_y + \mathbf{k}\widehat{S}_z) \tag{24.2-2}$$

where $\widehat{\mathbf{S}}$ is the spin angular momentum operator and where **i**, **j**, and **k** are the unit vectors in the x, y, and z directions. The quantity g is called the *anomalous* g *factor of the electron*, and corrects for the failure of the electron to obey nonrelativistic mechanics. Its value is 2.0023 . . . .

The only eigenvalue of the operator $\widehat{S}^2$ for an electron is $\hbar^2(1/2)(3/2)$, so that the magnitude of the spin magnetic dipole of an electron is

$$|\boldsymbol{\mu}| = g\frac{e}{2m_e}\hbar\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)} = g\frac{e}{2m_e}\hbar\sqrt{\frac{3}{4}} = g\beta_e\sqrt{\frac{3}{4}} \tag{24.2-3}$$

and its z component is

$$\mu_z = \pm\frac{1}{2}g\beta_e \tag{24.2-4}$$

The constant β_e is called the *Bohr magneton*:

$$\beta_e = \frac{e\hbar}{2m_e} = 9.2740 \times 10^{-24}\ \mathrm{J\,T^{-1}} \tag{24.2.-5}$$

For a magnetic field B_z in the direction of the z axis, the magnetic energy of an electron is

$$E_{\mathrm{mag}} = -\mu_z B_z = \pm\frac{g\beta_e B_z}{2} \tag{24.2-6}$$

The difference between the two energies is exploited in ESR spectroscopy.

EXAMPLE 24.7

a. For a magnetic field of 0.500 T, find the difference in the energies of the two electron spin states.

b. Find the ratio of the populations of these two states at 298.15 K.

Solution

a. $\Delta E_{\mathrm{mag}} = g\beta_e B_z = (2.0023)(9.2740 \times 10^{-24}\ \mathrm{J\,T^{-1}})(0.500\ \mathrm{T}) = 9.28 \times 10^{-24}\ \mathrm{J}$

b.

$$\frac{p_{\mathrm{up}}}{p_{\mathrm{down}}} = \exp\left(\frac{-9.28 \times 10^{-24}\ \mathrm{J}}{(1.3807 \times 10^{-23}\ \mathrm{J\,K^{-1}})(298\ \mathrm{K})}\right) = e^{-0.00226} = 0.99775$$

Exercise 24.4

Find the frequency and wavelength of photons with energy equal to the energy difference in Example 24.7.

Nuclear Magnetic Dipoles

Like the electron, the proton does not obey nonrelativistic mechanics. The proton's magnetic dipole operator is

$$\widehat{\boldsymbol{\mu}} = g_{\mathrm{p}} \frac{e}{2m_{\mathrm{p}}} \widehat{\mathbf{I}} \tag{24.2-7}$$

where $\widehat{\mathbf{I}}$ is the spin angular momentum operator of the proton, and m_{p} is the mass of the proton. The factor g_{p} is analogous to the anomalous g factor of the electron, and is called the *nuclear* g *factor* of the proton. Its value to six significant digits is 5.58569.

The proton has the same spin angular momentum properties as the electron, with a spin quantum number I equal to $1/2$. The magnitude of the spin angular momentum of a proton is

$$|\mathbf{I}| = \hbar\sqrt{I(I+1)} = \hbar\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)} = \hbar\sqrt{\frac{3}{4}} \tag{24.2-8}$$

The z component of the spin angular momentum is

$$I_z = M_I \hbar = \pm\frac{1}{2}\hbar \tag{24.2-9}$$

where M_I is the quantum number for the z component of I. The magnitude of the magnetic dipole μ for a proton is

$$|\boldsymbol{\mu}| = \mu = g_{\mathrm{p}} \frac{e}{2m_{\mathrm{p}}} \hbar\sqrt{\frac{1}{2}\left(\frac{1}{2}+1\right)} = \sqrt{\frac{3}{4}} g_{\mathrm{p}} \beta_{\mathrm{N}} = 2.44324 \times 10^{-26}\ \mathrm{J\,T^{-1}} \tag{24.2-10}$$

and its z component is

$$\mu_z = \pm\frac{1}{2} g_{\mathrm{p}} \beta_{\mathrm{N}} = \pm 1.41061 \times 10^{-6}\ \mathrm{J\,T^{-1}} \tag{24.2-11}$$

The constant β_{N} is analogous to the Bohr magneton and is called the *nuclear magneton*:

$$\beta_{\mathrm{N}} = \frac{e\hbar}{2m_{\mathrm{p}}} = 5.050787 \times 10^{-27}\ \mathrm{J\,T^{-1}} \tag{24.2-12}$$

In some tabulations (such as CODATA 63) the value given for the magnetic moment of the proton is the magnitude of the z component, equal to $1.41061 \times 10^{-26}\ \mathrm{J\,T^{-1}}$.

EXAMPLE 24.8

Find the difference in the energies of the two spin states of a proton in a magnetic field of 0.500 T. Compare with the result of Example 24.7 for the electron.

Solution

$$\Delta E_{\text{mag}} = g_{\text{p}}\beta_{\text{N}}B_z = (5.58569)(5.050787 \times 10^{-27}\ \text{J T}^{-1})(0.500\ \text{T})$$

$$= 1.41 \times 10^{-26}\ \text{J}$$

$$\frac{\Delta E_{\text{proton}}}{\Delta E_{\text{electron}}} = \frac{1.41 \times 10^{-26}\ \text{J}}{9.28 \times 10^{-24}\ \text{J}} = 1.52 \times 10^{-3} = \frac{1}{658}$$

Exercise 24.5

Find the ratio of the populations of the two energy proton levels in the previous example at 298.15 K.

Many other nuclei besides the proton have nonzero spin angular momenta. Chemists ordinarily encounter nuclei only in their ground states, so we take each nucleus to have a fixed magnitude of its spin angular momentum:

$$|\mathbf{I}| = \hbar\sqrt{I(I+1)} \tag{24.2-13}$$

where I is a fixed quantum number for a given nucleus: $I = 1$ for ^{2}H, $I = 1/2$ for ^{13}C, $I = 0$ for ^{12}C and ^{16}O, and so on. Each nucleus has a characteristic magnetic dipole moment:

$$|\boldsymbol{\mu}| = |g_{\text{N}}|\beta_{\text{N}}\sqrt{I(I+1)} = \hbar\gamma\sqrt{I(I+1)} \tag{24.2-14}$$

where g_{N} is a characteristic factor for the given nucleus, called the *nuclear* g *factor*. The quantity γ is called the *magnetogyric ratio*. It has a different value for each nucleus. The value of the magnetogyric ratio for the proton is

$$\gamma_{\text{p}} = \frac{e}{2m_{\text{p}}}g_{\text{p}} = \frac{g_{\text{p}}\beta_{\text{N}}}{\hbar}$$

$$= 2.67522 \times 10^8\ \text{s}^{-1}\ \text{T}^{-1} = 2.67522 \times 10^8\ \text{Hz T}^{-1} \tag{24.2-15}$$

where we use the hertz (Hz, same as s^{-1}) as the unit of frequency. For another nucleus, the magnetogyric ratio must be calculated from the g_{N} value:

$$\gamma_{\text{N}} = \frac{e}{2m_{\text{p}}}g_{\text{N}} = (4.78941 \times 10^7\ \text{J T}^{-1})g_{\text{N}} \tag{24.2-16}$$

The nuclear magneton β_{N} of Eq. (24.2-12) contains the mass and charge of the proton but is used for all nuclei. The necessary correction for different masses and charges is incorporated into the nuclear g factor g_{N} of the specific nucleus. Table A.24 of Appendix A lists the nuclear g factors and spin quantum numbers of several common nuclides. Surprisingly, some nuclides have negative values of g_{N}. In these cases the magnetic dipole of the nucleus has the direction that would be expected for a negative particle. It is as though such a nucleus contained both positive and negative charges, with the negative charges concentrated near the exterior of the nucleus.

The values that the z components of the nuclear spin can take on are

$$I_z = \hbar M_I \quad (M_I = I, I-1, \ldots, -I+1, -I) \tag{24.2-17}$$

For a proton, the quantum number M_I can equal 1/2 or −1/2. For a deuterium (^{2}H) nucleus M_I can equal 1, 0 or −1, and so on. The z component of the magnetic dipole can take on values

$$\mu_z = g_N \beta_N M_I \quad (M_I = I, I-1, \ldots, -I+1, -I) \tag{24.2-18}$$

If a nucleus is placed in a magnetic field B_z in the z direction the magnetic energy is proportional to B_z:

$$E_{\text{mag}} = -\mu_z B_z = -g_N \beta_N M_I B_z = -\gamma\hbar\, M_I B_z \tag{24.2-19}$$

A proton could be in either of two energy states with $M_I = \pm 1/2$, as could a ^{13}C nucleus. A deuterium nucleus could be in any of three energy states with $M_I = 1, 0$, or -1, and so on.

PROBLEMS

Section 24.2: Electronic and Nuclear Magnetic Dipoles

24.4 It is not known if the electron has any internal structure, but *string theory* hypothesizes that all “fundamental” particles consist of vibrations in tiny strings about 10^{-35} m in size.

a. Assume that a charge equal to the charge on an electron is moving in a circular orbit 1.00×10^{-35} m in radius. Calculate the speed of the charge if it produces a magnetic dipole equal to that of an electron. Compare this hypothetical speed with the speed of light.

b. Find the energy of a particle with mass equal to that of an electron with a de Broglie wavelength equal to the circumference of a circle 1.00×10^{-35} m in radius. Compare this energy with the rest-mass energy of an electron.

24.5 Repeat the calculation of the previous problem for a charge equal to the charge on a proton moving in a circular orbit 1.00×10^{-15} m in radius (roughly equal to a typical nuclear size).

24.6 Assume that the earth’s magnetic field at some location is equal to 0.500 gauss (5.00×10^{-5} T).

a. Find the difference in the energy of the two spin states of an electron in this magnetic field.

b. Find the frequency and the wavelength of a photon with the energy of part a.

24.7 Assume that the earth’s magnetic field at some location is equal to 0.500 gauss (5.00×10^{-5} T).

a. Find the difference in the energy of the two spin states of a proton in this magnetic field.

b. Find the frequency and the wavelength of a photon with the energy of part a.

24.8 **a.** Find the value of the magnetogyric ratio for ^{7}Li nuclei.

b. Find the value of the magnetogyric ratio for ^{13}C nuclei.

c. Find the value of the magnetogyric ratio for ^{17}O nuclei.

24.3 Electron Spin Resonance Spectroscopy

From Eq. (24.2-6) the energy of an electron in a magnetic field B_z is

$$E_{\text{mag}} = g\beta_e B_z m_s = -\pm\frac{g\beta_e B_z}{2} \tag{24.3-1}$$

Transitions between the spin states give rise to absorption of radiation. These transitions are *magnetic dipole transitions* and the selection rule is

$$\boxed{\Delta m_s = \pm 1} \qquad (24.3\text{-}2)$$

so that transitions between $m_s = 1/2$ and $m_s = -1/2$ are allowed. The frequency of radiation absorbed or emitted depends on B_z and is given by

$$\nu = \frac{\Delta E_{\text{mag}}}{h} = \frac{g\beta_e B_z}{h} \qquad (24.3\text{-}3)$$

Radiation that can be absorbed or emitted in these transitions is said to be in "resonance" with the electrons. The spectroscopy based on these transitions is called *electron spin resonance (ESR)* spectroscopy. It has also been called *electron paramagnetic resonance (EPR)* spectroscopy.

EXAMPLE 24.9

Find the magnetic field necessary to cause ESR absorption or emission of radiation with wavelength 1.000 cm.

Solution

$$B_z = \frac{hc}{g\beta_e\lambda} = \frac{(6.6261 \times 10^{-34}\,\text{J s})(2.9979 \times 10^{10}\,\text{cm s}^{-1})}{(2.0023)(9.2740 \times 10^{-24}\,\text{J T}^{-1})(1.000\,\text{cm})} = 1.070\,\text{T}$$

Since every substance contains electrons, it might seem that every substance would absorb radiation at the same frequency if placed in the same magnetic field. However, most substances do not absorb at all because their electrons occupy space orbitals in pairs with opposite spins. Because of the Pauli exclusion principle, such electrons cannot change their spins unless both members of a pair change simultaneously. One electron gains the same amount of energy that the other electron loses and no net absorption takes place. Only a substance containing unpaired electrons will exhibit an ESR spectrum.

It would still seem that every substance with unpaired electrons would absorb at the same frequency. However, the magnetic field to which an electron is exposed is a vector sum of the externally applied field, $\mathbf{B}_0$, and the contribution from the nuclei in the molecule, $\mathbf{B}_{\text{internal}}$. If the applied field is in the z direction and the molecule has n nuclei,

$$B_z = B_0 + B_{\text{internal},z} = B_0 + \sum_{j=1}^{n} a_j M_{Ij} \qquad (24.3\text{-}4)$$

The nuclear contribution B_{internal} is called the *Fermi contact interaction*. M_{Ij} is the quantum number for the z component of the nuclear spin angular moment of nucleus number j and the constant a_j is called the *coupling constant* for that nucleus. The coupling constants for nuclei in many molecules have values near 1 gauss (1×10^{-4} T), but the coupling constant is appreciably nonzero only if the electron approaches closely to the nucleus. If an unpaired electron occupies an orbital that has a nodal surface at a particular nucleus the coupling constant for that nucleus and that orbital will be negligibly small. Since *s* orbitals are the only hydrogen-like orbitals that are nonzero at the nucleus, the coupling constant at a nucleus is sometimes said to be a measure of the "*s* character" at that nucleus of the orbital containing the unpaired electron.

An ESR spectrometer uses microwave radiation with wavelengths roughly equal to 1 cm and a magnetic field near 1 T. This magnetic field can easily be attained with a permanent magnet. The microwaves are conducted by wave guides to the sample chamber, which is a cavity with conducting walls in which standing electromagnetic waves can occur. Absorption by the sample is detected by its effect on these standing waves. Since a particular cavity can support standing waves of only a few frequencies, the frequency of the radiation is kept fixed and the applied magnetic field is varied. Absorption will occur when the magnetic field affecting the unpaired electron equals B_{res}, the value such that Eq. (24.3-3) is satisfied for the frequency being used:

$$B_0 + B_{\mathrm{internal}} = B_{\mathrm{res}} = B_0 + \sum_{j=1}^{n} a_j M_{Ij} = \frac{h\nu}{g\beta_e} \tag{24.3-5}$$

A single substance can produce several values of B_0 at which resonance occurs, because different nuclear spin states will be found in different molecules in the sample and because the coupling constants at different nuclei can be different from each other. In the hydrogen molecule ion, H_2^+, the electron couples equally with the two protons. The molecule could be in a state with both proton spins up, in either of two states with one proton spin up and one down, or in a state with both proton spins down. Since the sum of the M_I values can equal 1, 0, or −1, we obtain a spectrum with three lines, where each line is produced by a different set of molecules. The states are nearly equally populated and the middle line is twice as intense as the other two, because there are two states with one spin up and one spin down.

EXAMPLE 24.10

Assume that the benzene negative ion, $C_6H_6^-$, has its unpaired electron in a delocalized orbital with equal magnitude at each of the protons. Predict the ESR spectrum.

Solution

We assume that all of the coupling constants are equal. There will be one line for each value of the sum of the M_I values. This sum can equal 3, 2, 1, 0, −1, −2, or −3, so that seven lines occur in the spectrum, with a splitting between two adjacent lines equal to the coupling constant. For a field of 0.500 T, the difference in energy between two nuclear spin states with values of the sum of the M_I's differing by unity is given by Eq. (24.2-19):

$$\begin{aligned}\Delta E_{\mathrm{mag}} &= g_{\mathrm{N}}\beta_{\mathrm{N}}B_z = (5.5857)(5.0508 \times 10^{-27}\ \mathrm{J\,T^{-1}})(0.500\ \mathrm{T}) \\ &= 1.411 \times 10^{-26}\ \mathrm{J}\end{aligned}$$

At 300.0 K the ratio of the populations of two such states is

$$\begin{aligned}e^{-\Delta E_{\mathrm{mag}}/k_{\mathrm{B}}T} &= \exp\left(-\frac{1.411 \times 10^{-26}\ \mathrm{J}}{(1.3807 \times 10^{-23}\ \mathrm{J\,K^{-1}})(300.0\ \mathrm{K})}\right) \\ &= 0.99999659\end{aligned}$$

Since the nuclear states are nearly equally populated, the population of a level will be proportional to the degeneracy of the level, which is proportional to the number of ways of dividing a set of six proton spins into a subset with $m_s = 1/2$ and a subset with $m_s = -1/2$. The number of ways of dividing a set of n objects into a subset of m objects and a subset of $n - m$ objects is

$$\text{Number} = \frac{n!}{m!(n-m)!} \tag{24.3-6}$$

which is the formula for binomial coefficients. The intensities of the spectral lines are in the ratios 1 : 6 : 15 : 20 : 15 : 6 : 1.

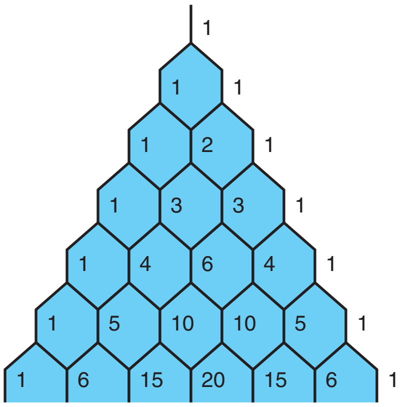


Figure 24.2 Diagram to Find the Splittings in the ESR Spectrum of the Benzene Negative Ion, $C_6H_6^-$. The use of this diagram requires that all of the splitting constants are equal. Otherwise the lines will not coincide, and there will be more than seven lines.

Figure 24.2 shows a mnemonic device for arriving at the spectrum of Example 24.10. Starting with the spectral line that would occur without any splitting, the effect of the first proton is represented by a splitting into two lines as shown at the top of the diagram. Each of these lines is then split into two lines, representing the effect of the second proton. Since all splitting constants are equal, two lines coincide after the second splitting, and there are three lines with relative intensities of 1 : 2 : 1, as shown at the second level of the diagram. The third level of the diagram represents the effect of the third proton, and so on. The relative intensities at each level are obtained by adding the relative intensities of the two lines at the previous level that combine to produce a given line. The result at each level gives relative intensities proportional to binomial coefficients.

Exercise 24.6

Predict the ESR spectrum of atomic hydrogen.

If an unpaired electron is affected by a nucleus with a spin quantum number other than 1/2, a given nucleus will produce more than two lines. For example, a deuterium nucleus (^{2}H) has $I = 1$ so that $M_I = 1, 0$, or -1. Deuterium atoms will produce a spectrum with three lines. However, unlike the spectrum of H_2^+, the three lines will be of nearly equal intensity, since there is one state with each value of M_I and the states are nearly equally populated. A nucleus with $I = 3$ would produce seven lines of equal intensity.

PROBLEMS

Section 24.3: Electron Spin Resonance Spectroscopy

24.9 The manganese nucleus has a spin quantum number $I = 5/2$. Describe the ESR spectrum of manganese atoms.

24.10 Predict the ESR spectrum of the cyclobutadiene negative ion, $C_4H_4^-$.

24.11 **a.** Predict the ESR spectrum of the hydrogen molecule ion, H_2^+.

b. Predict the ESR spectrum of D_2^+.

24.12 Predict the ESR spectrum of NO, nitric oxide. Assume the common isotopes, ^{14}N and ^{16}O.

24.13 Describe the ESR spectrum of a deuterium atom in its ground electronic state.

24.14 **a.** Assume that carbene, CH_2, is a linear molecule. Predict the ESR spectrum of CH_2.

b. Assume that CCl_2 is a bent molecule with a bond angle of roughly 120°. Predict the ESR spectrum of

CCl_2. Assume that the chlorines are both ^{35}Cl, which has a spin quantum number of 3/2.

24.15 Describe the ESR spectrum of the ethyl radical, $CH_3CH_2^-$. Make a reasonable assumption about the orbital in which the unpaired electron is found.

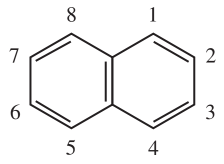
24.16 Assume that the methyl radical is planar (it is known to be nearly but not quite planar). Describe the ESR spectrum of the molecule.

24.17 Compare the ESR spectra of an isolated H atom with that of an isolated He^+ ion. Assume that the He nucleus is ^{4}He, which has $I = 0$.

24.18 The Hückel molecular orbital method gives the following LCAOMO for the unpaired electron in the naphthalene negative ion:

$$\psi = 0.42536(-\psi_1 + \psi_4 - \psi_5 + \psi_8) + 0.26286 (-\psi_2 + \psi_3 - \psi_6 + \psi_7)$$

where ψ_i is the unhybridized p orbital on carbon number i, numbered as in the diagram:



Assume that the coupling constant for each hydrogen is approximately proportional to the square of the coefficient for the carbon on which the hydrogen is bonded, and describe the ESR spectrum of the naphthalene negative ion.

24.19 For electrons in a magnetic field such that ESR absorption occurs at a frequency of $9.159 \times 10^9\ s^{-1}$, calculate the ratio of the populations of the two spin states at 298 K.

24.20 For electrons in a magnetic field of 1.44 T, calculate the ratio of the populations of the two spin states at 298 K.

24.4 Nuclear Magnetic Resonance Spectroscopy

Nuclear magnetic resonance (NMR) spectroscopy exploits transitions between different nuclear spin states in a magnetic field. It is the most important tool for determining the structure of organic molecules, and the 2003 Nobel Prize in medicine was awarded to chemist Paul C. Lauterbur and physicist Peter Mansfield for inventing *magnetic resonance imaging (MRI)*, which is used in medicine to obtain images of internal organs of patients through their differing densities of hydrogen atoms by focusing on the NMR absorption of hydrogen nuclei.[2]

Older NMR instruments are "continuous-wave" instruments. Radio-frequency energy is conducted by coaxial cable to the sample, which is located in the magnetic field of an electromagnet. The radiation can cause magnetic dipole transitions between different nuclear spin states. Since electromagnets cannot scan over a large range of magnetic fields without losing the necessary field homogeneity, a scanning instrument operates at a fixed magnetic field and the frequency of the radiation is scanned. The most common continuous-wave instruments obtain proton NMR spectra, but some are built to obtain spectra of two or more nuclei.

Most modern NMR instruments are *Fourier transform NMR spectrometers*, which frequently use superconducting electromagnets. Such instruments can obtain spectra of more than one kind of nucleus, and can obtain a spectrum more quickly than can a scanning instrument. They can also perform specialized experiments that are impossible with scanning instruments. The spectra that we now discuss are the same whether they are generated by a continuous-wave or a Fourier transform instrument.

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[2] See C. G. Fry, *J. Chem. Educ.*, **81**, 922 (2004) for a historical account.

The selection rule for magnetic dipole transitions of nuclear spins is

$$\Delta M_I = \pm 1 \tag{24.4-1}$$

so that the energy of the photon absorbed or emitted is

$$E_{\text{photon}} = h\nu = |g_{\text{N}}|\beta_{\text{N}} B_z = \gamma_{\text{N}} \hbar B_z = \frac{\gamma_{\text{N}} h B_z}{2\pi} \tag{24.4-2}$$

For the frequency ν the magnetic field must have the value

$$B_z = B_{\text{res}} = \frac{h\nu}{g_{\text{N}}\beta_{\text{N}}} = \frac{2\pi\nu}{\gamma_{\text{N}}} \tag{24.4-3}$$

where g_{N} is the nuclear g factor for the nucleus and γ_{N} is its magnetogyric ratio.

EXAMPLE 24.11

Find the value of the magnetic field necessary for protons to absorb at a frequency of 200.00 MHz.

Solution

$$B_z = \frac{h\nu}{g_{\text{N}}\beta_{\text{N}}} = \frac{(6.6261 \times 10^{-34}\ \text{J s})(200.00 \times 10^{6}\ \text{s}^{-1})}{(5.5857)(5.050787 \times 10^{-27}\ \text{J T}^{-1})} = 4.6973\ \text{T} = 46973\ \text{gauss}$$

Diamagnetic Shielding

If the frequency of the radiation is fixed and if the externally applied field were the only contribution to the magnetic field at the nucleus, every proton would absorb at the same value of the magnetic field, every ^{13}C nucleus would absorb at another value of the magnetic field, and so on. However, there are two contributions to the magnetic field at a given nucleus in addition to the externally applied magnetic field. The first is due to the fact that the externally applied magnetic field induces a net current in the electrons of the molecule. This produces a magnetic field in the opposite direction to the externally applied field. This phenomenon is called *diamagnetism* and is said to provide *shielding*. The diamagnetic contribution to the magnetic field at a given nucleus is proportional to the applied field and depends on the electron density around the nucleus. For nucleus number j in a given molecule, this diamagnetic contribution is

$$B_{j\text{diamagnetic}} = -\sigma_j B_0 \tag{24.4-4}$$

where σ_j is called the *shielding constant* for nucleus number j and where B_0 is the externally applied magnetic field. The shielding constant has a larger value when the probability of finding electrons around the nucleus is larger. Typical values of σ range from 15×10^{-6} to 35×10^{-6} (15 to 35 parts per million).

If we ignore other factors, the magnetic field at the jth nucleus is

$$B_j = (1 - \sigma_j)B_0 \tag{24.4-5}$$

and the applied magnetic field at which absorption by the jth nucleus occurs is

$$B_{0j} = \frac{h\nu}{g_N\beta_N} + \sigma_j B_{0j} \tag{24.4-6}$$

For proton NMR *tetramethyl silane* (TMS), $Si(CH_3)_4$, is chosen as a reference substance. It has a single sharp spectral line and a rather large shielding constant, $3.1 \times 10^{-5} = 31$ ppm (parts per million). The difference between the applied field necessary for the reference substance to absorb and that necessary for a given proton to absorb is called the *chemical shift* of that nucleus. One variable used to specify the chemical shift is δ, which is usually expressed in ppm. For nucleus number j,

$$\delta_j = \frac{B_{0\text{ref}} - B_{0j}}{B_{0\text{ref}}} \times 10^6 \text{ ppm} \tag{24.4-7}$$

From Eq. (24.4-6) we can write:

$$\delta_j = \frac{\sigma_{\text{ref}} B_{0\text{ref}} - \sigma_j B_{0j}}{B_{0\text{ref}}} \times 10^6 \text{ ppm} \approx (\sigma_{\text{ref}} - \sigma_j) \times 10^6 \text{ ppm} \tag{24.4-8}$$

The approximate equality in Eq. (24.4-8) is valid to four significant digits, because $B_{0\text{ref}}$ and B_{0j} will differ only by ten or twenty parts per million. The variable δ ordinarily lies between 0 and 15 ppm, but there are a few substances containing protons with negative values of δ (larger shielding constants than TMS). A second variable used to specify the chemical shift is τ:

$$\tau = 10 \text{ ppm} - \delta \tag{24.4-9}$$

The values of the shielding constant are related to the structure of the molecule, because a larger electron density around the proton generally remains in a larger shielding constant. If a proton is close to another nucleus of high electronegativity, it will generally have a smaller electron density around it and a smaller shielding constant. Its peak will appear "downfield" from the TMS peak at a relatively large value of δ. Table A.25 of Appendix A provides a list of typical values of δ for protons in different chemical environments. The values of δ can be different in different substances with similar functional groups, but the table is useful as a general guide.

An NMR spectrum is a graph in which a spectral line is represented by a peak. The area under the peak is proportional to the number of nuclei producing the spectral line. A low-resolution spectrum suffices to show the chemical shifts.

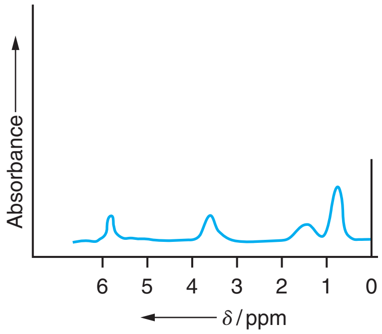

Figure 24.3 The Low-Resolution Proton NMR Spectrum of 1-Propanol (Simulated).

EXAMPLE 24.12

Figure 24.3 shows schematically the low-resolution proton NMR spectrum of 1-propanol. Interpret this spectrum.

Solution

The molecule contains protons in four kinds of electronic environments. The proton on the oxygen is bonded to an electronegative atom, and has a smaller shielding constant and a larger value of δ. The first peak from the left, with $\delta = 5.8$ and with relative area unity, is due to this proton. The protons bonded to the carbinol carbon produce the second peak from the left, with $\delta = 3.6$ ppm and with area equal to twice that of the first peak. The two protons on the second carbon are still more distant from the electronegative oxygen atom, and produce the third peak from the left, with $\delta = 1.5$ and twice the area of the first peak. The protons in the methyl group are most distant from the oxygen and produce the peak with $\delta = 0.9$ and area three times that of the first peak.

Exercise 24.7

Sketch the low-resolution proton NMR spectrum you would expect from propanal (propionaldehyde).

Spin–Spin Coupling and Spin–Spin Splitting (Multiplet Splitting)

The second molecular contribution to the magnetic field at a given nucleus is due to other nuclei with magnetic dipoles. A magnetic dipole in one nucleus induces a current in the electrons of the molecule, and this can produce a contribution to the magnetic field at the second nucleus if the second nucleus is not too distant from the first. This effect is called *spin–spin coupling*. Its contribution to the field at nucleus j is given by

$$B_{\text{spin–spin},\, j} = \sum_{i=1}^{n} J_{ji}\, M_{Ii} \tag{24.4-10}$$

where the sum includes a term for each other nucleus with nonzero spin and where M_{Ii} is the quantum number for the z projection of the spin angular momentum of nucleus number i. The coefficient J_{ij} is called the *spin–spin coupling constant* for nuclei numbers i and j. If J_{ij} is measured in Hz (s^{-1}) instead of in tesla, Eq. (24.4-10) is replaced by

$$\frac{\gamma B_{\text{spin–spin},\, j}}{2\pi} = \sum_{i=1}^{n} J_{ji}\, M_{Ii} \quad (J_{ij} \text{ measured in Hz}) \tag{24.4-11}$$

It is found that nucleus j affects nucleus i in the same way that nucleus i affects nucleus j, so that

$$J_{ij} = J_{ji} \tag{24.4-12}$$

The ratio of J_{ij} expressed in frequency units ($\text{s}^{-1} = \text{Hz}$) to the instrument's frequency is the same as the ratio of J_{ij} expressed in tesla to the magnetic field used in the instrument.

In aliphatic organic compounds, two protons that are bonded to a pair of atoms that are bonded directly together will ordinarily exhibit spin–spin coupling, but protons that are more distant from each other than this will not usually exhibit significant spin–spin coupling. In other words, two protons will usually have appreciable spin–spin coupling if the number of bonds from one proton to the other is no greater than three. In aromatic and conjugated organic compounds, spin–spin splitting from *meta* or *para* protons is observed because of the delocalized bonding.

The spin–spin coupling leads to a splitting of spectral lines into multiple lines that can be seen in a high-resolution spectrum. This splitting is known as *spin–spin splitting* or *multiplet splitting*. For example, in a molecule that contains no magnetic nuclei except for two protons that have significantly different shielding constants, the field at proton number 1 is

$$B_1 = B_0(1 - \sigma_1) + J_{12}M_{I2} \tag{24.4-13}$$

where J_{12} is measured in tesla. The field at proton number 2 is

$$B_2 = B_0(1 - \sigma_2) + J_{21}M_{I1} \tag{24.4-14}$$

There will be one value of B_0 at which the protons with $M_{I2} = 1/2$ will resonate and another value at which the protons with $M_{I2} = -1/2$ will resonate. Two lines will occur for proton number 1, corresponding to the two different values that M_I can have for the other proton. Similarly, two lines will occur for proton number 2. We say that there are two doublets. The two lines of each pair will be split by an amount equal to J_{12}, which is equal to J_{21} and the difference between the centers of the two pairs will be equal to $\sigma_1 - \sigma_2$. This spectrum is called a *first-order* spectrum, and applies if $B_0(\sigma_1 - \sigma_2)$ is fairly large compared with J_{12}.

EXAMPLE 24.13

A typical value of J_{ij} is $10\,\mathrm{s}^{-1} = 10\,\mathrm{Hz}$. For an NMR spectrometer with $\nu_{\mathrm{spec}} = 200\,\mathrm{MHz}$ ($2.00 \times 10^8\,\mathrm{s}^{-1}$), find the ratio of J_{ij} to a difference in chemical shifts of 1.5 ppm.

Solution

We express $\delta_1 - \delta_2$ in frequency units:

$$(1.5 \times 10^{-6})(2.00 \times 10^8\,\mathrm{s}^{-1}) = 300\,\mathrm{s}^{-1}$$

which is much larger than $10\,\mathrm{s}^{-1}$ so that the first-order analysis is justified.

If $B_0(\sigma_1 - \sigma_2)$ is not large compared with J_{12}, the two lines for each proton are not of equal area, and the difference between the centers of the pairs is not equal to $(\sigma_1 - \sigma_2)$, but is equal to $\sqrt{(\sigma_1 - \sigma_2)^2 + (J_{12}/B_0)^2}$, where J_{12} is measured in tesla. In addition, the line in each pair closer to the other pair of lines will have a larger intensity than the other line.[3] This is called a *second-order spectrum*. In the limit that $\sigma_1 - \sigma_2$ approaches zero, the distance between the centers of the pairs approaches J_{12}/B_0, the two inner lines coalesce into one line, and the outer lines disappear. Although spin–spin coupling occurs, spin–spin splitting is not observed between two protons that have the same chemical shift.

Some nuclei other than protons exhibit spin–spin coupling with protons, but nuclei with values of I greater than 1/2 do not ordinarily give spin–spin splitting. For example, ^{14}N, with $I = 1$, and ^{35}C and ^{37}Cl, with $I = 3/2$, do not split proton NMR lines. Splitting does occur between protons and ^{19}F or ^{13}C, which have $I = 1/2$. In organic

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[3] J. D. Roberts, *Nuclear Magnetic Resonance*, McGraw-Hill, New York, 1959, p. 55ff.

molecules, almost all of the carbon atoms are ^{12}C , which have no magnetic dipole. Almost all of the oxygen atoms are ^{16}O, which also have no magnetic dipole. In an organic molecule that contains only carbon, hydrogen, oxygen, nitrogen, and chlorine, only other protons provide noticeable spin–spin coupling for protons.

If there are more than two protons in a molecule, multiple splittings can occur. For example, consider a proton (number 1) on a carbon adjacent to a methyl group. Call the protons on the methyl group 2, 3, and 4. The three protons on the methyl group have the same chemical shift, so they do not give multiplet splitting with each other. Each of them will have the same splitting constant with the proton number 1.

$$J_{12} = J_{13} = J_{14} \tag{24.4-15}$$

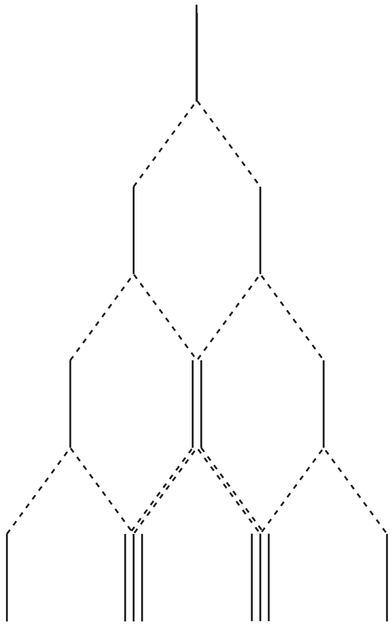

Figure 24.4 Mnemonic Device for the Spin–Spin Splitting for Three Protons.

The protons on the methyl group might all have spins up, two might have spin up, one might have spin up, or none might have spin up. Different molecules will occupy these states with relative populations in the ratios 1 : 3 : 3 : 1, since there are three ways to divide a set of three objects into a subset of two and a subset of one. Proton 1 will produce four lines (a quartet) with splitting equal to J_{12} and with intensities in the ratios 1 : 3 : 3 : 1. This pattern can be derived with the same kind of mnemonic device as was shown in Figure 24.2 for the ESR lines. This mnemonic device is shown in Figure 24.4, and gives the intensities in the ratios 1 : 3 : 3 : 1. If there is a single proton on the adjacent carbon, the protons on the methyl group will produce two lines with splitting equal to J_{12}, because of the splitting from the first proton. The total intensity of this doublet will equal three times the total intensity of the quartet.

If a proton exhibits spin–spin coupling with n other protons that have equal coupling constants with the first proton, there are $n + 1$ possible values for the sum in Eq. (24.4-10). There can be n protons with spin up, there can be $n - 1$ with spin up, and so on down to n protons with no spins up. This means that the spectral line of protons on the first carbon atom will be split into $n + 1$ lines. Since the energy differences are much smaller than k_BT, all of these states will be nearly equally populated, and the intensities of the lines will be proportional to the degeneracies of the levels. The degeneracy of the level with m protons having spin up out of a set of n protons is the number of ways of choosing a subset of m members and a subset of $n - m$ members out of a set of n members:

$$\text{Degeneracy} = \frac{n!}{m!(n-m)!} \tag{24.4-16}$$

which is the formula for binomial coefficients. For example, protons on the middle carbon of propane will be coupled to six protons on the two outer carbons, and will give seven lines with intensities in the ratios 1 : 6 : 15 : 20 : 15 : 6 : 1. Since protons on the outer carbons will be coupled to two protons on the center carton, they will give three lines with intensities in the ratios 1 : 2 : 1. This triplet will have three times the total area of the total area of the septet.

If a proton exhibits spin–spin coupling with two or more other protons that have different chemical shifts, the spin–spin coupling constants will have different values, since the coupling constants depend on the electronic environment of both protons. One way to predict the effect of the spin–spin coupling in such a case is to divide the other protons into sets of equal coupling constants. First determine the splitting due to the protons in one set. Then split each resulting line according to the splittings of the protons in the next set.

EXAMPLE 24.14

Predict the high-resolution proton NMR spectrum of 2-propanol.

Solution

The –OH proton will produce a line that is split into two lines by the proton on the –CH– carbon, but the methyl protons are too distant to give significant splitting. The line of the proton on the –CH– carbon is first split into seven lines by the six protons on the $–CH_3$ carbons, with relative intensities 1 : 6 : 15 : 20 : 15 : 6 : 1. Each of these lines will be split into two lines by the single –OH proton, giving a total of 14 lines. The six $–CH_3$ protons produce a doublet, because the only splitting is from the –CH– proton.

Figure 24.5 shows the high-resolution spectrum of 2-propanol dissolved in deuterated chloroform. Because of solvent interaction, the doublet from the hydroxyl proton occurs near 2 ppm instead of farther downfield. We discuss this effect later when we discuss ethanol. The group of peaks near 4 ppm is from the –CH– proton. The 14 lines overlap and are not completely resolved. The intense doublet near 1.3 ppm is from the six methyl protons.

The shielding term in Eq. (24.4-5), which gives rise to the chemical shift, is proportional to the applied field, whereas the spin–spin coupling term is independent of the applied field. If two instruments have different frequencies, say 60 MHz and 300 MHz, the spin–spin splitting terms will be the same in terms of frequency in both spectra, but the chemical shifts will be proportional to the magnetic field and thus larger in the higher-frequency instrument. Comparison of the spectra of the same substance from two such instruments can aid in interpretation of a spectrum with a number of overlapping sets of lines.

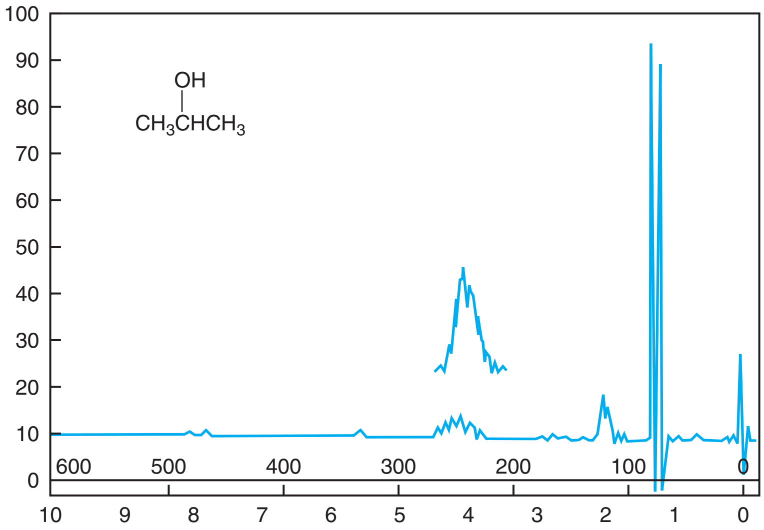

Figure 24.5 The High-Resolution Proton NMR Spectrum of 2-Propanol Dissolved in Deuterated Chloroform. From Charles J. Pouchert and John R. Campbell, *The Aldrich Library of NMR Spectra*, The Aldrich Chemical Co., 1974, Vol. I, p. 85.

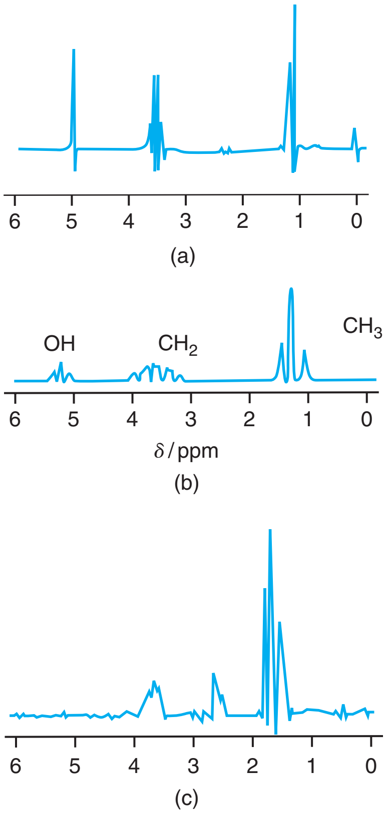

Figure 24.6 The Proton NMR Spectrum of Ethanol. (a) With a trace of water present. Because of exchange of the hydroxyl proton with water protons, the hydroxyl proton shows no spin–spin splitting. From G. W. Castellan, *Physical Chemistry*, 3rd ed., Addison-Wesley, Reading, MA, 1983, p. 606. (b) Highly purified ethanol. In the absence of water, the spin–spin splitting of the line from the hydroxyl proton is split into three lines by the methylene protons. From I. N. Levine, *Molecular Spectroscopy*, Wiley, New York, 1975, p. 353. (c) In deuterated chloroform. In this spectrum, the solvent interaction with chloroform moves the hydroxyl line to near 2.6 ppm. The splitting into three lines is not quite resolved. From C. J. Pouchert and J. R. Campbell, *The Aldrich Library of NMR Spectra*, The Aldrich Chemical Co., 1974, Vol. I, p. 79.

Impurity and Solvent Effects

If a substance contains impurities or if it is dissolved in a solvent, its proton NMR spectrum can be different from that of the pure substance. Figure 24.6a shows the proton NMR spectrum of ethanol containing a trace of water. Figure 24.6b shows the spectrum of carefully purified ethanol, and Figure 24.6c shows the spectrum of a dilute solution of ethanol in deuterated chloroform. We first consider the chemical shifts. In all three spectra the –CH_3 protons have a δ value near 1 ppm, as expected, since they are most distant from the electronegative O atom. The –CH_2– protons have a δ value between 3 and 4, because they are closer to the O atom than the –CH_3 protons. In the first spectrum, the spectral line of the –OH proton is at $\delta = 4.8$ ppm and in the second spectrum this peak is at $\delta = 5.3$ ppm. This is reasonable, because this proton is bonded to an electronegative O atom. However, in the solution with deuterated chloroform this spectral line is at $\delta = 2.3$ ppm. Ethanol molecules form hydrogen bonds with other ethanol molecules or with water molecules. When a hydrogen bond forms, the proton is attracted to the other molecule and is at a greater distance from the oxygen nucleus. It lies in a region of lower electron density and gives a spectral line at a greater value of δ. In the solution in deuterated chloroform, the ethanol molecules are distant from each other and cannot form hydrogen bonds. In the absence of hydrogen bonding the O–H bond distance, approximately 96 pm, is so small that the proton is imbedded in the electrons close to the oxygen and is more highly shielded, giving a smaller value of δ.

We now consider the spin–spin splitting. As expected the –CH_3 protons produce a triplet in all three spectra because of the splitting due to the –CH_2– protons. In the spectrum of the carefully purified ethanol the line of the –OH proton exhibits spin–spin splitting, being split into three lines by the two protons of the –CH_2– group. The –CH_2– protons produce a set of eight lines (not all completely resolved) from the four lines because of the –CH_3 protons, each of which is split into two lines by the –OH proton. In the solution spectrum this splitting is also present although poorly resolved. In the presence of a trace of water there is no spin–spin splitting in the –OH proton line. This is attributed to exchange of the proton with protons on water molecules. If the average time for this exchange process is shorter than the period of oscillation of the NMR radiation, the proton NMR spectrum will be an average of the spectrum of the proton that is leaving and the proton that is arriving, and these protons have equal probabilities of being spin up and spin down. An average line with no spin–spin splitting is observed for the –OH proton and the –CH_2– protons produce only the quartet expected from the splitting by the three protons on the –CH_3 group.

Saturation of a Signal

The difference in energy between the two states of protons in a typical magnetic field is much smaller than $k_B T$, so that the populations of the two states are nearly equal. If the populations are exactly equal, there would be no signal, because the stimulated emission and the absorption would cancel each other. It is possible with a strong signal to produce enough transitions to equalize the populations and cause the signal to disappear (this is called "saturating" the signal). In certain kinds of experiments, the effect of a spin–spin coupling can be removed by equalizing the populations of some nuclei (this is called *spin decoupling*).

EXAMPLE 24.15

Find the ratio of the populations of the two spin states of protons in a magnetic field of 4.6973 T at 298 K.

Solution

$$
\begin{aligned}
(\text{Population ratio}) &= e^{-\Delta E/k_{\mathrm{B}}T} = e^{-g_p\beta_{\mathrm{N}}B/k_{\mathrm{B}}T} \\
&= \exp\left(\frac{-(5.5857)(5.05079\times 10^{-27}\ \mathrm{J\,T^{-1}})(4.6973\ \mathrm{T})}{(1.3807\times 10^{-23}\ \mathrm{J\,K^{-1}})(298\ \mathrm{K})}\right) \\
&= e^{-3.2205\times 10^{-5}} = 0.9999678
\end{aligned}
$$

NMR Spectroscopy with Other Nuclei

Although proton NMR is the most common type of NMR spectroscopy, other nuclei are also used. It turns out that nuclei with I greater than 1/2 give broad lines that are not likely to be resolved well enough to give much useful information, so these nuclei are not used in NMR. The most prominent NMR nucleus after the proton is ^{13}C, although NMR of ^{19}F and ^{31}P is fairly common. The natural abundance of the ^{13}C isotope is approximately 1%, so that a ^{13}C nucleus is unlikely to have another ^{13}C nucleus in close proximity in a substance with the natural isotopic composition. In this case the ^{13}C–^{13}C spin–spin coupling can be ignored.

Almost every ^{13}C nucleus will be close to protons, so the spin–spin splitting between protons and ^{13}C nuclei is important in ^{13}C NMR. The technique of *spin decoupling* is used to simplify the spectra. The sample is strongly irradiated with radiation at the resonant frequency of some or all of the protons. This causes the ^{13}C multiplets to collapse to singlets. The simple explanation is that the irradiation causes the protons to make rapid transitions between the spin-up to the spin-down states so that they do not remain in a single spin state for long enough to provide the splitting. This explanation is similar to the explanation of the lack of spin–spin splitting in an alcohol with water present. There is a more complicated explanation in terms of precession of the spins.[4]

EXAMPLE 24.16

Calculate the resonance frequency of ^{13}C nuclei at the magnetic field that produces resonance with protons at 200.00 MHz.

Solution

From Example 24.11, $B_z = 4.6973$ T. From Table A.24 of Appendix A, $g_{\mathrm{N}} = 1.4048$.

$$
\begin{aligned}
\nu = \frac{g_{\mathrm{N}}\beta_{\mathrm{N}}B_z}{h} &= \frac{(1.4048)(5.050824\times 10^{-27}\ \mathrm{J\,T^{-1}})(4.6973\ \mathrm{T})}{6.6261\times 10^{-34}\ \mathrm{J\,s}} \\
&= 5.0300\times 10^{7}\ \mathrm{s^{-1}} = 50.300\ \mathrm{MHz}
\end{aligned}
$$

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[4] J. B. Lambert and E. P. Mazzola, *Nuclear Magnetic Resonance Spectroscopy*, Pearson, Upper Saddle River, NJ, 2004, p. 144ff.

PROBLEMS

Section 24.4: Nuclear Magnetic Resonance Spectroscopy

24.21 Find the magnetic field in tesla and in gauss necessary to carry out NMR experiments at 200.00 MHz with the ^{7}Li nucleus, which has a nuclear g_N factor equal to 2.171 and a nuclear spin number $I = 3/2$.

24.22 **a.** Describe qualitatively the high-resolution proton NMR spectrum of carefully purified propionic acid (propanoic acid).

b. Describe the spectrum of propionic acid with a small amount of water present.

c. Describe the spectrum of a dilute anhydrous solution of propionic acid in deuterated chloroform.

24.23 **a.** Describe qualitatively the high-resolution proton NMR spectrum of carefully purified acetic acid (ethanoic acid).

b. Describe the spectrum of acetic acid with a small amount of water present.

c. Describe the spectrum of a dilute anhydrous solution of acetic acid in deuterated chloroform.

24.24 Describe qualitatively the high-resolution proton NMR spectrum of

a. Methyl ethyl ketone (butanone)

b. Formaldehyde (methanal)

c. Formic acid (methanoic acid)

Look up the spectra and compare your predictions with the correct spectra.

24.25 Predict qualitatively the high-resolution proton NMR spectrum of CH_3F.

24.26 Sketch the proton NMR spectrum you would expect from each of the following. Indicate approximate chemical shifts.

a. Butanone (methyl ethyl ketone)

b. 2-Propanol (isopropyl alcohol)

c. Ethane

d. Ethanal (acetaldehyde)

24.27 **a.** A compound of empirical formula $C_2H_3Cl_3$ has a high-resolution proton NMR spectrum with a single line. What is the structural formula of the compound?

b. Predict the high-resolution proton NMR spectra of the other isomers of this compound.

24.28 Predict the proton NMR spectrum of each of the following substances. Include approximate values of the chemical shift relative to TMS. Give relative areas for the lines.

a. Acetone

b. Methyl acetate

c. Propane

24.29 The coupling constant for two protons in a given molecule is $J = 3.5$ Hz. In a proton NMR spectrum taken in a 200 MHz instrument, what is the spin–spin splitting between the lines when the spectrum is displayed with the axis in ppm?

24.30 Describe qualitatively the high-resolution proton NMR spectrum of

a. *tert*-Butyl alcohol (1,1-dimethylethanol)

b. *sec*-Butyl alcohol (1-methylpropanol)

c. Primary butyl alcohol (butanol)

Look up the spectra and compare your predictions with the correct spectra.

24.31 **a.** Tell how you would distinguish diethyl ether, *n*-butanol, and *tert*-butanol from each other using proton NMR.

b. Tell you how would distinguish acetone from propanal using proton NMR.

24.32 Tell how you would distinguish the following pairs of substances using proton NMR:

a. CH_3F and CH_3Cl

b. Methyl formate and acetic acid

24.33 **a.** Predict the ESR spectrum of the cyclopropenyl radical.

b. Predict the proton NMR spectrum of the cyclopropenyl radical.

24.5 Fourier Transform NMR Spectroscopy

Most modern NMR spectrometers use the Fourier transform technique, similar to that used in infrared spectroscopy. There is no need to scan the magnetic field, so spectra can be taken quickly. The spectrum can be obtained repeatedly and the individual spectra can be added, enhancing the signal and averaging out much of the noise. This is an advantage with ^{13}C, which has a natural abundance of only 1% and therefore gives only a weak NMR signal.

Fourier transform NMR spectroscopy can be described qualitatively in terms of the classical picture of *Larmor* precession.[5] In a magnetic field, a magnetic dipole has a torque acting on it, and this torque causes it to precess around the magnetic field in the same way that the toy gyroscope depicted in Figure E.3 of Appendix E precesses about the vertical direction. The direction of the dipole vector traces out a cone with the axis of the cone in the direction of the field. If the magnetic dipole is produced by the orbiting of a particle of charge Q and mass m about a center, its Larmor frequency (number of revolutions about the cone per second) of the magnetic moment in a magnetic field B is given by

$$\nu_{\text{Larmor}} = \frac{1}{2\pi}\frac{Q}{2m}B \tag{24.5-1}$$

The Larmor precession frequency of the magnetic moment of a proton is given by

$$\nu_{\text{Larmor}} = \frac{1}{2\pi}g_{\text{p}}\frac{e}{2m_{\text{p}}}B \tag{24.5-2}$$

EXAMPLE 24.17

Find the Larmor precession frequency of an unshielded proton in a magnetic field of 4.6973 T.

Solution

$$\nu_{\text{Larmor}} = \frac{1}{2\pi}(5.5856)\frac{1.6022 \times 10^{-19}\,\text{C}}{2(1.67265 \times 10^{-27}\,\text{kg})}(4.6973\,\text{T})$$

$$= 2.000 \times 10^{8}\,\text{s}^{-1} = 200.00\,\text{MHz}$$

This precession frequency is equal to the frequency of the electromagnetic radiation that induces the transitions involved in an NMR instrument. The term “magnetic resonance” refers to the classical picture of the precession synchronizing itself with the radiation.

We discuss proton NMR, but our treatment also applies to other nuclei with spin 1/2, such as ^{13}C and ^{19}F. The two spin functions α and β of a proton are like those of electrons, and correspond to spin angular momenta that can lie in either of two cones of directions, as depicted for electrons in Figure 17.12. The magnetic moment is parallel to the angular momentum and must lie on one of the same two cones. The NMR sample contains many molecules. In the presence of the external magnetic field the two spin states will have slightly different energies, and slightly more of the protons will be in the spin-up state than in the other, according to the Boltzmann distribution. From

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[5] R. S. Macomber, *J. Chem. Educ.*, **62**, 212 (1985).

Example 24.15 the population ratio for a 200 MHz instruments at room temperature is 0.9999678.

The vector sum of the magnetic dipoles in a sample is a macroscopic magnetization vector denoted by **M**. Since slightly more of the protons are in the spin-up state at thermal equilibrium, and since the spins are randomly oriented around the cones, **M** will point in the positive z direction. Even though **M** is a vector sum of many individual magnetic dipoles, it behaves like a single magnetic dipole when acted on by a magnetic field. A strong pulse of radio-frequency radiation is delivered to the sample, similar to the pulse of infrared radiation used in Fourier transform infrared spectroscopy. If the pulse is polarized so that its oscillating magnetic field is in the x direction, it imposes a torque on **M** so that the vector **M** rotates clockwise in the yz plane. The length of the pulse is chosen so that it rotates the magnetization vector by 90° onto the positive y axis. This pulse is called a 90° *pulse* or a $\pi/2$ *pulse*. The direction of the nuclear spins is independent of the orientation of the molecule, so that the magnetic moments of the nuclei are rotated without rotating the molecules.

After the pulse the magnetization vector **M** begins to precess in the xy plane as the individual spins precess. Since **M** lies in the xy plane equal numbers of nuclei now have spins up and spins down. This is a nonequilibrium distribution, and the spins begin to relax to the equilibrium population given by the Boltzmann distribution. There are two mechanisms of this relaxation, each of which produces an exponential decay with a characteristic relaxation time. The first mechanism is interaction of the spins with their surroundings, and its relaxation time is known as the *longitudinal relaxation time* or *spin–lattice relaxation time*, denoted by T_1. The second mechanism is the interaction of the spins with each other, and its relaxation time is known as the *transverse relaxation time* or *spin–spin relaxation time*, and is denoted by T_2. Figure 24.7a depicts the path of the precessing magnetization vector as it returns to its equilibrium position on the z axis.

The precessing magnetization vector induces an alternating voltage in a coil placed in the xy plane around the sample. The coil detects only the component of **M** in the xy plane. The signal detected by the coil comes from the component of **M** in the xy plane, as depicted in Figure 24.7b. The detected signal is called the *free induction decay* signal (abbreviated FID). A simple decaying oscillation is shown in Figure 24.8a, corresponding to a FID signal with a single frequency and a single relaxation time. If a substance has protons with different chemical shifts and spin–spin splittings, the protons precess at slightly different frequencies and produce a FID spectrum that is a sum of signals like that of Figure 24.8a with different frequencies. Figure 24.8b shows the sum of two decaying oscillations, one of which has twice the frequency of the other. The FID spectrum encodes the NMR spectrum as a function of time instead of as a function of frequency. The Fourier transform of the FID spectrum provides the spectrum as a function of frequency in the same way as in Fourier transform infrared spectroscopy. If the signal did not decay, the spectrum would consist of lines of zero width. Since the signal decays, the spectral lines have nonzero widths.

Multipulse NMR Experiments

Several techniques involve two or more pulses rather than the single pulse used in ordinary Fourier transform NMR.[6] These techniques can provide information that cannot easily be extracted from ordinary NMR spectra.

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[6] T. C. Farrar, *Introduction to Pulse NMR Spectroscopy*, Farragut Press, Chicago, 1989; J. B. Lambert and E. P. Mazzola, *op. cit.* (note 4).

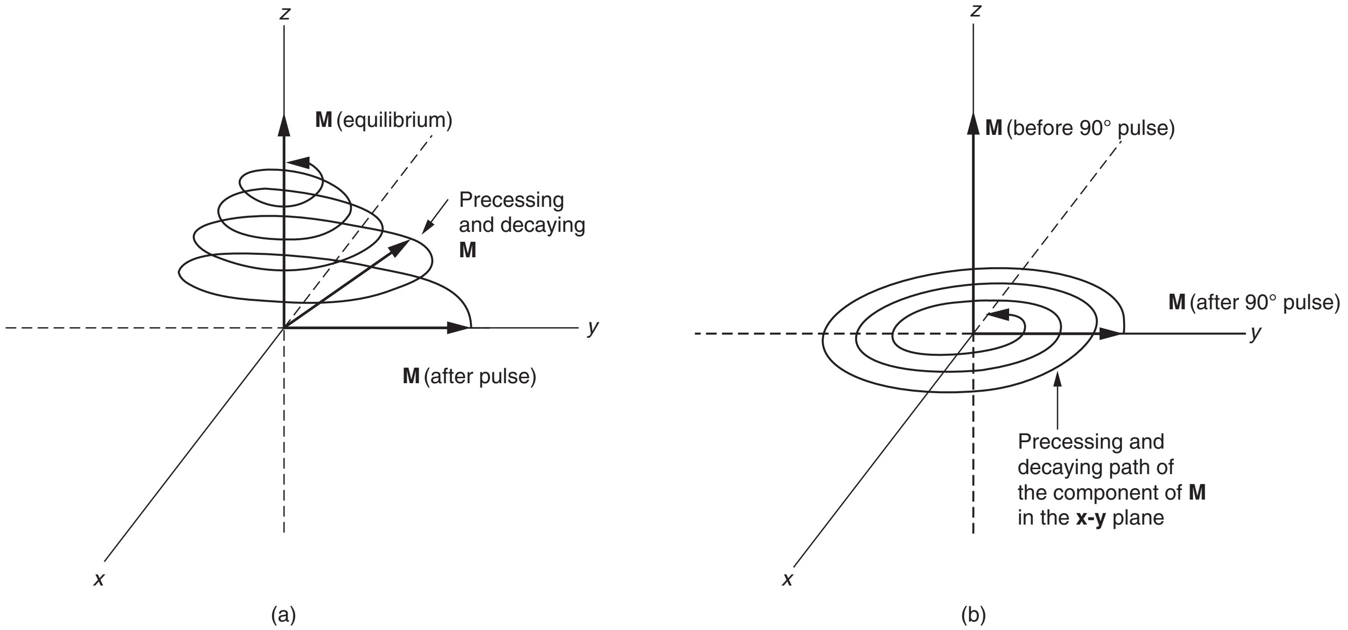

Figure 24.7 (a) The Decaying and Precession of the Magnetization Vector. (b) The Decaying and Precession of the Component of the Magnetization Vector in the *x*–*y* Plane.

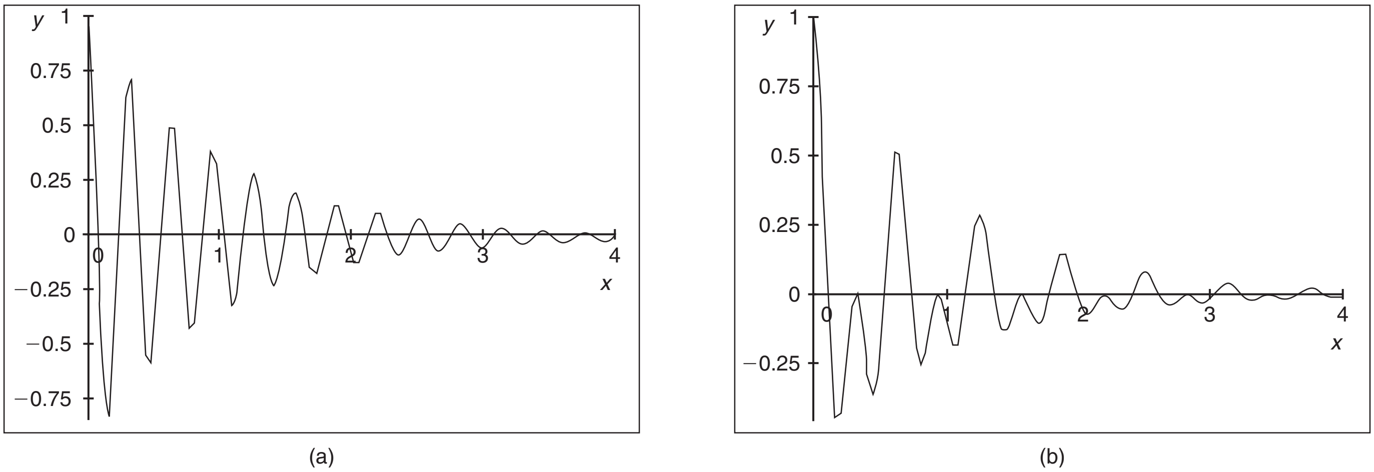

Figure 24.8 Two Decaying Oscillations Similar to FID signals. (a) A single frequency. (b) The sum of two frequencies.

The Spin–Echo Technique

This is the preferred method for measuring T_2, the spin–spin relaxation time. Consider a substance that has protons with several different chemical shifts. The procedure begins with a $\pi/2$ pulse (90° pulse) that rotates the magnetization vector from the z axis onto the y axis, as in simple Fourier transform NMR. Consider a substance with two protons, A and B, that have different chemical shifts. Let the contribution to **M** from proton A in all of the molecules be called $\mathbf{M}_\mathrm{A}$ and that from proton B in all of the molecules be called $\mathbf{M}_\mathrm{B}$. At the end of the first pulse, $\mathbf{M}_\mathrm{A}$ and $\mathbf{M}_\mathrm{B}$ will both lie on the positive y axis. Since the protons A and B have different chemical shifts, they will precess at slightly different rates. At a later time, $\mathbf{M}_\mathrm{A}$ and $\mathbf{M}_\mathrm{B}$ will have precessed by different angles in the xy plane, as depicted in Figure 24.9, where we assume that $\mathbf{M}_\mathrm{A}$ precesses more rapidly than $\mathbf{M}_\mathrm{B}$. We say that the individual sets of spins with different chemical shifts have begun to *dephase*. After a length of time that is chosen by the experimenter, a π *pulse* (180° *pulse*) is imposed, which is twice as long as the $\pi/2$ pulse. This pulse rotates the magnetization vector by 180° around the x axis. The new directions of $\mathbf{M}_\mathrm{A}$ and $\mathbf{M}_\mathrm{B}$ are shown in the figure. The slower-precessing vector is now ahead of the faster-precessing vector. The individual sets of spins continue to precess, but they now draw closer to each other and reverse the dephasing. The magnetization vector returns toward the value it had after the $\pi/2$ pulse. This is the "spin echo." Because of the spin–spin relaxation, the component of the magnetization vector in the xy plane does not completely return to its original value, with more of a difference for longer time

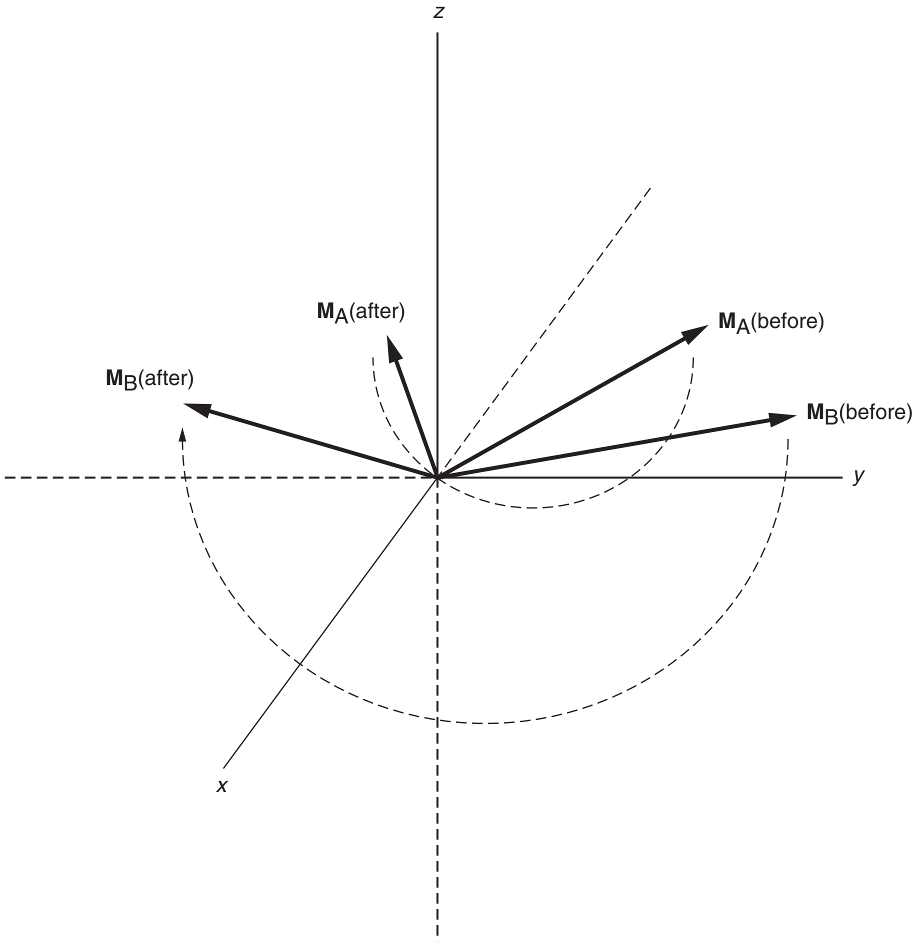

Figure 24.9 Two Precessing Contributions to the Magnetization before and after the 180° Pulse.

intervals. The experiment is repeated a number of times with different time intervals between the pulses. The dependence of the spin echo on the time between the pulses gives the value of T_2, the spin–spin relaxation time. Since the decay is exponential, the natural logarithm of the magnitude of the spin echo is plotted against the time required for the spin echo to occur. The negative slope of the line that fits the data is equal to the reciprocal of T_2.

Two-Dimensional NMR Experiments

These experiments use pulse sequences similar to that of the spin–echo experiment. There are a number of experiments with different pulse sequences. The different experiments are commonly named with acronyms. For example, COSY (**CO**rrelation **S**pectroscop**Y**) was the original two-dimensional NMR experiment.[7] Some other experiments are NOESY (**N**uclear **O**verhauser **E**ffect **S**pectroscop**Y**) and HETCOR (**HET**eronuclear **COR**relation). The usual goal of a COSY experiment is to determine which lines belong to which multiplet in a complicated spectrum with overlapping multiplets. We will give a simplified description of the COSY experiment for proton NMR (this is sometimes called HH-COSY).

In a COSY experiment two 90° pulses are used, separated by a time t_1 (the *evolution time*). The FID signal is acquired immediately after the second pulse. A number of runs are carried out with different values of t_1, so that there are two time variables, t_1 and the time that passes as the FID signal is monitored, denoted by t_2 (the *acquisition time*). The pulse sequence is shown schematically in Figure 24.10. With the externally imposed magnetic field B_z parallel to the z axis, the magnetic moment of an unshielded proton with spin up would precess around the z axis at the reference frequency (see

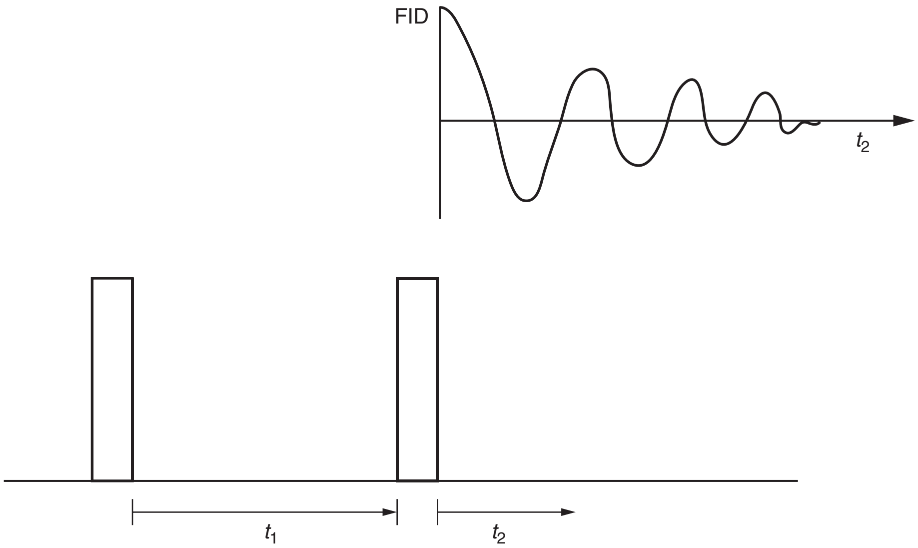

Figure 24.10 The Pulse Sequence for the COSY Experiment.

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[7] The COSY experiment was first proposed in 1971 by Prof. Jean Jeener of the Universite Libre de Bruxelles.

Example 24.17). In order to describe the COSY experiment we need to envision a Cartesian coordinate system that is rotating counterclockwise around the z axis at the reference frequency. The magnetic moment of an unshielded proton would be stationary in this rotating coordinate system. The vector sum of the proton magnetic moments of all protons is denoted by $\mathbf{M}$, as before. Before the first pulse $\mathbf{M}$ is parallel to the z axis. The first 90° pulse rotates $\mathbf{M}$ onto the positive y axis, just as in the simple NMR experiment and the spin–echo experiment.

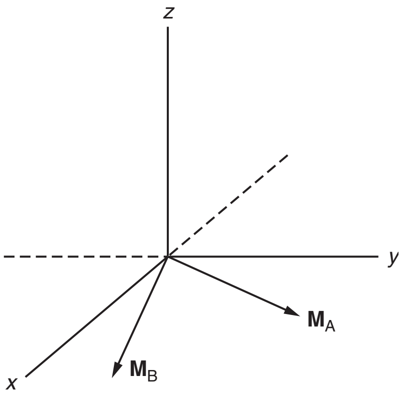

Figure 24.11 (a) The Magnetization Contributions $\mathbf{M}_A$ and $\mathbf{M}_B$ in the Rotating Coordinate System.

We first consider a substance that has two uncoupled protons, A and B, that have different chemical shifts (different shielding constants). We let $\mathbf{M}_A$ be the contribution to $\mathbf{M}$ of the A protons in all of the molecules of the sample and let $\mathbf{M}_B$ be the contribution to $\mathbf{M}$ of all of the B protons. Because of their different shielding constants, $\mathbf{M}_A$ and $\mathbf{M}_B$ precess at slightly slower rates than an unshielded proton, and lag behind the rotation of the coordinate system. They therefore move clockwise in the $x-y$ plane of the rotating coordinate system. We assume that proton B has a larger shielding constant than proton A, so it lags farther behind the rotating coordinate system than does proton A and moves through a greater angle in the rotating coordinate system, as shown in Figure 24.11a. We can express $\mathbf{M}_A$ and $\mathbf{M}_B$ in terms of their x and y components since they now lie in the xy plane.

$$\mathbf{M}_{\mathrm{A}} = \mathbf{i}\,M_{\mathrm{A}x} + \mathbf{j}\,M_{\mathrm{A}y} \tag{24.5-3}$$

and

$$\mathbf{M}_{\mathrm{B}} = \mathbf{i}\,M_{\mathrm{B}x} + \mathbf{j}\,M_{\mathrm{B}y} \tag{24.5-4}$$

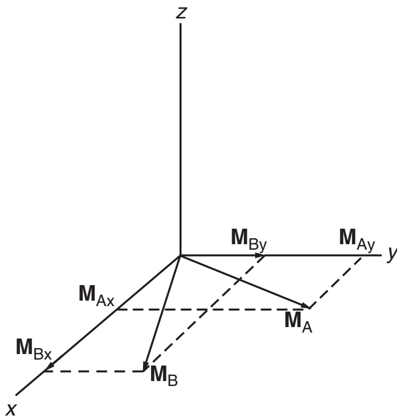

Figure 24.11 (b) The Magnetization Contributions $\mathbf{M}_A$ and $\mathbf{M}_B$ in the Rotating Coordinate System Represented by Their *x* and *y* Components.

where $\mathbf{i}$ is the unit vector in the x direction and $\mathbf{j}$ is the unit vector in the y direction. The components are also depicted in Figure 24.11b. At time t_1 a second 90° pulse is applied. We can find the effect of this pulse by considering the x and y components of the magnetization separately. The pulse has no effect on the x components, and rotates the y components clockwise onto the negative z axis, where they are not sensed by the detecting coil, which senses only magnetization in the $x-y$ plane. The x components $M_{\mathrm{A}x}$ and $M_{\mathrm{A}y}$ at the time of the second pulse ($t = t_1$) are:

$$M_{\mathrm{A}x}(t_1) = M_{\mathrm{A}}(0)\sin(2\pi\nu_{\mathrm{A}}t_1) \tag{24.5-5}$$

and

$$M_{\mathrm{B}x}(t_1) = M_{\mathrm{B}}(0)\sin(2\pi\nu_{\mathrm{B}}t_1) \tag{24.5-6}$$

where $M_{\mathrm{A}}(0)$ is the magnitude of $\mathbf{M}_{\mathrm{A}}$ at the end of the first pulse. The precession frequency of proton A is denoted by ν_{A}, and that for proton B is denoted by ν_{B}. These x components are the only magnetization vectors that remain in the $x-y$ plane after the second pulse. They continue to precess after the second pulse and produce the FID signal that is recorded as a function of t_2, the time that elapses after the second pulse.The FID is crudely depicted in Figure 24.10 along with the pulses.

The strength of the signal is determined by $M_{\mathrm{A}x}(t_1)$ and $M_{\mathrm{B}x}(t_1)$, the value of the x components at the time of the second pulse. If the value of t_1 is such that $\sin(2\pi\nu_{\mathrm{B}}t_1)$ is equal to zero or has a small value, proton B will make little or no contribution to the FID signal that is detected after the second pulse. Similarly, if the value of t_1 is such that $\sin(2\pi\nu_{\mathrm{A}}t_1)$ is equal to zero or has a small value, there will be little or no signal detected from proton A. The signals from proton A and proton B have effectively been separated from each other, occurring at different values of t_1. This dependence on t_1 is the reason that the method is called *correlation spectroscopy*.

The experiment consists of many repetitions of the pulse sequence with different values of t_1. Let us assume that 1000 repetitions are carried out with values of t_1 ranging from 0 to a convenient maximum value that allows a number of precession cycles (1 microsecond would allow 200 precession cycles in a 200 MHz instrument). The FID signal is recorded numerically as a discrete set of values. We assume that 1000 (10^3) data points are taken for each value of t_1. This gives us a total of 10^6 data points, each one corresponding to a specific value of t_1 and a specific value of t_2.

The Fourier transform for each FID signal is carried out (integrating over t_2), giving one spectrum as a function of a frequency ν_2 for each value of t_1. For some values of t_1 the FID signal contains a strong oscillation only for ν_A, whereas for other values of t_1 the signal contains a strong oscillation only for ν_B. For some values of t_1 there will be no strong oscillation. Each spectrum will contain no more than one strong peak. Since the calculation is carried out numerically each transform consists of a set of numerical values, one for each of a set of values of ν_2. Let us assume that each transform consists of 1000 points (this value doesn't have to equal the number of values of t_2 and an actual experiment might use more points than this). We now have a set of 10^6 numerical values, each one for a specific value of ν_2 and a specific value of t_1.

For a given value of ν_2, we have 1000 values of the FID signal intensity at different values of t_1. This is equivalent to a FID signal as a function of t_1. We now carry out another set of Fourier transforms (integrating over t_1) and obtain 1000 spectra in terms of a frequency ν_1, with one spectrum for each value of ν_2. We have carried out 10^6 Fourier transformations. Before the development of rapid computers and the fast Fourier transform algorithm, this would have required a great deal of computer time, but can now be done fairly quickly.

The results can be represented by a three-dimensional graph, with ν_1 plotted on one axis and ν_2 plotted on another. The strength of the absorption is plotted in a third dimension. Figure 24.12 depicts schematically a perspective view of a three-dimensional figure depicting the absorptions of protons A and B. The diagonal from lower left to upper right in the ν_1—ν_2 plane represents equal values of ν_1 and ν_2. The

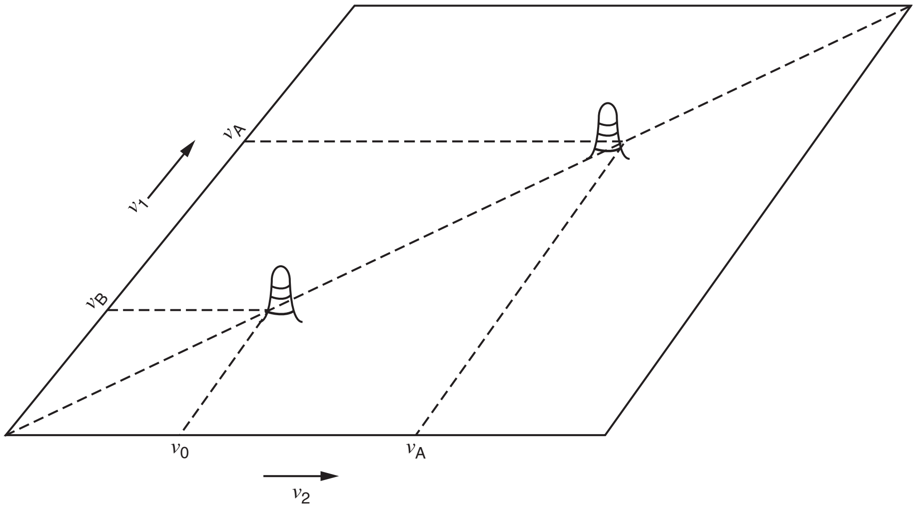

Figure 24.12 Schematic Perspective View of the Three-Dimensional Graph Representing the COSY Spectrum of Two Uncoupled Protons.

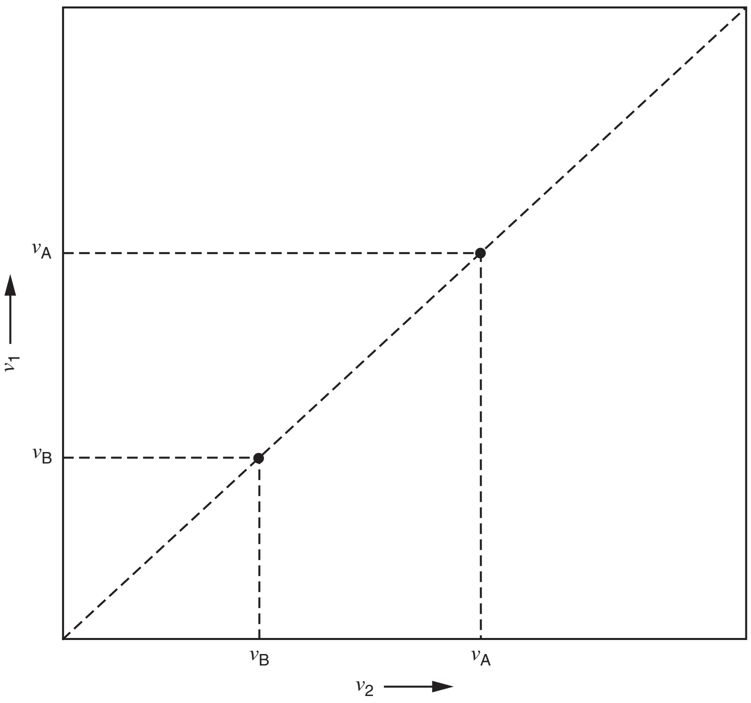

Figure 24.13 The Two-Dimensional COSY Spectrum of Two Uncoupled Protons.

peaks appear only on this diagonal at $\nu_1 = \nu_2 = \nu_A$ and at $\nu_1 = \nu_2 = \nu_B$, because it turns out that the two sets of FID signals are equivalent. It is more common to make a two-dimensional plot in which the spectral lines are represented by contours of equal intensity, so that spectral lines appear as blobs of closely spaced contour curves, as in Figure 24.13. Because of the use of two-dimensional plots, COSY experiments and other similar experiments are referred to as *two-dimensional NMR*.

Now consider the case that protons A and B have a nonzero coupling constant J_{AB}. The magnetic field at each proton has a spin–spin coupling contribution from the other proton. This contribution is transmitted through the electrons in the bonds between the protons and is generally significant only if there are no more than three bonds between the protons. The contribution to the magnetic field from a coupled proton is a time-dependent contribution because of the precession of the spins. There is a tendency of the rate of precession of one proton to modify the precession of the other proton. We say that magnetism is transferred from one proton to the other. The precession of a pair of coupled protons can be represented as a combination of two precession rates, one corresponding to the precession rate of each of the protons. Both frequencies are encoded in the FID signal. When the FID signal is Fourier transformed, both the frequency ν_A and the frequency ν_B can appear in the same FID signal. The same is true of the spectrum obtained by the second Fourier transform. The result is a symmetrical two-dimensional spectrum as shown in Figure 24.14. The multiplet splitting still splits the spectral lines, so there are four small peaks in a square, as seen in the diagram.

The advantage of the COSY procedure is the appearance of the off-diagonal spectral features, which clearly identify the coupled pairs of protons. In our case of two coupled protons, the spectrum is simple and this is not a useful advantage. In the case of more complicated substances, overlapping multiplets can be difficult to assign, and the COSY

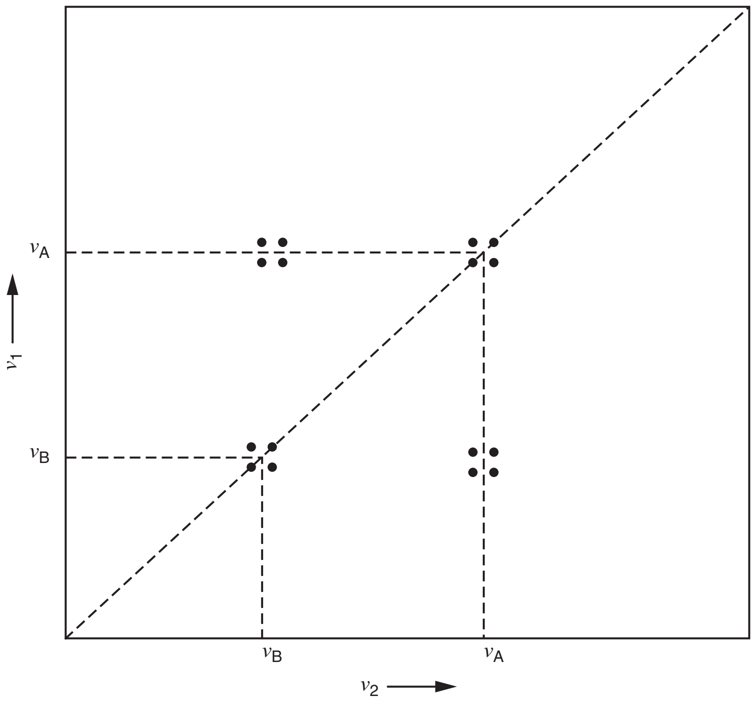

Figure 24.14 The Two-Dimensional COSY Spectrum of Two Coupled Protons.

results can eliminate any uncertainty. Figure 24.15 shows the HH-COSY spectrum of methyl vinyl ketone. The couplings between protons are clearly identified from the off-diagonal spectral features.

The HETCOR experiment is similar to the COSY experiment except that it deals with multiplet coupling between nuclei of different types, such as protons and ^{13}C nuclei. Other experiments such as the HETCOR experiment and the NOESY experiment are discussed in the books by Farraro, Farraro and Nakamoto, and Croasman and Carlson.[8]

PROBLEMS

Section 24.5: Fourier Transform NMR Spectroscopy

24.34 Construct an accurate graph of the function

$$I(t) = (\cos(t) + 5\cos(2t))e^{-t/10}$$

This function resembles a FID signal containing two frequencies.

24.35 Find the Fourier transform $I(t)$ of the function $e^{-a|\omega|}$.

24.36 Find the inverse Fourier transform $c(\omega)$ of the function $I(t) = e^{-at^2}\sin(bt)$. Construct an accurate graph of this Fourier transform.

24.37 **a.** Find the inverse Fourier transform $c(\omega)$ of the function $I(t) = e^{-|at|}\sin(bt)$. If $a = 1/T_1$, this function could represent a FID signal of a single frequency $b/2\pi$ decaying because of the spin–lattice relaxation.

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[8] Thomas C. Farrar, *Introduction to Pulse NMR Spectroscopy*, The Farragut Press, Chicago, 1989; Thomas C. Farrar and Edwin D. Becker, *Pulse and Fourier Transform NMR*, Academic Press, New York, 1971; W. R. Croasman and R. M. K. Carlson, *Two-Dimensional NMR Spectroscopy—Applications for Chemists and Biochemists*, VCH Publishers, Inc., New York, 1987.

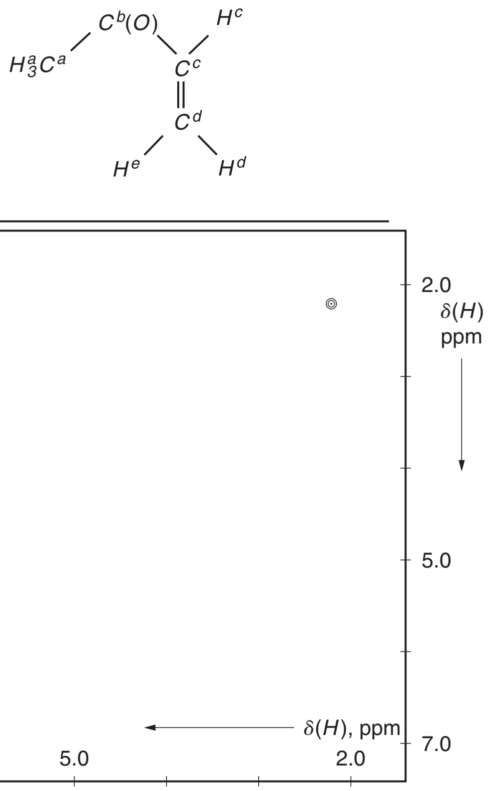

Figure 24.15 The Two-Dimensional COSY Spectrum of Methyl Vinyl Ketone in Deuterated Benzene. From T. C. Farrar, *Introduction to Pulse NMR Spectroscopy*, Farragut Press, Chicago, 1989, p. 181.

b. Construct an accurate graph of the Fourier transform from part a for several different values of a and b. Tell in words how the spin–spin relaxation time affects the width of the spectral line.

24.38 There is a useful theorem for the Fourier transform of a product of two functions, called the *convolution theorem* or the *Faltung theorem* (Faltung is German for “folding”). The convolution of two functions $f(x)$ and $g(x)$ is defined as the integral

$$\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} f(y)g(x-y)dy$$

This integral is a function of x, and its Fourier transform is equal to $F(k)G(k)$ where $F(k)$ is the Fourier transform of $f(x)$ and $G(k)$ is the Fourier transform of $g(x)$.[9] Use this theorem to find the inverse Fourier transform of $I(t) = e^{-at^2}\sin(bt)$. Verify that your answer is the same as that of Problem 24.36.

24.39 The Fourier transform of e^{iat} is proportional to the Dirac delta function. Argue that the integral

$$\int_{-\infty}^{\infty} e^{iat}e^{i\omega t}dt$$

diverges (becomes infinite) if $a = \omega$ and vanishes if $a \neq \omega$.

Summary of the Chapter

Magnetic resonance spectroscopy is absorption spectroscopy in which the sample substance is placed in a magnetic field, causing spin states that are degenerate in the

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[9] Philip M. Morse and Herman Feshbach, *Methods of Theoretical Physics*, Part I, McGraw-Hill, New York, 1953, p. 464ff.

absence of the field to have different energies. The two principal types of magnetic resonance spectroscopy are electron spin resonance (ESR) and nuclear magnetic resonance (NMR). In ESR spectroscopy, a substance with unpaired electrons absorbs radiation of a fixed frequency when the externally applied magnetic field is such that the magnetic field is

$$B_{\text{res}} = \frac{h\nu}{g\beta_e}$$

where g is known as the g factor of the electron, and β_e is called the Bohr magneton. Since the magnetic field "felt" by the electrons includes a term due to nuclear spins in the molecule, structural information can be obtained from the ESR spectrum.

NMR spectroscopy involves transitions of nuclear spins from one state to another in a magnetic field with absorption of radiation. The applied magnetic field at a given nucleus must be

$$B_{\text{res}} = \frac{h\nu}{g_{\text{N}}\beta_{\text{N}}}$$

where g_{N} is the nuclear g factor for the particular nucleus, and β_{N} is the nuclear magneton (same for every nucleus).

The field at a given nucleus contains two contributions in addition to the externally applied field. One is due to shielding of the electrons around the nucleus and is expressed by the chemical shift. The other is due to the presence of other spins in the molecule and gives rise to spin–spin splitting of spectral lines. Interpretation of the chemical shifts and spin–spin splittings gives structural information.

Fourier transform NMR techniques have become the standard for many laboratories. In these techniques, the precession of magnetization vectors is sensed to produce a free-induction decay (FID) signal. This signal is subjected to a Fourier transformation to obtain a spectrum as a function of frequency. Two-dimensional NMR techniques can provide additional information.

ADDITIONAL PROBLEMS

24.40 **a.** Would H_2 have an ESR spectrum? If so, describe the spectrum.

b. Would H_2 have an NMR spectrum? If so, describe the spectrum.

24.41 Describe qualitatively the following spectra:

a. The ESR spectrum of an isolated ^{17}O atom ($I = 5/2$).

b. The ESR spectrum of $^{16}O_2$ ($I = 0$).

c. The ESR spectrum of an isolated ^{35}Cl atom ($I = 3/2$).

d. The proton NMR spectrum of benzene.

24.42 Tell how you would distinguish between each pair of substances.

a. Dimethyl ether and ethanol

b. 3-Pentanone and 2-pentanone

c. 1-Chloropropane and 2-chloropropane (The spin–spin coupling between protons and chlorines does not lead to spin–spin splitting.)

24.43 Label each statement as either true or false. If a statement is true only under special circumstances, label it as false.

a. Every molecule exhibits an electron spin resonance spectrum.

b. Every molecule exhibits a nuclear magnetic resonance spectrum.

c. Every molecule containing hydrogen exhibits a proton NMR spectrum.

d. Two protons with the same chemical shift can exhibit spin–spin coupling but not spin–spin splitting.

e. The classical picture of Larmor precession is not useful in understanding NMR.

24.44 Tell how you would distinguish between each pair of substances.

a. Methyl acetate and propanoic acid

b. $^{1}H^{35}Cl$ and $^{2}H^{35}Cl$

c. $HC{\equiv}CH$ and $HC{\equiv}CCl$

4

The Reconciliation of the Macroscopic and Molecular Theories of Matter

25

Equilibrium Statistical Mechanics. I. The Probability Distribution for Molecular States

PRINCIPAL FACTS AND IDEAS

1. Statistical mechanics is the mathematical connection between the microscopic states of mechanics and the macroscopic states of thermodynamics.
2. Statistical mechanics identifies macroscopic states with averages over microscopic states.
3. A model system that represents a dilute gas is a set of noninteracting particles.
4. For this model system we can derive a formula for the probability of a molecular state.

25.1

The Quantum Statistical Mechanics of a Simple Model System

In Part III of this textbook, we discussed the quantum-mechanical states of single atoms and molecules. We now focus on systems containing many molecules. There are two principal types of states that we need to discuss: (1) the mechanical states (*microscopic states* or *microstates*) of the entire system, and (2) the thermodynamic states (*macroscopic states* or *macrostates*) of the system.

Macroscopic states involve variables that pertain to the entire system, such as the pressure P, the temperature T, and the volume V. For a fluid system of one substance and one phase, the equilibrium macrostate is specified by only three variables, such as P, T, and V. If we assume that classical mechanics is an adequate approximation, the microstate of such a system is specified by the position and velocity of every particle in the system. If quantum mechanics must be used for a dilute gas, there are several quantum numbers required to specify the state of each molecule in the system. This is a very large number of independent variables or a very large number of quantum numbers. Statistical mechanics is the theory that relates the small amount of information in the macrostates and the large amount of information in the microstates.

A Simple Model System

In order to introduce the principles of statistical mechanics we discuss a *model system*, which means a nonexistent system that is simpler to analyze than a real system. Our model system consists of four harmonic oscillators, all with the same frequency ν. The harmonic oscillators in the model system can be distinguished from each other and do not exert forces on each other. This is of course not a large system containing many molecules, but will serve to introduce some of the concepts of statistical mechanics.

The Hamiltonian operator of the system is a sum of four harmonic oscillator Hamiltonians:

$$\widehat{H}_{\text{system}}(1,2,3,4) = \widehat{H}(1) + \widehat{H}(2) + \widehat{H}(3) + \widehat{H}(4) \tag{25.1-1}$$

$\widehat{H}(1)$ is the Hamiltonian operator of harmonic oscillator number 1, and so forth, as shown in Eq. (15.4-1). The numbers in the parentheses are abbreviations for x_1, x_2, x_3, and x_4, the coordinates of the four oscillators. There are no terms involving two or more coordinates in the same term because the oscillators do not interact with each other.

The Hamiltonian operator in Eq. (25.1-1) corresponds to a time-independent Schrödinger equation that can be solved by separation of variables, using a trial solution:

$$\Psi(1,2,3,4) = \psi_1(1)\psi_2(2)\psi_3(3)\psi_4(4) \tag{25.1-2}$$

When the solution is carried out, the factors $\psi_1(1)$, $\psi_2(2)$, $\psi_3(3)$, and $\psi_4(4)$ are harmonic oscillator energy eigenfunctions with quantum numbers v_1, v_2, v_3, and v_4. Since the oscillators are distinguishable from each other, the system wave function does not have to be symmetrized or antisymmetrized, and there are no restrictions on the values of the quantum numbers. The system energy eigenvalues corresponding to Eq. (25.1-2) are

$$E = \varepsilon_{v_1} + \varepsilon_{v_2} + \varepsilon_{v_3} + \varepsilon_{v_4} \tag{25.1-3}$$

where ε_{ν_1}, ε_{ν_2}, ε_{ν_3}, and ε_{ν_4} are harmonic oscillator energy eigenvalues corresponding to the quantum numbers ν_1, ν_2, ν_3, and ν_4. In this chapter, we will use a lowercase ε for a molecular energy eigenvalue and a lowercase ψ for a molecular wave function. We will use reserve E for a system energy eigenvalue and capital Ψ for a system wave function.

Exercise 25.1

a. Assume that the four oscillators in our model system are indistinguishable and are fermions. Antisymmetrize the wave function of Eq. (25.1-2) by writing 24 terms with appropriate positive and negative signs. Exchange a few pairs of coordinates to satisfy yourself that the wave function is antisymmetric. Show that no two quantum numbers can be equal to each other. Write the wave function as a Slater determinant.

b. Assume that the four oscillators in our system are indistinguishable and are bosons. Symmetrize the wave function of Eq. (25.1-2) by writing 24 terms with positive signs. Exchange a few pairs of coordinates to satisfy yourself that the wave function is symmetric. Show that it is possible for two or more quantum numbers to be equal to each other.

From the expression for the energy eigenvalues of a harmonic oscillator the energy of the system is

$$E = h\nu(v_1 + v_2 + v_3 + v_4) + 4\left(\frac{1}{2}h\nu\right) \tag{25.1-4}$$

The final term is the zero-point energy. We change the zero of potential energy so that the ground-state vibrational energy is equal to zero, and Eq. (25.1-4) becomes

$$E = h\nu(v_1 + v_2 + v_3 + v_4) \tag{25.1-5}$$

We require three variables such as the energy, volume, and amount of substance to specify the equilibrium macrostate of a fluid system. The energy of our model system is independent of its volume, so its macrostate is specified by two variables, the energy and the number of particles in the system. We consider the macrostate corresponding to $E = 4h\nu$ and $N = 4$. The 35 system microstates compatible with this macrostate are listed in Table 25.1, and any one of these microstates might be occupied, given the specified macrostate.

We have labeled the microstates with an index k that ranges from 1 to 35. The set of numbers $N_0(k), N_1(k), N_2(k), N_3(k)$, and $N_4(k)$ specify the number of oscillators occupying each oscillator state for a given system microstate number k. Such a set of numbers is called a *distribution*. We denote a distribution by $\{N\}$, a symbol that stands for the entire set of N's. The distribution for each of the 35 system states is exhibited in Table 25.1. Several of the system states have the same distribution, and we denote the number of system states corresponding to a given distribution by $W(\{N\})$. There are two distributions with $W = 12$, one with $W = 6$, one with $W = 4$, and one with $W = 1$.

Exercise 25.2

Assuming that the four harmonic oscillators in our system are indistinguishable fermions, make a list of the possible microstates of the system.

Table 25.1 Vibrational States for a System of Four Harmonic Oscillators

System State No. (k)	v_1	v_2	v_3	v_4	N_0	N_1	N_2	N_3	N_4	$W(\{N\})$
1	1	1	1	1	0	4	0	0	0	1
2	0	1	1	2	1	2	1	0	0	12
3	0	1	2	1	1	2	1	0	0	
4	0	2	1	1	1	2	1	0	0	
5	1	0	1	2	1	2	1	0	0	
6	1	0	2	1	1	2	1	0	0	
7	2	0	1	1	1	2	1	0	0	
8	2	1	0	1	1	2	1	0	0	
9	1	2	0	1	1	2	1	0	0	
10	1	1	0	2	1	2	1	0	0	
11	2	1	1	0	1	2	1	0	0	
12	1	2	1	0	1	2	1	0	0	
13	1	1	2	0	1	2	1	0	0	
14	0	0	2	2	2	0	2	0	0	6
15	0	2	0	2	2	0	2	0	0	
16	2	0	0	2	2	0	2	0	0	
17	0	2	2	0	2	0	2	0	0	
18	2	0	2	0	2	0	2	0	0	
19	2	2	0	0	2	0	2	0	0	
20	0	0	1	3	2	1	0	1	0	12
21	0	0	3	1	2	1	0	1	0	
22	0	1	0	3	2	1	0	1	0	
23	0	3	0	1	2	1	0	1	0	
24	1	0	0	3	2	1	0	1	0	
25	3	0	0	1	2	1	0	1	0	
26	0	1	3	0	2	1	0	1	0	
27	0	3	1	0	2	1	0	1	0	
28	1	0	3	0	2	1	0	1	0	
29	3	0	1	0	2	1	0	1	0	
30	1	3	0	0	2	1	0	1	0	
31	3	1	0	0	2	1	0	1	0	
32	0	0	0	4	3	0	0	0	1	4
33	0	0	4	0	3	0	0	0	1	
34	0	4	0	0	3	0	0	0	1	
35	4	0	0	0	3	0	0	0	1	

The Postulates of Statistical Mechanics

Although we know the macrostate of our model system, we have no information about which of the 35 microstates the system occupies. We make an assumption that is called the *first postulate of statistical mechanics*:

> **Postulate 1.** *A macroscopic property of a system can be equated to the average (mean value) of the corresponding property over all of the system microstates that are compatible with the macroscopic state of the system.*

To define the type of average to be taken, we make another fundamental assumption, called the *second postulate of statistical mechanics*:

Postulate 2. *All system microstates of equal energy are equally probable and enter in the average of postulate 1 with equal weight.*

A more complete version of the second postulate assumes random *a priori* phases of the time-dependent factors in the wave functions and involves quantum-mechanical density matrices.[1] We present only the simplest version of statistical mechanics.

Postulate 2 is equivalent to assuming that over some long period of time during which the system remains in a given macrostate, it would spend equal time in each of the microstates that correspond to the given macrostate. This assumption is sometimes called the *ergodic hypothesis*. For a system of many particles there are very many possible microstates corresponding to a single macrostate and there is no guarantee that all of them would be occupied in any period of time, no matter how long, or that each of them would be occupied for the same length of time. The postulates must be regarded as hypotheses whose use is justified only by comparing their consequences with experiment.

The Probability Distribution of Molecular States

We now seek the probability that a randomly selected oscillator would occupy a particular vibrational state. All of the harmonic oscillators are alike, so we focus on oscillator number 1. Of the 35 system microstates, there are 15 states with $v_1 = 0$. Since all of the 35 possible system microstates are equally probable, the probability that a randomly chosen oscillator will have $v = 0$ is

$$p_0 = \frac{15}{35} = 0.42857 \tag{25.1-6a}$$

There are 10 states for which $v_1 = 1$, so that

$$p_1 = \frac{10}{35} = 0.28571 \tag{25.1-6b}$$

The other probabilities are

$$p_2 = \frac{6}{35} = 0.17143 \tag{25.1-6c}$$

$$p_3 = \frac{3}{35} = 0.08571 \tag{25.1-6d}$$

$$p_4 = \frac{1}{35} = 0.02857 \tag{25.1-6e}$$

Exercise 25.3

Show that the same probabilities occur if oscillator number 2 is examined.

These probabilities were obtained by averaging over system microstates, so we call them an *average probability distribution*. When we use these probabilities to calculate an average molecular quantity we will actually have a double average: an average over molecular states using a probability distribution that was itself obtained by averaging

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[1] L. E. Reichl, *Statistical Physics*, University of Texas Press, Austin, 1980.

over system microstates. The *mean value* is the most common type of average. The mean of a set of values $w_1, w_2, \ldots, w_N$ is given by

$$\langle w \rangle = \frac{1}{N}(w_1 + w_2 + \cdots + w_N) = \frac{1}{N}\sum_{i=1}^{N} w_i \tag{25.1-7}$$

If some of values are equal to each other, we can write a sum with fewer terms. We arrange the values so that the values from w_1 to w_M are all different from each other and all of the other values are equal to one or another of the first M values. Let N_i be the number of values equal to w_i. We can write the mean value with a shorter sum:

$$\langle w \rangle = \frac{1}{N}\sum_{i=1}^{M} N_i w_i = \sum_{i=1}^{M} p_i w_i \tag{25.1-8}$$

where $p_i = N_i/N$. The quantity p_i is the fraction of the values that equal w_i and is also equal to the probability that a randomly chosen value will equal w_i.

According to our first postulate, macroscopic quantities are equal to averages of appropriate mechanical quantities. The macroscopic energy is defined thermodynamically in terms of work and heat. It is denoted by U and is called the internal energy or thermodynamic energy. We now assert that the internal energy U is equal to $\langle E \rangle$, the average mechanical energy of the system. In our example, we consider only states with $E = 4h\nu$, so $U = 4h\nu$. The average energy of an oscillator is given by

$$\langle \varepsilon \rangle = \sum_{v=0}^{4} p_v \varepsilon_v = p_0 0 + p_1 h\nu + p_2 2h\nu_3 + p_3 3h\nu + p_4 4h\nu \tag{25.1-9}$$

This must equal $U/4$, which is equal to $h\nu$.

Exercise 25.4

Calculate $\langle \varepsilon \rangle$ using the probabilities in Eq. (25.1-6) and show that to five significant digits $\langle \varepsilon \rangle = (1.0000)h\nu$.

When we discuss a real system, the average distribution will be impossible to calculate because of the large number of microstates. We will seek another approach, which we now illustrate with our model system. Return to Table 25.1 and look at the W values of the different distributions. Since all of the system microstates are equally probable, the distribution with the largest W is the *most probable distribution*. In our example, there are two distributions that correspond to $W = 12$, so we call the average of these two distributions the most probable distribution.

Table 25.2 and Figure 25.1 exhibit the average distribution, the most probable distribution, and the Boltzmann distribution of Eq. (22.5-2) that corresponds to the same average energy per oscillator. All three distributions have the same general trend, that molecular states of higher energy are less probable. The Boltzmann distribution does not stop at $v = 4$, because it applies to a system of many oscillators with an average energy equal to $h\nu$.

Exercise 25.5

Show that the most probable distribution gives the correct value of $\langle \varepsilon \rangle$.

Table 25.2 Average, Most Probable, and Boltzmann Probability Distributions for the Vibrational States of Four Harmonic Oscillators

Value of v	p_v (Average)	p_v (Most Probable)	p_v (Boltzmann)
0	0.42857	0.3750	0.50000
1	0.28571	0.3750	0.25000
2	0.17143	0.1250	0.12500
3	0.08571	0.1250	0.06250
4	0.02857	0	0.03125
5	0	0	0.01562
6	0	0	0.00781

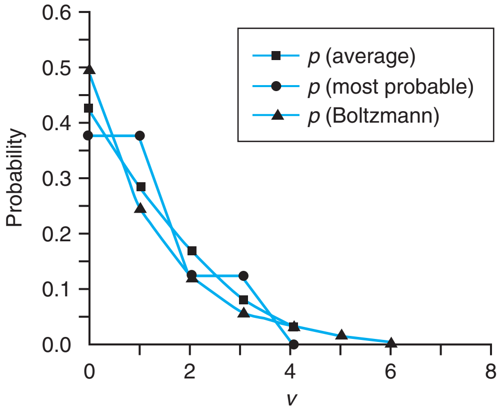

Figure 25.1 The Average Distribution and the Most Probable Distribution for the Vibrational Energy of Four Harmonic Oscillators.

EXAMPLE 25.1

Obtain the Boltzmann probability distribution for our model system that corresponds to an average energy per oscillator of $h\nu$.

Solution

The Boltzmann distribution of Eq. (22.5-1) is not normalized. The normalized Boltzmann probability distribution is given by

$$(\text{Probability of a state } i) = p_i = \frac{1}{z} e^{-\varepsilon_i / k_B T} \qquad (25.1\text{-}10)$$

where the divisor z is chosen to give normalization:

$$z = \sum_{i=0}^{\infty} e^{-\varepsilon_i / k_B T} \qquad (25.1\text{-}11)$$

Note that the Boltzmann probability distribution is not restricted to the states that we have listed, so that the upper limit of the sum is infinite. The formula for z is the sum of a geometric progression, a well-known sum:

$$\sum_{v=0}^{\infty} a^v = \frac{1}{1-a} \qquad (25.1\text{-}12)$$

where we must require that $a < 1$. Since $h\nu/k_\mathrm{B}T > 0, e^{-h\nu/k_\mathrm{B}T} < 1$ and our sum is:

$$z = \sum_{v=0}^{\infty} e^{-vh\nu/k_\mathrm{B}T} = \sum_{v=0}^{\infty} \left(e^{-h\nu/k_\mathrm{B}T}\right)^{v} = \frac{1}{1 - e^{-h\nu/k_\mathrm{B}T}} \tag{25.1-13}$$

so that the normalized Boltzmann probability distribution is

$$p_v = (1 - e^{-h\nu/k_\mathrm{B}T})\, e^{-vh\nu/k_\mathrm{B}T} \tag{25.1-14}$$

We will show later in the chapter that the formula for the mean energy is given by

$$\langle \varepsilon \rangle = \frac{h\nu}{e^{h\nu/k_\mathrm{B}T}{}_{-1}} \tag{25.1-15}$$

In order to have $\langle \varepsilon \rangle$ equal to $h\nu s$ we must have a value of the temperature given by

$$e^{h\nu/k_\mathrm{B}T} - 1 = 1 \quad \text{or} \quad \frac{h\nu}{k_\mathrm{B}T} = \ln(2) \tag{25.1-16}$$

which gives the normalized Boltzmann distribution for our model system of four harmonic oscillators:

$$p_{v(\mathrm{Boltzmann})} = \frac{1}{2} e^{-v\ln(2)} = \frac{1}{2}\left(e^{-\ln(2)}\right)^{v} = \frac{1}{2} 2^{-v} \tag{25.1-17}$$

Exercise 25.6

Sum the values for the Boltzmann distribution in Table 25.2 for $v = 0$ to $v = 6$ and see how close the result is to 1.000. The error in a partial sum of a geometric progression is equal to the magnitude of the last term included. Does your sum conform to this?

PROBLEMS

Section 25.1: The Quantum Statistical Mechanics of a Simple Model System

25.1 **a.** Find the total number of system vibrational states for a system of three harmonic oscillators with a total energy of $3h\nu$.

b. Find the average molecular probability distribution for the vibrational states of the system of part a, as was done in Section 25.1.

c. Find the most probable probability distribution for the vibrational states of the system of part a, as was done in Section 25.1.

25.2 **a.** List the system states for a system of four harmonic oscillators with a total energy of $3h\nu$.

b. Find the average molecular probability distribution for the vibrational states of the system of part a.

c. Find the most probable probability distribution for the vibrational states of the system of part a.

25.3 **a.** Find the total number of system vibrational states for a system of two harmonic oscillators with a total energy of $4h\nu$.

b. Find the average molecular probability distribution for the vibrational states of the system of part a.

c. Find the most probable probability distribution for the vibrational states of the system of part a.

25.4 Consider a system of four distinguishable rigid rotating diatomic molecules with a total energy of $20hB$, where B is the rotational constant.

a. Make a list of the possible system states analogous to that of Table 25.1. Don't forget the degeneracies.

b. Find the average distribution of molecular levels, analogous to that of Eq. (25.1-7).

c. Find the most probable distribution.

25.5 The standard deviation of a statistical sample of N members, $w_1, w_2, \ldots, w_N$, is defined by

$$s = \left[\frac{1}{N-1}\sum_{i=1}^{N}(w_i - \langle w\rangle)^2\right]^{1/2}$$

Calculate the standard deviation of the energy of an oscillator in our model system.

25.2 The Probability Distribution for a Dilute Gas

We now want to consider macroscopic systems of many molecules. We focus on the simplest macroscopic system, a dilute gas of a single substance. We assume that the macroscopic state of our dilute gas is specified by the internal energy U, the volume V, and the amount of the single substance n. We consider only system microstates corresponding to the energy eigenvalue E equal to U and corresponding to the correct volume and the correct number of molecules.

In a dilute gas the molecules are on the average far enough from each other that the intermolecular forces are negligible, as can be seen in Problem 25.9. In this case the system Hamiltonian operator can be written as a sum of Hamiltonian operators for independent molecules:

$$\widehat{H}_{\text{sys}} = \sum_{i=1}^{N}\widehat{H}(i) \tag{25.2-1}$$

where $\widehat{H}(i)$ is the molecular Hamiltonian operator for molecule number i, and where N is the number of molecules in the system. The label (i) stands for the coordinates of all of the nuclei and electrons in molecular number i. There are no terms in which the coordinates of particles in two or more molecules occur because the intermolecular forces have been neglected. In addition to the dilute gas, there are crystal models due to Einstein and to Debye in which Eq. (25.2-1) applies. We discuss these models in a later chapter.

The system Hamiltonian of Eq. (25.2-1) corresponds to a Schrödinger equation that can be solved by the separation of variables, a method that we have used a number of times. It gives energy eigenvalues that are a sum of molecular energy eigenvalues

$$E_k = \sum_{i=1}^{N}\varepsilon_{k_i} \tag{25.2-2}$$

and energy eigenfunctions that are products of molecular energy eigenfunctions

$$\Psi_k = \prod_{i=1}^{N}\psi_{k_i}(i) \tag{25.2-3}$$

where the subscript k_i is an abbreviation for the values of the quantum numbers that are needed to specify the molecular state of molecule number i, given that the system state is Ψ_k. We assume that the molecule energy eigenvalues ε_{k_i} and molecule wave functions ψ_{k_i} are known to a usable approximation.

The molecules in our system are indistinguishable from each other in the same way that electrons are indistinguishable from each other. If the total number of electrons, protons, and neutrons in a molecule is an odd number, the molecule is a fermion, because exchanging two molecules changes the sign of the wave function an odd number of times. The system wave function must be antisymmetrized and the Pauli exclusion principle applies. No two fermion molecules in the system can occupy exactly the same state. If the molecule contains an even number of electrons, protons, and neutrons it is a boson, and the wave function must be symmetrized. The Pauli exclusion principle does not apply.

Exercise 25.7

Identify each of the following as a fermion or boson:

a. A ^{13}C atom
b. F_2 if both atoms are ^{19}F
c. NO if both atoms are the common isotopes
d. CH_4 if all atoms are the common isotopes
e. CH_4 if the C atom is ^{13}C

The Average Distribution

We want to find the probability that a randomly chosen molecule is in a given molecule state. We first consider the average distribution. If the system is in microstate k, let the number of molecules in level j be denoted by $N_j(k)$. The set of numbers $N_1(k)$, $N_2(k)$, $N_3(k)$, and so forth, is a molecular distribution that specifies the occupation of all of the molecular energy levels if the system is in system microstate k. We denote this distribution by the single symbol $\{N(k)\}$. This distribution is analogous to the distribution on a single line of Table 25.1 for our model system of four oscillators.

We must average over all system microstates that have E equal to U and N equal to $N_{\text{Av}}n$, and correspond to the correct value of V. We denote the number of such microstates by W. This degeneracy of a system energy level is analogous to the degeneracy of 35 for the energy level $E = 4h\nu$ in the model system of four harmonic oscillators. For a many-particle system, W will be a very large number. The number of molecules in molecule energy level j averaged over all of these system microstates is:

$$\bar{N}_j = \frac{1}{\Omega}\sum_{k=1}^{\Omega} N_j(k) \tag{25.2-4}$$

We call the distribution $\{\bar{N}\}$ the *average distribution*. Unfortunately, the average distribution in Eq. (25.2-4) cannot be computed because Ω is a very large number.

The Most Probable Distribution

Since we cannot find the average distribution, we will seek the most probable distribution.[2] In our model system of four oscillators, we saw that the average distribution

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[2] Our discussion follows that of N. Davidson, *Statistical Mechanics*, McGraw-Hill, New York, 1962, Chapter 6.

and the most probable distribution resembled each other. Although we do not prove this fact, the average distribution and the most probable distribution become identical in the limit of an infinitely large system, which is called the *thermodynamic limit*.

Let $W(\{N\})$ be the number of system microstates that correspond to a given distribution $\{N\}$. The sum of the W's for all distributions that correspond to the correct values of E, V, and N obeys

$$\sum_{\{N\}} W(\{N\}) = \Omega \tag{25.2-5}$$

where the sum includes one term for each distinct distribution. By the second postulate of statistical mechanics, all system microstates with the correct values of E, V, and N are equally probable. The distribution with the largest value of W is therefore the most probable distribution.

We now obtain an expression for W for a given distribution. Consider energy level number j with degeneracy g_j. Let N_j be the number of molecules occupying states in level j. We will assume that our system contains very many molecules. Since we have already assumed that it is a dilute gas, we must assume that it is confined in an extremely large volume. Equation (22.1-4) shows that when the dimensions of a rectangular container become very large, the translational energy levels of a particle confined in the container become very close together. The degeneracies of the translational energy levels also become very large, and if necessary, we can group energy levels of nearly equal energies together to get very large degeneracies. These assumptions correspond to

$$N_j \gg 1 \tag{25.2-6}$$

and

$$g_j \gg N_j \tag{25.2-7}$$

where N_j is the number of molecules occupying molecule energy level j, and g_j is the degeneracy of the level. The condition of Eq. (25.2-7) is called *dilute occupation*.

We first assume that the molecules are fermions, so that no more than one molecule can occupy each state. We need the number of ways to divide the g_j states of level j into N_j occupied states and $g_j - N_j$ unoccupied states. We denote this number by t_j. Counting up this number of ways is an elementary statistics problem.[3] Consider first a set of N balls and N boxes, with each box able to hold no more than one ball. The first ball can go into any of N boxes, the second ball can go into any of $N - 1$ boxes, and so forth, until the final ball has only one empty box to go into. Since the choices are independent, the number of ways of making all of the choices is the product of the number of ways of making the individual choices:

$$\text{Number of ways of choosing} = N(N-1)(N-2)\cdots(3)(2)(1) = N! \tag{25.2-8}$$

where $N!$ stands for *N factorial*, the product of all of the integers starting with N and ranging down to 1. We say that $N!$ is the number of *permutations* of N objects.

Now consider the number of ways to pick N occupied states from g possible states, where $g > N$. This is analogous to having more boxes than balls. There are g choices

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[3] J. E. Freund, *Modern Elementary Statistics*, 7th ed., Prentice-Hall, Englewood Cliffs, NJ, 1988, p. 97ff.

for the first pick, there are $g - 1$ choices for the second pick, until there are $g - (N - 1)$ choices for the Nth pick.

$$\begin{aligned}\text{Number of ways of choosing} = P(g, N) &= g(g-1)(g-2)\cdots(g-(N-1)) \\ &= \frac{g!}{(g-N)!} \qquad (25.2\text{-}9)\end{aligned}$$

The quantity $P(g, N)$ is called the number of permutations of N objects chosen from g objects. However, in our case the order in which the N occupied states are chosen is immaterial, so we must divide by $N!$, the number of ways of permuting N objects. The result is called the number of *combinations* of g objects taken N at a time.

$$t = C(g, N) = \frac{g!}{(g-N)!N!} \qquad (25.2\text{-}10)$$

The expression in Eq. (25.2-10) is also the expression for a *binomial coefficient*, which is the coefficient of the $a^N b^{g-N}$ term in the expression for $(a + b)^g$.

We now apply Eq. (25.2-10) to energy level j. There are N_j factors in the quotient $g_j!/(g_j - N_j)!$ that do not cancel. Since in our case of dilute occupation $g_j \gg N_j$, all of the factors in the product are nearly equal to g_j, and the product of these factors is approximately equal to $g_j^{N_j}$. To a good approximation for fermion molecules

$$t_i \approx \frac{g_j^{N_j}}{N_j!} \qquad (25.2\text{-}11)$$

This expression gives $t_j = 1$ for $N_j = 0$ (an unoccupied level) since 0! is defined to equal unity and since any number raised to the zero power equals unity.

EXAMPLE 25.2

Find the percent error in approximating Eq. (25.2-6) by Eq. (25.2-11):

a. For $g_j = 100$ and $N_j = 3$

b. For $g_j = 1000000$ and $N_j = 3$

Solution

a. For $g_j = 100$ and $N_j = 3$

$$t_j = \frac{(100)(99)(98)}{100!} = \frac{970200}{100!}$$

$$t_j(\text{approx}) = \frac{(100)^3}{100!} = \frac{1000000}{100!} \qquad 3.07\%\ \text{error}$$

We do not evaluate 100! because it is a large number.

b. For $g_j = 1000000$ and $N_j = 3$

$$t_j = \frac{(1000000)(999999)(999998)}{1000000!} = \frac{9.9999700 \times 10^{17}}{1000000!}$$

$$t_j(\text{approx}) = \frac{(1000000)^3}{1000000!} = \frac{1.00000 \times 10^{18}}{1000000!} \qquad 0.00030\%\ \text{error}$$

Exercise 25.8

Find the percent error in approximating Eq. (25.2-10) by Eq. (25.2-11) if $g_j = 1000000000$ and $N_j = 3$.

For a system of bosons, we imagine N_j objects in g_j compartments in a long box, with $g_j - 1$ movable partitions between the compartments. Since there is no limit on the number of objects in a compartment, all possible orders (permutations) of the objects and partitions are allowed. Then realize that the partitions are indistinguishable from each other, and the objects are indistinguishable from each other. The version of Eq. (25.2-10) for bosons is therefore

$$t_j = \frac{(g_j + N_j - 1)!}{(g_j - 1)!N_j!} \quad \text{(bosons)} \tag{25.2-12}$$

There are N_j factors in the quotient $(g_j + N_j - 1)!/(g_j - 1)!$ that do not cancel. In the dilute occupation case $N_j \ll g_j$, so that Eq. (25.2-11) also applies to a system of boson molecules.

Exercise 25.9

Show that in the dilute occupation case, Eq. (25.2-11) also applies to boson molecules.

We will now apply Eq. (25.2-11) to our dilute gas, whether our molecules are bosons or fermions. For two independent energy levels the total number of ways to choose states is the product of the number of ways of choosing states for each level. For the entire distribution the number of system microstates is given by a product containing one factor as in Eq. (25.2-11) for each molecular energy level:

$$W(\{N\}) = \prod_{j=1}^{\infty} t_j \approx \prod_{j=1}^{\infty} \frac{g_j^{N_j}}{N_j!} \tag{25.2-13}$$

There are infinitely many molecule energy levels, as shown in the product limits. From now on we will omit the upper limits on sums or products over the energy levels, but will understand the product to include all possible molecular energy levels.

Only those distributions can be considered that conform to the specified values of N, E, and V. These constraints correspond to

$$\sum_j N_j = N \tag{25.2-14a}$$

$$\sum_j N_j \varepsilon_j = E \tag{25.2-14b}$$

$$\varepsilon_j \text{ must correspond to the correct volume for every } j \tag{25.2-14c}$$

The problem of finding the most probable distribution is now the problem of finding the distribution that corresponds to the largest value of $W(\{N\})$ subject to the constraints given by Eqs. (25.2-14a) and (25.2-14b).

In order to use the methods of calculus, we assume that the N_j's are able to take on any real values instead of taking on only integral values. A value of N_j corresponding to the maximum value of $W(\{N\})$ can be rounded to the closest integer to give the desired value. The maximum value subject to constraints is found by *Lagrange's method of undetermined* multipliers.[4] If we wish to find a relative maximum or minimum of a function $f = f(x, y, z)$ subject to two constraints we first express the constraints by equations of the form

$$u(x, y, z) = 0 \tag{25.2-15a}$$

and

$$w(x, y, z) = 0 \tag{25.2-15b}$$

We then find the point at which the following simultaneous equations are satisfied:

$$\frac{\partial}{\partial x}[f + \alpha u + \beta w] = 0 \tag{25.2-16a}$$

$$\frac{\partial}{\partial y}[f + \alpha u + \beta w] = 0 \tag{25.2-16b}$$

$$\frac{\partial}{\partial z}[f + \alpha u + \beta w] = 0 \tag{25.2-16c}$$

The parameters α and β are called *undetermined multipliers*. They can depend on other variables, but not on x, y, or z. If there are more than two constraints, there is an undetermined multiplier for each constraint.

It is easier to find the maximum of $\ln(W)$ than a maximum in W, because W equals a product of many factors, whereas $\ln(W)$ equals a sum of many terms, which is easier to differentiate than a product. The logarithm is a monotonic function of its argument, so that the largest value of $\ln(W)$ occurs together with the largest value of W. To find the maximum of $\ln(W)$ subject to the constraints of Eqs. (25.2-14a) and (25.2-14b), there is a set of simultaneous equations, one for each N_i:

$$\frac{\partial}{\partial N_i}\left[\ln(W) + \alpha\left(\sum_j N_j - N\right) - \beta\left(\sum_j N_j\varepsilon_j - E\right)\right] = 0 \quad (i = 1, 2, 3, \ldots) \tag{25.2-17}$$

The method is not changed by using the symbol $-\beta$ instead of β for one of the multipliers.

The logarithm of W is given by

$$\ln[W(\{N\})] = \sum_j [N_j \ln(g_j) - \ln(N_j!)] \tag{25.2-18}$$

We must find an approximation for $\ln(N_j!)$ that can be differentiated. This is *Stirling's approximation*:

$$N! \approx (2\pi N)^{1/2} N^N e^{-N} \tag{25.2-19}$$

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[4] H. Anton, *Calculus*, 3rd ed., Wiley, New York, 1988, p. 1032ff; R. G. Mortimer, *Mathematics for Physical Chemistry*, 3rd ed., Elsevier Academic Press, San Diego, 2005, p. 228ff.

For $\ln(N!)$

$$\ln(N!) \approx \frac{1}{2}\ln(2\pi N) + N\ln(N) - N \tag{25.2-20}$$

Stirling's approximation is more nearly correct for larger values of N. Because we assume that N_j is a large number, the first term is much smaller than the other terms. We omit it and write

$$\ln(N!) \approx N\ln(N) - N \tag{25.2-21}$$

You can see why we assumed that our system is very large. Not only did we require that $g_j \gg N_j$ for a typical energy level, we also need to assume that N_j is a large number in order to use this approximation.

Exercise 25.10

Using a table of factorials or a calculator that computes factorials, find the percent error in the results of the expression of Eq. (25.2-20) and that of Eq. (25.2-21) for $N = 10, N = 60$, and $N = 200$. Find the difference between the results of Eq. (25.2-20) and of Eq. (25.2-21) for $N = 1 \times 10^9$.

Substitution of Eqs. (25.2-18) and (25.2-21) into Eq. (25.2-17) gives a set of simultaneous equations (one equation for each value of i):

$$\frac{\partial}{\partial N_i}\left(\sum_j [N_j\ln(g_j) - N_j\ln(N_j) + N_j + \alpha N_j - \beta N_{j\varepsilon_j}] - \alpha N + \beta_E\right) = 0$$

The terms $-\alpha N$ and βE are independent of the N's and have zero derivatives. Because N_1, N_2, N_3, and so on, are all independent variables and since all of the N variables except for N_i are held fixed in the differentiation, only the term in the sum with $j = i$ has a nonzero derivative, and we have

$$\ln(g_i) - \ln(N_i) - 1 + 1 + \alpha - \beta\varepsilon_i = 0 \quad (i = 1, 2, 3, \ldots) \tag{25.2-22}$$

Fortunately, each equation contains only one variable. We solve Eq. (25.2-22) for N_i:

$$N_i = g_i e^{\alpha} e^{-\beta\varepsilon_i} \tag{25.2-23}$$

The probability that a randomly selected molecule is found in energy level j is equal to the fraction of molecules in that energy level:

$$p_j = \frac{N_j}{N} = \frac{1}{N} g_j e^{\alpha} e^{-\beta\varepsilon_j} \quad \text{(probability of level } j\text{)} \tag{25.2-24}$$

where we return to the use of the subscript j to designate a molecule energy level. All of the states of a level are equally probable since they have the same energy, so the probability of a molecular state is

$$p_i = \frac{N_i}{N} = \frac{1}{N} e^{\alpha} e^{-\beta\varepsilon_i} \quad \text{(probability of state } i\text{)} \tag{25.2-25}$$

where we now use the subscript i to designate a molecule state.

Equations (25.2-24) and (25.2-25) are for a gas with dilute occupation, in which the distinction between fermions and bosons is unimportant. If Eq. (25.2-10) or (25.2-12) is used in the expression for W instead of the expression in Eq. (25.2-11), the results for noninteracting fermions and bosons are

$$N_j = \frac{g_j e^{\alpha} e^{-\beta\varepsilon_j}}{1 + e^{\alpha} e^{-\beta\varepsilon_j}} \quad \text{(fermions)} \tag{25.2-26}$$

$$N_j = \frac{g_j e^{\alpha} e^{-\beta\varepsilon_j}}{1 - e^{\alpha} e^{-\beta\varepsilon_j}} \quad \text{(bosons)} \tag{25.2-27}$$

Exercise 25.11

Show that Eqs. (25.2-26) and (25.2-27) are correct.

For sufficiently large energies, the second terms in the denominators of both the expressions in Eqs. (25.2-26) and (25.2-27) become negligible, and both expressions approach

$$N_j = g_j e^{\alpha} e^{-\beta\varepsilon_j} \tag{25.2-28}$$

which is the same as Eq. (25.2-25).

PROBLEMS

Section 25.2: The Probability Distribution for a Dilute Gas

25.6 It would be impossible to write down the antisymmetrized wave function of a system containing more than a few fermions. Estimate the number of terms in an antisymmetrized wave function for a system containing a number of fermions equal to Avogadro's constant, using Stirling's approximation.

25.7 The number of distinct ways to choose states for N_j fermions from a level with degeneracy g_j is given by Eq. (25.2-10).

- **a.** Find the percent differences between the result of this formula and the result of Eq. (25.2-11) for $g_j = 1000$ and $N_j = 5$.
- **b.** Repeat the calculation for $g_j = 1000000$ and $N_j = 5$.

25.8 The number of distinct ways to choose states for N_j bosons from a level with degeneracy g_j is given by Eq. (25.2-12).

- **a.** Find the percent differences between the result of this formula and the result of Eq. (25.2-11) for $g_j = 1000$ and $N_j = 5$.
- **b.** Repeat the calculation for $g_j = 1000000$ and $N_j = 5$.

25.9 In order for the dilute-gas approximation to hold, the potential energy of interaction of the molecules must be negligible. The potential energy of two molecules can be represented by the Lennard–Jones formula

$$u_{LJ}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{25.2-29}$$

where r is the distance between the centers of the molecules and where ε and σ are parameters that have different values for each gas. For helium, $\sigma = 2.56 \times 10^{-10}$ m and $\varepsilon = 1.41 \times 10^{-22}$ J. Estimate the potential energy of 1.00 mol of argon gas at 1.00 atm and 298.15 K as follows: Calculate the volume per molecule, and assume that each molecule occupies a cubical volume. Estimate the average nearest-neighbor distance as the distance from the center of one cube to the center of the next cube. Evaluate the potential energy of a pair of nearest-neighbor molecules. Assume that each molecule is surrounded by twelve nearest-neighbor molecules and neglect interactions with more distant molecules. Remember that each intermolecular potential energy is shared by two molecules. Compare the potential energy with the kinetic energy, which is given by gas kinetic theory as $3nRT/2$, where n is the amount of gas in moles.

25.10 In order for the dilute-gas approximation to hold, the potential energy of interaction of the molecules must be negligible. The potential energy of two molecules can be represented by the Lennard–Jones formula exhibited in the previous problem. For carbon dioxide, $\sigma = 4.5 \times 10^{-10}$ m and $\varepsilon = 2.61 \times 10^{-21}$ J. Estimate the energy of attraction of 1.00 mol of carbon dioxide at molar volume 0.50 L mol^{-1} and temperature 298.15 K as follows: Calculate the volume per molecule, and assume that each molecule occupies a cubical volume. Estimate the average nearest-neighbor distance as the distance from the center of one cube to the center of the next cube. Evaluate the potential energy of a pair of nearest-neighbor molecules. Assume that each molecule is surrounded by twelve nearest-neighbor molecules and neglect interactions with more distant molecules. Remember that each intermolecular potential energy is shared by two molecules. Compare the potential energy with the kinetic energy, which is given by gas kinetic theory as $3nRT/2$, where n is the amount of gas in moles.

25.11 **a.** Use Lagrange's method of undetermined multipliers to find the constrained maximum of the function $f = e^{-(x^2+y^2)}$ subject to the constraint $x + y = 2$.

b. Find the maximum in an alternate way by replacing y by $2 - x$ in the original function and then finding the maximum by setting the derivative of the function with respect to x equal to zero.

25.12 **a.** Use Lagrange's method of undetermined multipliers to find the constrained maximum in the first octant (x and y both positive) of the function $f = e^{-(x^2+y^2)}$ subject to the constraint $x^2 + y^2 = 1$.

b. Find the maximum in an alternate way by replacing x^2 by $1 - y^2$ in the original function and then finding the maximum by setting the derivative of the function with respect to y equal to zero.

25.13 Find the maximum of the function $f = \sin(x)e^{-y^2}$ subject to the constraint $x - y = 0$.

25.3 The Probability Distribution and the Molecular Partition Function

In this section, we evaluate the parameters α and β and introduce the molecular partition function, a function that can be used to calculate values of thermodynamic variables for a dilute gas.

The Molecular Partition Function and the Parameter α

To remove the parameter α from the distribution in Eq. (25.2-23) we substitute this distribution into the constraint of Eq. (25.2-14a):

$$\sum_j g_j e^{\alpha} e^{-\beta\varepsilon_j} = N \tag{25.3-1}$$

The e^{α} factor in Eq. (25.3-1) can be factored out of the sum and the resulting equation can be solved for e^{α}:

$$e^{\alpha} = N\left[\sum_j g_j e^{-\beta\varepsilon_j}\right]^{-1} = \frac{N}{z} \tag{25.3-2}$$

where we define the *molecular partition function* z:

$$z = \sum_j g_j e^{-\beta\varepsilon_j} \quad \text{(definition of the molecular partition function)} \tag{25.3-3}$$

This sum is over the molecular energy levels.

The most probable distribution can now be written

$$N_j = \frac{N}{z} g_j e^{-\beta \varepsilon_j} \tag{25.3-4a}$$

The probability of finding a randomly selected molecule in molecule energy level j is equal to the fraction of molecules that are in this level:

$$p_j = \frac{N_j}{N} = \frac{1}{z} g_j e^{-\beta \varepsilon_j} \quad \text{(probability of level } j\text{)} \tag{25.3-4b}$$

The name "partition function" was chosen because z is related to the way in which the molecules are partitioned among the possible molecular states. The German name for a partition function is *Zustandsumme*, literally translated as "state sum" or "sum over states." This name is more descriptive than "partition function" and is occasionally used in the English language, with or without translation. The German name is the reason for using the letter z to denote the molecular partition function, but the letter q is also used by some authors.

Each term in Eq. (25.3-3) is proportional to the number of states in that level, so we can write the molecular partition function as a sum over states instead of a sum over levels:

$$z = \sum_i e^{-\beta \varepsilon_i} \quad \text{(sum over molecule states)} \tag{25.3-5}$$

The molecular partition function can be interpreted as a sum of probabilities of states, with the probability of a state of zero energy set equal to unity. Its value can be thought of as an effective total number of states accessible to a molecule under the given conditions.

The Parameter β

In order to determine what the parameter β represents, we substitute the expression for N_j given in Eq. (25.3-4a) into the constraint of Eq. (25.2-14b):

$$\frac{1}{z}\sum_j \varepsilon_j g_j e^{-\beta \varepsilon_j} = \langle \varepsilon \rangle = \frac{E}{N} = \frac{U}{N} \tag{25.3-6}$$

where we have again equated the system energy eigenvalue E to the thermodynamic energy U. Equation (25.3-6) can be written in another way, using a mathematical trick that identifies a derivative and interchanges the order of summing and differentiating.

$$\begin{aligned} \frac{U}{N} &= \frac{1}{z}\sum_j \varepsilon_j g_j e^{-\beta \varepsilon_j} = -\frac{1}{z}\sum_j \frac{\partial}{\partial \beta}\left(g_j e^{-\beta \varepsilon_j}\right) \\ &= -\frac{1}{z}\frac{\partial}{\partial \beta}\left[\sum_j g_j e^{-\beta \varepsilon_j}\right] = -\frac{1}{z}\frac{\partial z}{\partial \beta} = -\left(\frac{\partial \ln(z)}{\partial \beta}\right)_V \end{aligned} \tag{25.3-7}$$

The energy eigenvalues depend on the volume, so V must be held fixed in the differentiation. The interchange of summing and differentiating an infinite series is valid if the series is uniformly convergent. This means that the series converges at least at a given rate for all values of the variables involved. We assume this to be the case.

The Molecular Partition Function of a Dilute Monatomic Gas

The parameters α and β can depend on thermodynamic variables. Since α is now expressed in terms of β, finding out how β depends on thermodynamic variables will complete the task of finding the most probable distribution. The expression of Eq. (25.3-7) is used to do this, and it is necessary to know how the thermodynamic energy U depends on thermodynamic variables for a specific system.

For this system we choose a monatomic dilute gas confined in a rectangular box of dimensions $a \times b \times c$. It is an experimental fact that the thermodynamic energy of a monatomic gas such as helium, neon, or argon is given for ordinary temperatures by the relation

$$U = \frac{3}{2}nRT + U_0 = \frac{3}{2}Nk_BT + U_0 \tag{25.3-8}$$

where R is the ideal gas constant and T is the absolute temperature, and where U_0 is a constant. The constant k_B is Boltzmann's constant, equal to $R/N_{Av} = 1.3807 \times 10^{-23}\ \mathrm{J\,K^{-1}}$. We choose to set U_0 equal to zero.

We now apply the expression for U in Eq. (25.3-7) to obtain a formula to compare with Eq. (25.3-8). Atoms have only translational and electronic energy. The degeneracy of an energy level is the product of the translational degeneracy and the electronic degeneracy, and the energy is the sum of the translational and the electronic energy. The molecular partition function is

$$z = \sum_{j_{tr}} \sum_{j_{el}} g_{j_{tr}} g_{j_{el}} e^{-\beta(\varepsilon_{j_{tr}} + \varepsilon_{j_{el}})} \tag{25.3-9}$$

where j_{tr} is an abbreviation for the translational quantum numbers and j_{el} is an abbreviation for the electronic quantum numbers. The two energies and degeneracies are independent of each other, so the partition function is a product of two independent sums:

$$z = \sum_{j_{tr}} g_{j_{tr}} e^{-\beta\varepsilon_{j_{tr}}} \sum_{j_{el}} g_{j_{el}} e^{-\beta\varepsilon_{j_{el}}} = z_{tr} z_{el} \tag{25.3-10}$$

The factor z_{tr} is called the *translational partition function* and the factor z_{el} is called the *electronic partition function*. Since there are no general formulas for $\varepsilon_{j_{el}}$, z_{el} must be summed explicitly:

$$z_{el} = g_{0_{el}} e^{-\beta\varepsilon_{0_{el}}} + g_{1_{el}} e^{-\beta\varepsilon_{1_{el}}} + \cdots \tag{25.3-11}$$

It is an experimental fact for inert gases such as helium, neon, and argon that the electronic energy can be ignored near room temperature, and we will see in the next section that this leads to a constant value for z_{el}. We now focus on the translational partition function.

If the potential energy is chosen to equal zero inside the box, the translational energy eigenvalues are given by Eq. (22.1-4):

$$\varepsilon_{tr} = \varepsilon_{n_x n_y n_z} = \frac{h^2}{8m}\left[\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right] \tag{25.3-12}$$

where m is the molecular mass. We write the translational partition function as a sum over states:

$$z_{\text{tr}} = \sum_{n_x=1}^{\infty}\sum_{n_y=1}^{\infty}\sum_{n_z=1}^{\infty} \exp\left(\frac{-\beta h^2(n_x^2/a^2 + n_y^2/b^2 + n_z^2/c^2)}{8m}\right) \tag{25.3-13}$$

Each value of n_x can occur with every value of n_y, and so on, so the sum factors into three separate sums:

$$z_{\text{tr}} = z_x z_y z_z \tag{25.3-14}$$

where

$$z_x = \sum_{n_x=1}^{\infty} \exp\left(\frac{-\beta h^2 n_x^2}{8ma^2}\right) \tag{25.3-15}$$

and where z_y and z_z are given by analogous formulas.

Exercise 25.12

By writing all the terms on both sides of the equation, show that

$$\sum_{i=1}^{3}\sum_{j=1}^{3} a_i b_j = \left(\sum_{i=1}^{3} a_i\right)\left(\sum_{j=1}^{3} b_j\right)$$

where a_i and b_j represent arbitrary quantities.

Figure 25.2 shows a representation of the sum of Eq. (25.3-15) in which each term is equal to the area of a rectangle with unit width and with height equal to the value of the term. The rectangle for a given value of n_x is drawn to the left of that value on the horizontal axis, so the areas begin at $n_x = 0$ while the sum begins at $n_x = 1$. Also shown in the figure is a curve representing the function

$$f(n_x) = \exp\left(\frac{-\beta h^2 n_x^2}{8ma^2}\right) \tag{25.3-16}$$

where n_x now takes on any positive real value, not just integral values. This function is equal to the terms in the sum shown in Eq. (25.3-15) for integral values of n_x and interpolates between these values for nonintegral values of n_x.

We approximate the sum by the area under the curve, which is equal to the integral

$$z_x \approx \int_0^{\infty} \exp\left(\frac{-\beta h^2 n_x^2}{8ma^2}\right) dn_x = \left(\frac{2\pi m}{h^2\beta}\right)^{1/2} a \tag{25.3-17}$$

The approximation of Eq. (25.3-17) will be a good approximation if nearly all of the areas between the rectangles and the curve in Figure 25.2 are small, as will be shown

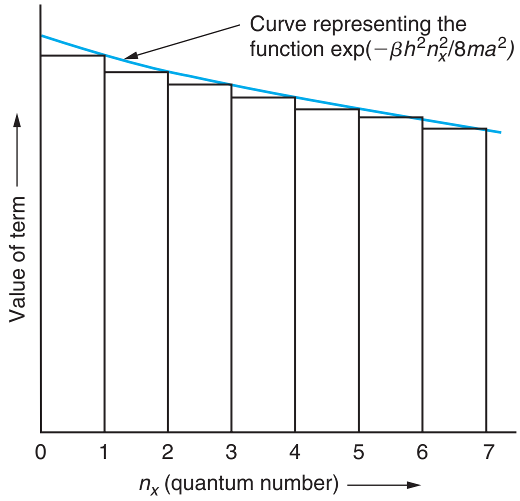

Figure 25.2 A Graphical Representation of the Translational Partition Function (Schematic).

in Exercise 25.14. The factors z_y and z_z are similar to z_x except for the replacement of a by b or c, so the translational partition function can be written as

$$z_{\mathrm{tr}} = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} abc = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} V \tag{25.3-18}$$

where $V = abc$, the volume of the box containing the gas. The thermodynamic properties of a dilute gas are independent of the shape of the container in which it is confined, so we will use the second version of Eq. (25.3-18).

The parameter β can now be evaluated. We substitute Eq. (25.3-18) into Eq. (25.3-7), assuming that z_{el} is equal to a constant:

$$\begin{aligned}\frac{U}{N} &= \left(\frac{\partial}{\partial\beta}\ln(z_{\mathrm{tr}}z_{\mathrm{el}})\right)_V = \left(\frac{\partial}{\partial\beta}\ln(z_{\mathrm{tr}})\right)_V + \left(\frac{\partial}{\partial\beta}\ln(z_{\mathrm{el}})\right)_V \\ &= \left(\frac{\partial}{\partial\beta}\ln(z_{\mathrm{tr}})\right)_V + 0 \\ &= \left(\frac{\partial}{\partial\beta}\ln\left(\left(\frac{2\pi m}{h^2\beta}\right)^{3/2} V\right)\right)_V = -\frac{3}{2}\frac{d\ln(1/\beta)}{d\beta} = \frac{3}{2}\frac{d\ln(\beta)}{d\beta} = \frac{3}{2\beta}\end{aligned} \tag{25.3-19}$$

To make Eq. (25.3-19) agree with Eq. (25.3-8) we set

$$\boxed{\beta = \frac{1}{k_{\mathrm{B}}T}} \tag{25.3-20}$$

The translational partition function is now

$$\boxed{z_{\mathrm{tr}} = \left(\frac{2\pi m k_{\mathrm{B}}T}{h^2}\right)^{3/2} V \quad \text{(any gaseous substance)}} \tag{25.3-21}$$

EXAMPLE 25.3

Find the value of z_{tr} for argon atoms confined in a box of volume 25.0 L (0.0250 m^3) at 298.15 K.

Solution

$$m = \frac{0.039948\ \text{kg mol}^{-1}}{6.02214 \times 10^{23}\ \text{mol}^{-1}} = 6.63 \times 10^{-26}\ \text{kg}$$

$$z_{\text{tr}} = \left(\frac{(2\pi)(6.63 \times 10^{-26}\ \text{kg})(1.3807 \times 10^{-23}\ \text{J K}^{-1})(298.15\ \text{K})}{(6.6261 \times 10^{-34}\ \text{J s})^2}\right)^{3/2}(0.0250\ \text{m}^3)$$

$$= 6.11 \times 10^{30}$$

The large magnitude of the translational partition function in Example 25.3 is typical. There are a great many translational states that are effectively accessible to an atom or molecule at room temperature. The probability of any one state is very small. A state of zero energy would have a probability of $1/(6.11 \times 10^{30}) = 1.64 \times 10^{-31}$. The probability of a state of higher energy has an even smaller value.

Exercise 25.13

a. Find the value of z_{tr} for helium atoms confined in a box of volume 25.0 L at 298.15 K. Compare this value with that of argon in Example 25.3 and comment on the difference.
b. Repeat the calculation for xenon atoms.

We can now assess the accuracy of replacing the sum given by Eq. (25.3-16) by the integral shown in Eq. (25.3-17).

EXAMPLE 25.4

a. Assuming that n_x, n_y, and n_z are equal to each other and that our gas is confined in a cubical box 1.00 m on a side, find the value of n_x that will make the energy of a neon atom equal to $3k_BT/2$ at 300 K.
b. Find the change in energy if n_x is replaced by $n_x + 1$ and show that this change is small compared with $3k_BT/2$ at 300 K.

Solution

a.

$$\frac{3}{2}k_BT = \frac{h^2}{8ma^2}(3n_x^2)$$

$$n_x^2 = \frac{4ma^2k_BT}{h^2}$$

$$= \frac{4(0.02018\,\mathrm{kg\,mol^{-1}})(1.00\,\mathrm{m})^2(1.3807\times10^{-23}\,\mathrm{J\,K^{-1}})(300\,\mathrm{K})}{(6.022\times10^{23}\,\mathrm{mol^{-1}})(6.6261\times10^{-34}\,\mathrm{J\,s})^2}$$

$$= 1.2\times10^{21}$$

$$n_x = 3.5\times10^{10}$$

b.

$$\varepsilon = \frac{3}{2}k_BT = (1.5)(1.3807\times10^{-23}\,\mathrm{J\,K^{-1}})(298.15\,\mathrm{K}) = 6.175\times10^{-21}\,\mathrm{J}$$

$$\Delta\varepsilon = \frac{\partial\varepsilon}{\partial n_x}\Delta n_x = \frac{\partial}{\partial x}\left(\frac{h^2}{8ma^2}(3n_x^2)\right)\Delta n_x = \frac{h^2}{8ma^2}6n_x\Delta n_x = \frac{2\varepsilon}{n_x}\Delta n_x = \frac{2\varepsilon}{n_x} = \frac{3k_BT}{n_x}$$

$$= \frac{3(1.3807\times10^{-23}\,\mathrm{J\,K^{-1}})(300\,\mathrm{K})}{3.5\times10^{10}} = 3.6\times10^{-31}\,\mathrm{J}$$

$\Delta\varepsilon$ is smaller than ε by a factor of roughly 10^{-10}.

Exercise 25.14

Replace β by $1/k_BT$ in Eq. (25.3-15). Find the value of the term in this sum corresponding to $n_x = 3.51010$. Find the difference between this term and the term corresponding to $n_x + 1$ and show that this difference is small compared with the value of the term.

Since the typical difference between one term in the sum and the next term is very small, the integral approximation to the translational partition function is quite accurate (to 8 or 9 significant digits).

In the derivation of the most probable distribution there was no restriction to a particular dilute gas. We showed that $\beta = 1/(k_BT)$ for a dilute monatomic gas with negligible electronic excitation, but this relation must be valid for all dilute gases. With this identification the probability of a molecular energy level of any dilute gas is

$$p_j = \frac{N_j}{N} = \frac{1}{z}g_je^{-\varepsilon_j/k_BT} \quad \begin{pmatrix}\text{dilute gas}\\ \text{energy levels}\end{pmatrix} \tag{25.3-22}$$

and the probability distribution for molecular states is

$$p_i = \frac{N_i}{N} = \frac{1}{z}e^{-\varepsilon_i/k_BT} \quad \begin{pmatrix}\text{dilute gas}\\ \text{states}\end{pmatrix} \tag{25.3-23}$$

The molecular partition function is given by

$$z = \sum_j g_je^{-\varepsilon_j/k_BT} \quad \text{(sum over levels)} \tag{25.3-24}$$

or

$$z = \sum_i e^{-\varepsilon_i/k_BT} \quad \text{(sum over states)} \tag{25.3-25}$$

The probability distribution of Eq. (25.3-23) is the same as the *Boltzmann probability distribution* of Eq. (22.5-2). It has the following general characteristics: (1) At a finite temperature the equilibrium probability of a molecular state decreases exponentially as a function of the molecular energy. States with energy much larger than k_BT are not significantly populated. (2) In the limit of zero temperature, only the lowest-energy level is occupied. (3) If the temperature is increased, the probabilities of states of high energy increase. (4) In the limit of infinite temperature, all molecular states are equally populated.

EXAMPLE 25.5

Consider two states with an energy difference of 1.00 eV. Find the ratio of their probabilities at (a) 298.15 K; (b) 1000.0 K; and (c) 10000.0 K.

Solution

a. $$\mathit{ratio} = \exp\left(-\frac{(1.00\,\mathrm{eV})(1.6022\times10^{-19}\,\mathrm{J\,Ev^{-1}})}{(1.3807\times10^{-23}\,\mathrm{J\,K^{-1}})(298.15\,\mathrm{K})}\right) = 1.25\times10^{-17}$$

b. $$\mathit{ratio} = \exp\left(-\frac{(1.00\,\mathrm{eV})(1.6022\times10^{-19}\,\mathrm{J\,Ev^{-1}})}{(1.3807\times10^{-23}\,\mathrm{J\,K^{-1}})(1000.0\,\mathrm{K})}\right) = 9.13\times10^{-6}$$

c. $$\mathit{ratio} = \exp\left(-\frac{(1.00\,\mathrm{eV})(1.6022\times10^{-19}\,\mathrm{J\,Ev^{-1}})}{(1.3807\times10^{-23}\,\mathrm{J\,K^{-1}})(10000.0\,\mathrm{K})}\right) = 0.313$$

Our probability distribution is valid for equilibrium macroscopic states. Nonequilibrium system states can occur in which a molecular state of high energy has a higher population than a state of low energy. This situation is achieved in lasers. A distribution with a larger population for a state of higher energy is said to correspond to a negative temperature. Smaller values of the reciprocal temperature correspond to larger values of the temperature. As a positive temperature approaches very large values, the reciprocal temperature approaches zero. If the reciprocal temperature can pass through zero and become negative, this must correspond to being "hotter" than any positive reciprocal temperature. Negative temperatures pertain to nonequilibrium systems and cannot be identified with the thermodynamic temperature, which is an equilibrium concept and must be positive.

Exercise 25.15

In a certain laser, the population of a state of energy 2.08 eV is 50% larger than the population of a state of energy zero. Find the negative temperature corresponding to this situation.

We can rewrite the expression for the thermodynamic energy shown in Eq. (25.3-7) in terms of T, using the chain rule (see Appendix B):

$$U = -N\left(\frac{\partial \ln(z)}{\partial T}\right)_V\left(\frac{\partial T}{\partial \beta}\right) = Nk_BT^2\left(\frac{\partial \ln(z)}{\partial T}\right)_V \quad \text{(any dilute gas)} \tag{25.3-26}$$

Exercise 25.16

Verify Eq. (25.3-26) by evaluating $d\beta/dT$, which is equal to the reciprocal of $dT/d\beta$.

Consider the effect of changing the zero of energy by adding a constant $\mathcal{V}'$ to the value of the potential energy of a molecule. (See Problem 15.6 for the effect on an energy eigenvalue.) Let ε_j' represent the new value of the energy eigenvalue of level number j:

$$\varepsilon_j' = \varepsilon_j + \mathcal{V}' \tag{25.3-27}$$

Denote the new value of the partition function by z':

$$\begin{aligned} z' &= \sum_j g_j e^{-\varepsilon_j'/k_\mathrm{B}T} = \sum_j g_j e^{-(\varepsilon_j+\mathcal{V}')/k_\mathrm{B}T} \\ &= e^{-\mathcal{V}'/k_\mathrm{B}T} \sum_j g_j e^{-\varepsilon_j/k_\mathrm{B}T} = e^{-\mathcal{V}'/k_\mathrm{B}T} z \end{aligned} \tag{25.3-28}$$

The probability distribution is

$$\begin{aligned} p' &= \frac{1}{z''} g_j e^{-(\varepsilon_j+\mathcal{V}')/k_\mathrm{B}T} = \frac{1}{z e^{-\mathcal{V}'/k_\mathrm{B}T}} g_j e^{-\varepsilon_j/k_\mathrm{B}T} e^{-\mathcal{V}'/k_\mathrm{B}T} \\ &= \frac{1}{z} g_j e^{-\varepsilon_j/k_\mathrm{B}T} \end{aligned} \tag{25.3-29}$$

The probability distribution is independent of the choice of the zero of energy, as we would expect, but the value of the partition function changes by the factor $e^{-\mathcal{V}'/k_\mathrm{B}T}$. A change in the zero of energy adds a constant to the thermodynamic energy.

Exercise 25.17

Using Eq. (25.3-26), show that the thermodynamic energy using the new zero of energy is given by

$$U' = U + N\mathcal{V}' \tag{25.3-30}$$

PROBLEMS

Section 25.3: The Probability Distribution and the Molecular Partition Function

25.14 Write the translational partition function for a monatomic dilute gas at 298.15 K and a volume of $0.0244\ \mathrm{m}^3$ as a constant times $M^{3/2}$, where M is the molar mass in $\mathrm{kg\ mol^{-1}}$. Evaluate the partition function for He, Ne, Ar, Kr, and Xe. Explain the dependence on molar mass.

25.15 **a.** Find the value of the molecular partition function of a neon atom confined in a cubical volume of $1.000\ \mathrm{m}^3$ at 298.15 K.

b. Find the probability of the translational state of a neon atom corresponding to $n_x = n_y = n_z = 3.5 \times 10^{10}$ (the values in Example 25.4) at this temperature and volume.

25.16 The value of the molecular partition function of an argon atom confined in a volume of 0.0250 m^3 (25.0 L) at 298.15 K is given in Example 25.3.

a. Find the value of n_x (assumed equal to n_y and n_z) that will make the energy of an argon atom equal to $3k_BT/2$ at this temperature, assuming that the volume is a cube.

b. Find the probability of the state with this value of n_x, n_y, and n_z.

25.17 Calculate the ratio of the population of the $v = 1$ vibrational state of CO to the $v = 0$ vibrational state at (a) 298.15 K, (b) 500 K, (c) 1000 K, and (d) 5000 K. (e) What is the limit as $T \to \infty$?

25.18 Calculate the ratio of the population of the $v = 2$ vibrational state of I_2 to the $v = 0$ vibrational state at (a) 298.15 K, (b) 500 K, (c) 1000 K, and (d) 5000 K. (e) What is the limit as $T \to \infty$?

25.19 Calculate the ratio of the population of the $J = 1$ rotational level of CO to the $J = 0$ rotational level at (a) 298.15 K, (b) 1000 K. (c) What is the limit as $T \to \infty$?

25.20 Calculate the ratio of the population of the $J = 2$ rotational level of I_2 to the $J = 0$ rotational level at (a) 298.15 K, (b) 1000 K. (c) What is the limit as $T \to \infty$?

25.4 The Calculation of Molecular Partition Functions

In the previous section we obtained a general formula for the translational partition function. In this section we obtain formulas for the other factors in the molecular partition function for dilute gases and carry out example calculations of partition functions.

Monatomic Gases

We have already determined that the molecular partition function for a dilute monatomic gas is the product of a translational partition function and an electronic partition function. We obtained a formula for the translational partition function in Eq. (25.3-21):

$$z_{\mathrm{tr}} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V \qquad (25.4\text{-}1)$$

With our replacement of β by $1/(k_B T)$, Eq. (25.3-11) for the electronic partition function becomes

$$z_{\mathrm{el}} = g_0 e^{-\varepsilon_0/k_B T} + g_1 e^{-\varepsilon_1/k_B T} + \cdots \qquad (25.4\text{-}2)$$

Except for hydrogen-like atoms, there is no simple formula for atomic electronic energy eigenvalues, so the sum in Eq. (25.4-2) must be added up explicitly. However, for a typical monatomic gas such as helium or argon, the ground electronic energy level is a nondegenerate ^1S state, and the first excited state is at least 1 eV higher than the ground-level. In this case, all terms past the first term are negligible at ordinary temperatures, and we can write, to an excellent approximation:

$$z_{\mathrm{el}} \approx g_0 e^{-\varepsilon_0/k_B T} \qquad (25.4\text{-}3)$$

If the energy of the ground-level is chosen to equal zero and if the ground-level is nondegenerate, we have

$$z_{\mathrm{el}} \approx 1 \quad (\varepsilon_0 = 0,\ g_0 = 1) \qquad (25.4\text{-}4)$$

EXAMPLE 25.6

For the case that $g_0 = 1$, $\varepsilon_0 = 0$ and $\varepsilon_1 = 1.00$ eV, show that $z_{\mathrm{el}} \approx 1$ is an adequate approximation at $T = 300$ K.

Solution

$$\frac{\varepsilon_1}{k_B T} = \frac{(1.00\,\mathrm{eV})(1.602 \times 10^{-19}\,\mathrm{J\,eV^{-1}})}{(1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}})(300\,\mathrm{K})} = 38.7$$

$$e^{-38.7} = 1.6 \times 10^{-17}$$

All terms are negligible except for the first term and $z_{\mathrm{el}} = 1$ to an excellent approximation.

The result of this example justifies our earlier assumption that there was no significant electronic excitation in our dilute monatomic gas.

Diatomic Gases

In addition to translational and electronic motion, a diatomic gas has rotational and vibrational motion. To a good approximation the energy is a sum of four separate terms, as in Eq. (22.2-37):

$$\varepsilon_j = \varepsilon_{j_{\mathrm{tr}}} + \varepsilon_{j_{\mathrm{rot}}} + \varepsilon_{j_{\mathrm{vib}}} + \varepsilon_{j_{\mathrm{el}}} \tag{25.4-5}$$

Equation (25.4-5) leads to a factoring of the molecular partition function:

$$\begin{aligned} z &= \sum_{j_{\mathrm{tr}}} g_{j_{\mathrm{tr}}} e^{-\beta\varepsilon_{j_{\mathrm{tr}}}} \sum_{j_{\mathrm{rot}}} g_{j_{\mathrm{rot}}} e^{-\beta\varepsilon_{j_{\mathrm{rot}}}} \sum_{j_{\mathrm{vib}}} g_{j_{\mathrm{vib}}} e^{-\beta\varepsilon_{j_{\mathrm{vib}}}} \sum_{j_{\mathrm{el}}} g_{j_{\mathrm{el}}} e^{-\beta\varepsilon_{j_{\mathrm{el}}}} \\ &= z_{\mathrm{tr}} z_{\mathrm{rot}} z_{\mathrm{vib}} z_{\mathrm{el}} \quad \left(\begin{array}{c}\text{diatomic or polyatomic}\\ \text{substances}\end{array}\right) \end{aligned} \tag{25.4-6}$$

The Translational and Electronic Partition Functions

The translational energy is given by the same formula as for atoms, and the translational partition function is given by Eq. (25.3-21). As with atoms, there is no general formula for the electronic energy. Part of the Born–Oppenheimer energy acts as a potential energy of vibration, and the rest is a constant that is assigned to be the electronic energy. There are two ways to assign this energy. The first is to assign the minimum value of the Born–Oppenheimer energy as $\varepsilon_{\mathrm{el}}$ and to assign the remainder to be the vibrational potential energy, as was done in Eq. (22.2-41). The second choice is to include the zero-point vibrational energy as part of the electronic energy as in Eq. (22.2-43), setting the vibrational ground-state energy equal to zero. Both these choices are depicted in Figure 25.3. With either choice, the electronic energy is taken as a different constant for each electronic state, and the formula in Eq. (25.4-2) is summed explicitly. Except for a few unusual cases, such as NO, only the first term is significantly different from zero, as is the case with atoms. For example, the ground-level of O_2 is a ${}^3\Sigma_g^-$ state with a degeneracy of 3, and all excited states are high enough in energy to be ignored at

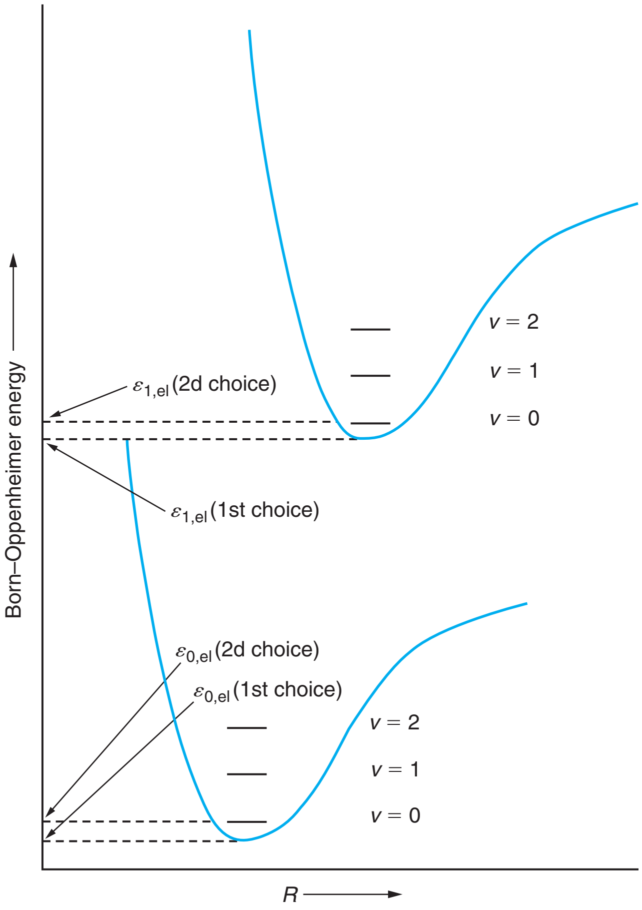

Figure 25.3 The Electronic Energy (Born–Oppenheimer Energy) as a Function of Internuclear Distance for Two Electronic States.

ordinary temperatures. The electronic partition function of O_2 at ordinary temperatures is equal to 3.000 if the energy of the ground-level is chosen to equal zero.

The Rotational Partition Function

We treat diatomic molecules in the harmonic oscillator–rigid rotor approximation. The rotational energy is given by Eq. (22.2-40):

$$\varepsilon_{\mathrm{rot}} = \varepsilon_J = \frac{\hbar^2}{2I_e}J(J+1) = hB_eJ(J+1) = hc\tilde{B}_eJ(J+1) \qquad (25.4\text{-}7)$$

where we have expressed the energy in terms of the rotational constant, B_e, given by Eq. (22.2-48)

$$B_e = \frac{h}{8\pi^2 I_e} = \frac{h}{8\pi^2 \mu r_e^2} \qquad (25.4\text{-}8)$$

or by the parameter $\tilde{B}_{\mathrm{e}}$, equal to B_{e}/c where c is the speed of light. The equilibrium moment of inertia is denoted by I_{e}, the reduced mass of the nuclei is denoted by μ, and the equilibrium internuclear distance is denoted by r_{e}.

The degeneracy of the rotational level number J is $2J + 1$. The rotational partition function of a dilute diatomic gas is given by the sum over levels:

$$z_{\mathrm{rot}} = \sum_{J=0}^{\infty} g_J e^{-\varepsilon_J/k_{\mathrm{B}}T} = \sum_{J=0}^{\infty} (2J+1) e^{-hB_{\mathrm{e}}J(J+1)/k_{\mathrm{B}}T} \tag{25.4-9}$$

Figure 25.4 shows the sum of Eq. (25.4-7) represented by the combined areas of a set of rectangles, as was done with the translational partition function in Figure 25.2. Because $J = 0$ is the lower limit of the sum, we draw the rectangle for a given value of J to the right of that integer value of J. Figure 25.4 also shows a curve representing the function that is obtained by allowing J to take on all real values. The sum is approximately equal to the area under the curve, which is equal to the integral

$$z_{\mathrm{rot}} \approx \int_0^{\infty} (2J+1) e^{-hB_{\mathrm{e}}J(J+1)/k_{\mathrm{B}}T} dJ \tag{25.4-10}$$

We let $u = J(J+1)$ so that $du = (2J+1)dJ$:

$$z_{\mathrm{rot}} \approx \int_0^{\infty} e^{-hB_{\mathrm{e}}u/k_{\mathrm{B}}T} du = \frac{k_{\mathrm{B}}T}{hB_{\mathrm{e}}} = \frac{k_{\mathrm{B}}T}{hc\tilde{B}_{\mathrm{e}}} = \frac{8\pi^2 I_{\mathrm{e}} k_{\mathrm{B}}T}{h^2} = \frac{8\pi^2 \mu r_{\mathrm{e}^2} k_{\mathrm{B}}T}{h^2} \tag{25.4-11}$$

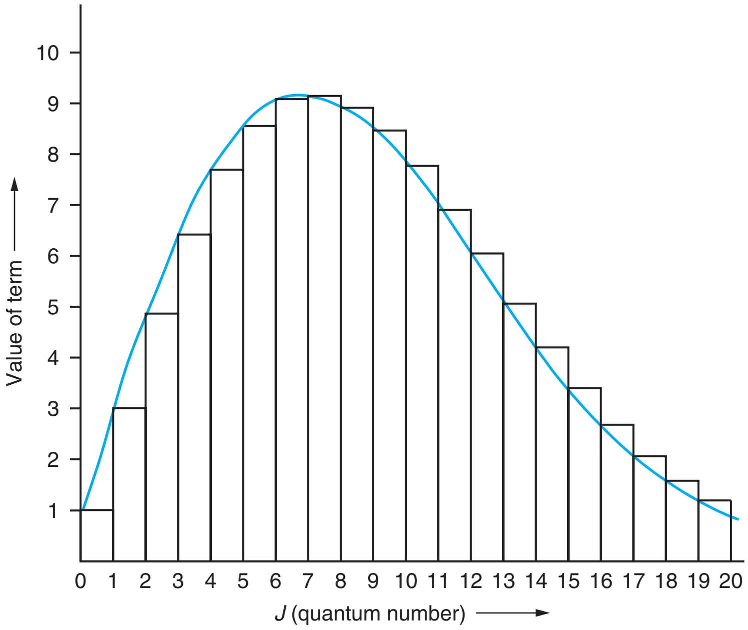

Figure 25.4 A Graphical Representation of the Rotational Partition Function (Drawn for *CO* at 298.15 K). This figure is analogous to Figure 25.2 for the translational partition function. The area under the bar graph is equal to the rotational partition function for a diatomic molecule, and the area under the curve is equal to the integral approximation to the rotational partition function.

The formula given in Eq. (25.4-11) applies to heteronuclear diatomic molecules, but must be modified for homonuclear diatomic molecules, for which either odd values of J or even values of J do not occur, as discussed in Chapter 22. This restriction corresponds to omitting half of the rectangles in Figure 25.4, approximately cutting the value of the sum in half. For diatomic molecules the *symmetry number* σ is defined in Section 22.5.

$$\sigma = \begin{cases} 2 & \text{homonuclear diatomic molecules} \\ 1 & \text{heteronuclear diatomic molecules} \end{cases} \tag{25.4-12}$$

We can write for all diatomic molecules

$$z_{\mathrm{rot}} = \frac{1}{\sigma}\frac{8\pi^2 I_{\mathrm{e}} k_{\mathrm{B}} T}{h^2} = \frac{1}{\sigma}\frac{k_{\mathrm{B}}T}{hB_{\mathrm{e}}} = \frac{1}{\sigma}\frac{k_{\mathrm{B}}T}{hc\tilde{B}_{\mathrm{e}}} \quad \left(\begin{matrix}\text{diatomic}\\ \text{substances}\end{matrix}\right) \tag{25.4-13}$$

In the translational partition function, the replacement of a sum by an integral gave an excellent approximation. In the rotational partition function it is a very good approximation at ordinary temperatures for molecules containing heavy atoms, a good approximation for molecules containing atoms of moderate mass, and a fairly poor approximation for molecules containing light atoms such as hydrogen. The approximation is better for larger values of the rotational partition function, so it is a better approximation at higher temperatures. If the formula in Eq. (25.4-13) gives a value smaller than 10, this approximation might not be adequate. Partial sums of the series representing the rotational partition function can be summed explicitly, and formulas with corrections can also be used (see Problem 25.31).[5]

EXAMPLE 25.7

Calculate the rotational partition function for $^{35}\mathrm{Cl}_2$ at 298.15 K.

Solution

$$\mu = \frac{0.03497\ \mathrm{kg\ mol^{-1}}}{2(6.0221 \times 10^{23}\ \mathrm{mol^{-1}})} = 2.903 \times 10^{-26}\ \mathrm{kg}$$

From Table A.22 in Appendix A, $r_{\mathrm{e}} = 1.988 \times 10^{-10}$ m.

$$I_{\mathrm{e}} = (2.903 \times 10^{-26}\ \mathrm{kg})(1.988 \times 10^{-10}\ \mathrm{m})^2 = 1.147 \times 10^{-45}\ \mathrm{kg\ m^2}$$

$$z_{\mathrm{rot}} = \frac{1}{2}\frac{8\pi^2(1.147 \times 10^{-45}\ \mathrm{kg\ m^2})(1.3807 \times 10^{-23}\ \mathrm{J\ K^{-1}})(298.15\ \mathrm{K})}{(6.6261 \times 10^{-34}\ \mathrm{J\ s})^2} = 424.7$$

Exercise 25.18

Repeat the calculation of the rotational partition function of $^{35}\mathrm{Cl}_2$ at 298.15 K using the value of $\tilde{B}_{\mathrm{e}}$ from Table A.22 in Appendix A.

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[5] N. Davidson, *op. cit.*, p. 111ff (note 2); R. S. McDowell, *J. Chem. Phys.*, **88**, 356 (1988).

The value in Example 25.7 is typical for molecules of moderate size near room temperature, and is large enough to be a good approximation.

The Vibrational Partition Function

If the zero-point vibrational energy is included as part of the electronic energy, the vibrational energy of a diatomic molecule is given by

$$\varepsilon_{\text{vib}} = \varepsilon_v = h\nu_{\text{e}}v = hc\tilde{\nu}_{\text{e}}v \tag{25.4-14}$$

where v is the vibrational quantum number. The vibrational frequency ν_{e} is given by Eq. (22.2-30):

$$\nu_{\text{e}} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{25.4-15}$$

where k is the vibrational force constant and μ is the reduced mass of the nuclei. The parameter $\tilde{\nu}_{\text{e}}$ is equal to ν_{e}/c where c is the speed of light.

Since the vibrational levels are nondegenerate, the vibrational partition function of a diatomic molecule is

$$z_{\text{vib}} = \sum_{v=0}^{\infty} e^{-h\nu_{\text{e}}v/k_{\text{B}}T} = \sum_{v=0}^{\infty} a^v \tag{25.4-16}$$

where $a = \exp(-h\nu/k_{\text{B}}T)$. This sum is a **geometric progression** with infinitely many terms, given by a well-known formula

$$\sum_{v=0}^{\infty} a^v = \frac{1}{1-a} \tag{25.4-17}$$

This formula is valid if $|a| < 1$, which is satisfied by $a = \exp(-h\nu_{\text{e}}/k_{\text{B}}T)$. The vibrational partition function is given by

$$\boxed{z_{\text{vib}} = \frac{1}{1 - e^{-h\nu_{\text{e}}/k_{\text{B}}T}} = \frac{1}{1 - e^{-hc\tilde{\nu}_{\text{e}}/k_{\text{B}}T}}} \tag{25.4-18}$$

EXAMPLE 25.8

Calculate the vibrational partition function of $^{35}\text{Cl}_2$ at 298.15 K. The vibrational frequency is $1.6780 \times 10^{13}\ \text{s}^{-1}$.

Solution

Let $x = h\nu_{\text{e}}/k_{\text{B}}T$:

$$x = \frac{(6.6261 \times 10^{-34}\ \text{J s})(1.6780 \times 10^{13}\ \text{s}^{-1})}{(1.3807 \times 10^{-23}\ \text{J K}^{-1})(298.15\ \text{K})} = 2.701$$

$$z_{\text{vib}} = \frac{1}{1 - e^{-x}} = \frac{1}{1 - e^{-2.701}} = 1.0720$$

The excited vibrational states are not significantly populated at room temperature, as shown by the closeness of the value of z_{vib} in the previous example to unity. For a typical diatomic molecule at room temperature, very many translational states are effectively accessible, a few hundred rotational states are effectively accessible, but only one vibrational state and one electronic state are accessible.

EXAMPLE 25.9

Calculate the vibrational partition functions for H_2 and for I_2 at 298.15 K.

Solution

For $\mathrm{H_2}$, $\tilde{\nu}_{\mathrm{e}} = 4401.2\ \mathrm{cm^{-1}}$, and for $\mathrm{I_2}$, $\tilde{\nu}_{\mathrm{e}} = 214.5\ \mathrm{cm^{-1}}$. For $\mathrm{H_2}$,

$$\frac{hc\tilde{\nu}_{\mathrm{e}}}{k_{\mathrm{B}}T} = \frac{(6.6261 \times 10^{-34}\,\mathrm{J\,s})(2.9979 \times 10^{10}\,\mathrm{cm\,s^{-1}})(4401.2\,\mathrm{cm^{-1}})}{(1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}})(298.15\,\mathrm{K})} = 21.239$$

$$z_{\mathrm{vib}} = \frac{1}{1 - e^{-21.239}} = 1.0000000006$$

For $\mathrm{I_2}$,

$$\frac{hc\tilde{\nu}_{\mathrm{e}}}{k_{\mathrm{B}}T} = \frac{(6.6261 \times 10^{-34}\,\mathrm{J\,s})(2.9979 \times 10^{10}\,\mathrm{cm\,s^{-1}})(214.5\,\mathrm{cm^{-1}})}{(1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}})(298.15\,\mathrm{K})}$$

$$= 1.03510$$

$$z_{\mathrm{vib}} = \frac{1}{1 - e^{-1.03510}} = 1.5508$$

The vibrational partition function of $\mathrm{H_2}$ is very close to unity because its vibrational energy levels are very widely spaced, and only the ground vibrational state is significantly populated at room temperature. The vibrational energy levels of $\mathrm{I_2}$ are much closer, and there is some population of the first few excited vibrational states. However, the effective number of occupied vibrational states is still smaller than 2.

Exercise 25.19

Show that if the vibrational energy is written as

$$\varepsilon''_{\mathrm{vib}} = h\nu\left(v + \frac{1}{2}\right) \tag{25.4-19}$$

the vibrational partition function is

$$z''_{\mathrm{vib}} = \frac{e^{-h\nu/2k_{\mathrm{B}}T}}{1 - e^{-h\nu/k_{\mathrm{B}}T}} = \frac{e^{-h\nu_{\mathrm{e}}/2k_{\mathrm{B}}T}}{1 - e^{-h\nu_{\mathrm{e}}/k_{\mathrm{B}}T}} \tag{25.4-20}$$

Calculate the value of this vibrational partition function for $^{35}\mathrm{Cl_2}$ at 298.15 K. Compare your result with that of Example 25.8, and explain the difference.

Corrections to the Product Partition Function

Writing the partition function as a product of four factors as in Eq. (25.4-6) depends on the assumption that only the ground electronic level is needed in the electronic partition function. If additional electronic terms must be included, the same rotational and vibrational partition functions do not necessarily apply to different electronic states since all electronic states do not usually have the same force constant and internuclear distance. If different values of B_e and ν_e apply to different electronic states we must compute a different rotational and vibrational partition function for each electronic state. The partition function becomes

$$z = z_{tr}[g_0 e^{-\varepsilon_0/k_BT} z_{rot,0} z_{vib,0} + g_1 e^{-\varepsilon_1/k_BT} z_{rot,1} z_{vib,1} + \ldots] \qquad (25.4\text{-}21)$$

where $z_{rot,0}$ and $z_{vib,0}$ are the rotational and vibrational partition functions corresponding to electronic state number 0, $z_{rot,1}$ and $z_{vib,1}$ correspond to electronic state number 1, and so on. If the excited electronic states make a fairly small contribution, it might be a usable approximation to assume that all electronic states have roughly the same values of B_e and ν_e. If so, we can write the partition function in the factored form of Eq. (25.4-6) even if more than one term is included in z_{el}. The values of B_e and ν_e of the ground electronic level are used since this term makes the largest contribution.

EXAMPLE 25.10

The ground electronic level of NO (a relatively stable molecule with an unpaired electron) is a $^2\Pi_{1/2}$ term. The first excited level is a $^2\Pi_{3/2}$ term with an energy 2.380×10^{-21} J above the ground-level. Both levels have a degeneracy equal to 2. All other electronic states are more than 7×10^{-19} J above the ground-level. For the ground-level $\nu_e = 5.7086 \times 10^{13}\ \text{s}^{-1}$ and $B_e = 5.0123 \times 10^{10}\ \text{s}^{-1}$.

a. Find the molecular partition function of NO at 298.15 K and at a volume equal to the molar volume at 101325 Pa. Assume that the ground-level values of B_e and ν_e apply to both electronic states.

b. Find the molecular partition function for NO for the conditions of part a, using the values for the first excited state, $\nu_e = 5.7081 \times 10^{13}\ \text{s}^{-1}$ and $B_e = 5.1569 \times 10^{10}\ \text{s}^{-1}$.

Solution

a.

$$m(\text{NO}) = \frac{0.014003074\ \text{kg mol}^{-1} + 0.015994915\ \text{kg mol}^{-1}}{6.02214 \times 10^{23}\ \text{mol}^{-1}}$$

$$= 4.98127 \times 10^{-26}\ \text{kg}$$

$$V = \frac{nRT}{P} = \frac{(1.000\ \text{mol})(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})}{101325\ \text{Pa}} = 0.024466\ \text{m}^3$$

$$z_{tr} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V$$

$$= \left(\frac{2\pi(4.98127 \times 10^{-26}\ \text{kg})(1.3807 \times 10^{-23}\ \text{J K}^{-1})(298.15\ \text{K})}{(6.6261 \times 10^{-34}\ \text{J s})^2}\right)^{3/2}$$

$$\times (0.024466\ \text{m}^3)$$

$$= 3.8893 \times 10^{30}$$

$$z_{\mathrm{rot}} = \frac{8\pi^2 k_{\mathrm{B}} T}{h^2} = \frac{k_{\mathrm{B}} T}{h B_{\mathrm{e}}} = \frac{(1.3807 \times 10^{-23}\ \mathrm{J\,K^{-1}})(298.15\ \mathrm{K})}{\left(6.6261 \times 10^{-34}\ \mathrm{J\,s}\right)\left(5.0123 \times 10^{10}\ \mathrm{s^{-1}}\right)} = 123.95$$

$$\frac{h\nu_{\mathrm{e}}}{k_{\mathrm{B}} T} = \frac{(6.6261 \times 10^{-34}\ \mathrm{J\,s})(5.7086 \times 10^{13}\ \mathrm{s^{-1}})}{\left(1.3807 \times 10^{-23}\ \mathrm{J\,K^{-1}}\right)(298.15\ \mathrm{K})} = 9.1889$$

$$z_{\mathrm{vib}} = \frac{1}{1 - e^{-h\nu_{\mathrm{e}}/k_{\mathrm{B}}T}} = \frac{1}{1 - e^{-9.1889}} = 1.0001$$

$$z_{\mathrm{elec}} \approx 2 + 2e^{-\varepsilon_1/k_{\mathrm{B}}T} = 2 + 2\exp\left(\frac{-2.380 \times 10^{-21}\ \mathrm{J}}{\left(1.3807 \times 10^{-23}\ \mathrm{J\,K^{-1}}\right)(298.15\ \mathrm{K})}\right)$$

$$\approx 2 + 2e^{-0.57815} = 3.1218$$

$$z = z_{\mathrm{tr}} z_{\mathrm{rot}} z_{\mathrm{vib}} z_{\mathrm{elec}} = (3.8893 \times 10^{30})(123.95)(1.00010)(3.1218)$$

$$= 1.5052 \times 10^{33}$$

b. z_{tr} is unchanged. A calculation as in part a shows that z_{vib} for the excited state is equal to that of the ground-state to the number of significant digits given. Denote partition functions for the ground-state by the subscript (gs) and those for the excited state by (ex):

$$z_{\mathrm{rot(ex)}} = \frac{8\pi^2 k_{\mathrm{B}} T}{h^2} = \frac{k_{\mathrm{B}} T}{h B_{\mathrm{e}}} = \frac{(1.3807 \times 10^{-23}\ \mathrm{J\,K^{-1}})(298.15\ \mathrm{K})}{\left(6.6261 \times 10^{-34}\ \mathrm{J\,s}\right)\left(5.1569 \times 10^{10}\ \mathrm{s^{-1}}\right)}$$

$$= 120.47$$

$$z = z_{\mathrm{tr}}\left[(z_{\mathrm{rot(gs)}} z_{\mathrm{vib(gs)}})(2) + (z_{\mathrm{rot(ex)}} z_{\mathrm{vib(ex)}})(2)e^{-0.57815}\right]$$

$$= 3.8893 \times 10^{30}\left[(123.95)(1.00010)(2) + (120.47)(1.0001)(2)(.5609325)\right]$$

$$= 1.4900 \times 10^{33}$$

The partition function of part a is in error by about 1.0%.

The molecular partition function for a diatomic gas can also be corrected by going beyond the harmonic oscillator–rigid rotor approximation, including the correction terms in Eq. (22.2-45) for the energy levels.[6] We do not discuss these corrections.

Polyatomic Gases

In the harmonic oscillator–rigid rotor approximation polyatomic molecules obey the same separation of their energy into four independent terms as in Eq. (25.4-5). In this approximation the molecular partition function of a polyatomic substance factors into the same four factors as in Eq. (25.4-6). The translational partition function is given by

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[6] N. Davidson, *op. cit.*, p. 116ff (note 2).

the same formula as for atoms and diatomic molecules, Eq. (25.3-21). The electronic partition function is obtained by explicit summation as in Eq. (25.4-2), and the one-term approximation of Eq. (25.4-4) is usually valid if the molecule does not have unpaired electrons.

The Rotational Partition Function

For a linear polyatomic molecule like acetylene or cyanogen, the rotational energy levels are the same as those of diatomic molecules in Eq. (22.2-18). Equation (25.4-13) can be used for the rotational partition function with the appropriate symmetry number and moment of inertia. The rotational energy levels of nonlinear polyatomic molecules are more complicated than those of diatomic molecules. The derivation of the rotational partition function for nonlinear molecules is complicated, and we merely cite the result:[7]

$$z_{\mathrm{rot}} = \frac{\sqrt{\pi}}{\sigma}\left(\frac{8\pi^2 k_{\mathrm{B}}T}{h^2}\right)^{3/2}(I_A I_B I_C)^{1/2} \quad \left(\begin{array}{c}\text{nonlinear polyatomic}\\ \text{substance}\end{array}\right) \tag{25.4-22}$$

where I_A, I_B, and I_C are the principal moments of inertia as defined in Eq. (22.4-2). The symmetry number σ is equal to the number of ways of orienting a model of the molecule such that each nuclear location is occupied by a nucleus of the same isotope of the same element as in the other orientations, as described in Section 22.4 of Chapter 22. The inclusion of the symmetry number corresponds to the fact that of the conceivable sets of values of the quantum numbers J, M, and K only a fraction $1/\sigma$ actually occur. The rotational partition function of a polyatomic molecule is generally large enough so that Eq. (25.4-22) is a good approximation. A more accurate expression for spherical top molecules has been derived.[8]

EXAMPLE 25.11

Calculate the rotational partition function of CCl_4 at 298.15 K, assuming all chlorine atoms to be the ^{35}Cl isotope. The molecule is a spherical top, with bond lengths equal to 1.766×10^{-10} m, and with all three moments of inertia equal to 4.829×10^{-45} kg m^2.

Solution

The symmetry number is counted as follows: With a given Cl at in a fixed position, say on the z axis, there are three orientations. There are four ways to place a Cl atom on the z axis, so the symmetry number is $3 \times 4 = 12$. We can write

$$\begin{aligned} z_{\mathrm{rot}} &= \frac{\sqrt{\pi}}{12}\left(\frac{8\pi^2(1.3807\times 10^{-23}\ \mathrm{J\,K^{-1}})(298.15\ \mathrm{K})}{(6.6261\times 10^{-34}\ \mathrm{J\,s})^2}\right)^{3/2}(4.829\times 10^{-45}\ \mathrm{kg\,m^2})^{3/2} \\ &= 31570 \end{aligned}$$

This value is large enough to be a very good approximation.

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[7] N. Davidson, *op. cit.*, p. 169ff (note 2).

[8] R. S. McDowell, *J. Quant. Spectrosc. Radiat. Transfer.*, **38**, 337 (1987).

The Vibrational Partition Function

In the harmonic oscillator approximation, the vibrational energy of a polyatomic molecule is the sum of the energies of normal modes, each of which acts like a harmonic oscillator, as in Eq. (22.4-19). A nonlinear polyatomic molecule has $3n - 6$ normal modes, and a linear polyatomic molecule has $3n - 5$ normal modes, where n is the number of nuclei in the molecule. Choosing the energy of the ground vibrational state to equal zero, we have

$$\varepsilon_{\text{vib}} = \sum_{i=1}^{3n-5(6)} h\tilde{\nu}_i v_i = \sum_{i=1}^{3n-5(6)} hc\tilde{\nu}_i v_i \tag{25.4-23}$$

where ν_i represents the classical vibration frequency of normal mode number i, and v_i is the quantum number for this normal mode. The parameter $\tilde{\nu}$ is the frequency of vibration divided by the speed of light, and is the quantity usually found in tables. The upper limit of the sum is equal to $3n - 5$ for linear polyatomic molecules and equal to $3n - 6$ for nonlinear molecules.

Since the vibrational energy is a sum of $3n - 5$ or $3n - 6$ terms and since the quantum numbers for each vibration are independent of each other, the vibrational partition function of a polyatomic substance is a product of factors, and each factor is analogous to that of a diatomic molecule:

$$z_{\text{vib}} = \prod_{i=1}^{3n-5(6)} \frac{1}{1 - e^{-h\nu_i/k_B T}} = \prod_{i=1}^{3n-5(6)} \frac{1}{1 - e^{-hc\tilde{\nu}_i/k_B T}} \tag{25.4-24}$$

where the upper limit of the product indicates $3n - 5$ for a linear polyatomic molecule and $3n - 6$ for a nonlinear polyatomic molecule.

EXAMPLE 25.12

The vibrational frequencies of carbon dioxide are $\nu_1 = 4.162 \times 10^{13}\ \text{s}^{-1}$, $\nu_2 = 2.000 \times 10^{13}\ \text{s}^{-1}$ (two bends at this frequency), and $\nu_3 = 7.043 \times 10^{13}\ \text{s}^{-1}$. Calculate the vibrational partition function at 298.15 K.

Solution

Let

$$x_1 = \frac{h\nu_1}{k_B T} = \frac{(6.6261 \times 10^{-34}\ \text{J s})(4.162 \times 10^{13}\ \text{s}^{-1})}{\left(1.3807 \times 10^{-23}\ \text{J K}^{-1}\right)(298.15\ \text{K})} = 6.699$$

By similar calculations $x_2 = 3.219$ and $x_3 = 11.337$. The vibrational partition function is

$$\begin{aligned} z_{\text{vib}} &= \frac{1}{1 - e^{-6.699}}\left(\frac{1}{1 - e^{-3.219}}\right)^2 \frac{1}{1 - e^{-11.337}} \\ &= (1.0012)(1.0417)^2(1.000012) = 1.0865 \end{aligned}$$

The lowest-frequency vibrations (the two bending modes) make the largest contributions to z_{vib}, but the size of the vibrational partition function indicates that there is very little vibrational excitation.

Exercise 25.20

Calculate the vibrational partition function of sulfur dioxide at 298.15 K. The vibrational frequencies are $1.556 \times 10^{13}\ \mathrm{s}^{-1}$, $3.451 \times 10^{13}\ \mathrm{s}^{-1}$, and $4.080 \times 10^{13}\ \mathrm{s}^{-1}$.

Nuclear Contributions to the Partition Function

The four factors of the molecular partition function that we have discussed are not the complete partition function, because the nuclear contributions have not been included. However, excitation of a typical nucleus to its first excited state requires a very large energy compared with chemical energies (usually millions of electron volts). Excited nuclear states are therefore nearly completely unpopulated at room temperature, and only the nuclear ground-states contribute to the partition function. The degeneracy of nuclear spin states must sometimes be included. For example, if a molecule of *ortho*-hydrogen (see Section 22.3) is not in an external magnetic field, the three states with different projections of the total nuclear angular momentum have the same energy. In this case *ortho*-hydrogen must have a factor of 3 included in its partition function for its nuclear spin degeneracy. There is only one value of the spin projection for *para*-hydrogen, so that *para*-hydrogen requires a factor equal to unity in its partition function. In the presence of a catalyst that can dissociate the hydrogen molecules, *ortho*- and *para*-hydrogen can interconvert rapidly, and can be considered a single substance that requires a factor of 4 in its partition function for the nuclear spin degeneracy.

PROBLEMS

Section 25.4: The Calculation of Molecular Partition Functions

25.21 **a.** Calculate the value of the rotational partition function of CO gas at 298.15 K and at 500.0 K.

b. Find the J value that has the largest population for CO at 298.15 K and at 500.0 K.

c. Find the probability of the energy level corresponding to this value of J at 298.15 K.

25.22 **a.** Calculate the value of the rotational partition function of I_2 gas at 500.0 K.

b. Find the J value that has the largest population for I_2 at 500.0 K. Assume that only even values of J occur.

c. Find the probability of the energy level corresponding to this value of J.

25.23 Calculate the value of the molecular partition function of argon gas at 298.15 K for a volume of $0.02500\ \mathrm{m}^3$ and also for a volume of $1.00\ \mathrm{m}^3$ at the same temperature. Explain in words what the difference between the two values means.

25.24 **a.** Calculate the rotational partition function for H_2 at 298.15 K, using Eq. (25.4-13).

b. Calculate the rotational partition function of H_2 at 298.15 K by adding up terms explicitly, assuming that the hydrogen is all *para*-hydrogen (only even values of J occur). Continue the sum until one additional term in the sum over levels does not change the first four digits of the sum. Compare your result with that of part a.

25.25 Calculate the value of the molecular partition function of Cl_2 gas at 298.15 K and a pressure of 1.000 bar. Find the Russell–Saunders term symbol for the ground-state of atomic chlorine and find the degeneracy of this level. Assume that the electronic partition function can be approximated by g_0, the degeneracy of the ground-level.

25.26 Calculate the value of the molecular partition function of Cl_2 gas at 298.15 K for volume of $0.02500\ \mathrm{m}^3$ and also for a volume of 1.00 m^3 at the same temperature. Explain in words what the difference between the two values means. Which factors in the partition function change values when the volume changes and which remain at the same value?

25.27 Calculate the molecular partition functions of helium gas and krypton gas at 298.15 K, assuming each gas is confined in a volume of 24.45 L. Explain the difference in the two results in terms of effective number of accessible states.

25.28 Calculate the molecular partition function of argon at 300.0 K and at 500.0 K, assuming the gas is confined in a volume of 100 L. Explain the difference in the two results in terms of the effective number of accessible states.

25.29 Calculate the molecular partition function of F_2 gas at 300.0 K and at 500.0 K, assuming the gas is confined in a volume of 100.0 L. Explain the difference in the two results in terms of the effective number of accessible states.

25.30 Calculate the four factors in the partition function of N_2 at 298.15 K if 1.000 mol is confined at 1.000 atm.

25.31 A formula for the rotational partition function of a diatomic substance that gives corrections to the formula of Eq. (25.4-13) is[9]

$$z_{\mathrm{rot}} = \sigma \frac{T}{\Theta_{\mathrm{rot}}}\left[1 + \frac{1}{3}(\Theta_{\mathrm{rot}}/T) + \frac{1}{15}(\Theta_{\mathrm{rot}}/T)^2 + \frac{4}{315}(\Theta_{\mathrm{rot}}/T)^3 + \ldots\right.$$

where Θ_{rot} is called the **rotational temperature**:

$$\Theta_{\mathrm{rot}} = \frac{h^2}{8\pi^2 I_e k_B} = \frac{hB_e}{k_B}$$

Calculate the rotational partition function of H_2 at 298.15 K and compare your answer with that of Eq. (25.4-13) and with the result of Problem 25.24.

25.32 Calculate the rotational partition function of Br_2 at 25.0 K using the formula in Problem 25.31. Compare your result with that obtained from Eq. (25.4-13).

25.33 Calculate the rotational partition function of Cl_2 at 500.0 K using the formula in Problem 25.31. Compare your result with that obtained using Eq. (25.4-13).

25.34 Calculate the rotational partition function of I_2 at 500.0 K using the formula in Problem 25.31. Compare your result with that obtained from Eq. (25.4-13).

25.35 What fraction of diatomic molecules has rotational energy greater than $k_B T$? Assume that the sums can be approximated by integrals.

25.36 The bond distances in H_2O are equal to 95.8 pm, and the bond angle is equal to 104.45°. Find the location of the center of mass and the principal moments of inertia. Calculate the rotational partition function at 298.15 K. Don't forget the symmetry number.

25.37 The C–H bond distances in methane are equal to 1.091×10^{-10} m and the bond angles are equal to the tetrahedral angle, $109°28' 16.394''$. Calculate the rotational partition function for methane at 298.15 K. Comment on the comparison between your value and that for carbon tetrachloride in Example 25.11. You must calculate the moments of inertia, all three of which are equal to each other. Since the molecule is a spherical top, any perpendicular axes are principal axes. One choice is to place the hydrogen atoms at alternating vertices of a cube and to place the axes through the centers of the faces of the cube. You will have to calculate the size of the cube using geometry. Another choice is to place the z axis on a C–H bond and to place another C–H bond in the xz plane and to use the fact that all H atoms contribute equally.

25.38 The bond distances in NH_3 are equal to 101.4 pm, and the bond angles are equal to 107.3°. Find the location of the center of mass and the principal moments of inertia. What is the symmetry number? Calculate the rotational partition function of NH_3 at 500 K. Don't forget the symmetry number.

25.39 In calculating rotational and vibrational partition functions, the upper limit of the sum is taken as infinity. However, states with very high values of the quantum numbers will not occur, because the molecule would dissociate before reaching such a high energy. Explain why this fact does not produce a serious numerical error in calculating the partition function.

25.40 Carry out the summation of the rotational partition function separately for the *ortho* and *para* forms of hydrogen gas. Compare with the result obtained with the integral approximation using a symmetry number of 2 and a nuclear spin degeneracy factor of 4.

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[9] N. Davidson, *op. cit.*, p. 118 (note 2).

Summary of the Chapter

The properties of macroscopic systems are determined by the behavior of molecules making up the system. Through statistical mechanics we can in principle calculate these properties from molecular properties.

The two principal postulates of statistical mechanics are: (1) Observed macroscopic properties of a system held at a fixed energy can be equated to an average over system mechanical states corresponding to that energy. (2) All system states of the same energy are given equal weight in this average.

For a dilute gas, we can average over molecular states with a molecular probability distribution. The most probable distribution was found as an approximation to the average distribution. It is the Boltzmann distribution

$$p_j = \frac{1}{z} g_j e^{-\varepsilon_j/k_\mathrm{B}T}$$

where p_j is the probability that a randomly selected molecule would be found in molecule energy level j, of degeneracy g_j, and energy ϵ_j. The quantity z is the molecular partition function. It can be written as a sum over levels,

$$z = \sum_j g_j e^{-\varepsilon_j/k_\mathrm{B}T}$$

and can also be written as a sum over states, in which case the sum is the same except for the absence of the degeneracy g_j.

For atomic gases, to an excellent approximation

$$z = z_\mathrm{tr} z_\mathrm{el}$$

and for diatomic or polyatomic gases, to a good approximation,

$$z = z_\mathrm{tr} z_\mathrm{rot} z_\mathrm{vib} z_\mathrm{el}$$

All factors except for the electronic partition function can be expressed with general formulas. The electronic partition function must be summed up term by term, but can often be approximated by a single term.

ADDITIONAL PROBLEMS

25.41 **a.** Show that the values of W in Table 25.1 are equal to $\frac{4}{N_0!N_1!N_2!N_3!N_4!}$, where N_0 is the number of times 0 appears in the list of quantum numbers, N_1 is the number of times 1 appears in the list, etc. Remember that 0! is defined to equal 1.

b. Find the value of Ω for the example system of four oscillators if the system energy equals $5h\nu$.

c. Find the value of Ω for the example system of four oscillators if the system energy equals $3h\nu$.

25.42 For a gas of diatomic molecules:

a. What is the effect on the translational partition function if the Kelvin temperature is doubled at constant volume?

b. What is the effect on the translational partition function if the Kelvin temperature is doubled at constant pressure?

c. What is the effect on the rotational partition function if the Kelvin temperature is doubled at constant volume? At constant pressure?

d. What approximately is the effect on the vibrational partition function of a typical small molecule if the Kelvin temperature is doubled from 150 K to 300 K?

e. What approximately is the effect on the electronic partition function of a typical small molecule if the Kelvin temperature is doubled from 150 K to 300 K?

25.43 Choose a diatomic gas and compute its translational, rotational, vibrational, and electronic partition functions at 298.15 K and 1.000 bar, looking up parameters as needed in Table A.22 in Appendix A or in some more complete table.[10] Unless you choose NO or a similar molecule with an unpaired electron, assume that only the ground electronic state needs to be included.

25.44 The ground electronic level of NO is a ${}^2\Pi_{1/2}$term. The first excited level is a ${}^2\Pi_{3/2}$ term with an energy 2.380×10^{-21} J above the ground-level. Both these states have degeneracy equal to 2. All other electronic states are more than 7×10^{-19} J above the ground-level and can be neglected. For the ground-level $\tilde{\nu}_e = 1904.20\,\mathrm{cm}^{-1}$, and $\tilde{B}_e = 1.67195\,\mathrm{cm}^{-1}$. Assume that the ground-level values of $\tilde{\nu}_e$ and $\tilde{B}_e$ can be used for the excited state.

a. Find the electronic factor in the molecular partition function of NO at 298.15 K and 1.000 atm.

b. Find the fraction of NO molecules in the first excited electronic state at 298.15 K.

25.45 Identify the following statements as either true or false. If a statement is true only under special circumstances, label it as false.

a. Dilute gases are the only systems that can be treated with statistical mechanics.

b. Dilute gases are the only systems for which molecular partition functions apply.

c. It is impossible for a state of higher energy to have a larger population than a state of lower energy.

d. The value of the molecular partition function can be interpreted as the effective number of states available to the molecule at the temperature and pressure of the system.

e. Sums over states and sums over levels can be used interchangeably.

f. For a system of macroscopic size, the average distribution of molecular states and the most probable distribution are essentially the same.

g. Fermion and boson probability distributions become more and more like the Boltzmann distribution as the occupation becomes more dilute.

h. Fermion and boson probability distributions become more and more like the Boltzmann distribution as the energy increases.

i. Molecular partition functions are exactly factored into translation, rotational, vibrational, and electronic factors.

j. Negative temperatures are not an equilibrium concept.

25.46 **a.** Represent the electron in a hydrogen atom as an electron in a cubic box 1.00×10^{-10} m on a side. Find the electronic partition function at 298.15 K, using Eq. (25.3-21) for the translational partition function. There are two spin states, so that each state has a degeneracy of 2.

b. There is a problem with part a in that the integral approximate used to derive Eq. (25.3-21) is inaccurate, because adjacent terms in the sum are not nearly equal to each other. Sum the electronic partition function by adding terms explicitly. Discontinue the sum when an additional term changes the value of the sum by less than one part in 1000. Set the energy of the ground-state equal to zero so that energy of an excited level is

$$E_{n_x,n_y,n_z} = \frac{h^2}{8ma^2}\left(n_{x^2} + n_{y^2} + n_{z^2} - 3\right)$$

c. There is a serious conceptual problem with the electronic partition function of the hydrogen atom, since there are infinitely many bound states with finite energy eigenvalues. Explain what this appears to do to the electronic partition function. Some have proposed as a solution to this problem that those states should be omitted that correspond to an expectation value of the atomic radius equal or greater than the size of the known universe.

d. Sum the electronic partition function explicitly for a temperature of 298.15 K, using the energy levels and degeneracies from Chapter 17, including states up to and including the $n = 3$ level, but setting the energy of the $n = 1$ level equal to zero so that the energy of the nth level is

$$E_n = (13.60\,\mathrm{eV})\left(1 - \frac{1}{n^2}\right)$$

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[10] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. Vol. IV. Constants of Diatomic Molecules*, Van Nostrand Reinhold, New York, 1979.

and so on. Repeat the calculation including states up to and including the $n = 5$ level. Compare your answers with each other and with those of parts a and b.

25.47 **a.** Calculate the rotational partition function for *para*-H_2 at 500.0 K, using the formula in Eq. (25.4-13).

b. Repeat the calculation using the formula in Problem 25.31.

c. Repeat the calculation using direct summation.

25.48 Find the ratio of the populations of the $v = 1$, $J = 1$ state and the $v = 0$, $J = 0$ state at 298 K for

a. H_2

b. HD, where D is deuterium, ^2H

c. D_2

25.49 Find the ratio of the populations of the $v = 1$, $J = 1$ state and the $v = 0$, $J = 0$ state at 298 K for:

a. $^1H^{35}Cl$

b. $^1H^{37}Cl$

c. $^2H^{35}Cl$

d. $^2H^{37}Cl$

25.50 **a.** For a temperature of 298 K, find the ratio of the population of the $v = 1$ vibrational state to the population of the $v = 0$ vibrational state of H_2.

b. For a temperature of 298 K, find the ratio of the population of the $v = 1$ vibrational state to the population of the $v = 0$ vibrational state of I_2.

c. Explain why the values in parts a and b are so different.

25.51 **a.** Calculate the ratio of the population of the $v = 1$ vibrational state of HF to the $v = 0$ vibrational state at (a) 298.15 K, (b) 500 K, (c) 1000 K, and (d) 5000 K. What is the limit as $T \to \infty$? Data are found in Table A.22 in Appendix A.

b. Calculate the ratio of the population of the $J = 1$ rotational level of HF to the $J = 0$ rotational level at (a) 298.15 K and (b) 1000 K. What is the limit as $T \to \infty$?

c. Find the value of J that has the largest population for HF at 298.15 K and at 1000 K.

26

Equilibrium Statistical Mechanics. II. Statistical Thermodynamics

PRINCIPAL FACTS AND IDEAS

1. Equilibrium thermodynamic variables of a dilute gas can be expressed in terms of the molecular partition function.
2. Explicit formulas can be derived for molecular partition functions for dilute gases, providing explicit formulas for thermodynamic functions.
3. Equilibrium constants for chemical reactions in dilute gases can be calculated theoretically from molecular partition functions.
4. The activated complex theory of reaction rates in dilute gas mixtures is based on the statistical mechanical theory of chemical equilibrium.

26.1

The Statistical Thermodynamics of a Dilute Gas

In the previous chapter we obtained the probability distribution for molecular states in a dilute gas and obtained a formula for the thermodynamic energy of a dilute gas in terms of the partition function. Statistical mechanics will not be very useful until we obtain formulas for the other thermodynamic functions, which is the topic of this chapter.

The Entropy of a Dilute Gas

If a macroscopic system such as a gas is at thermodynamic equilibrium, its entropy has a well-defined constant value. However, the molecules are moving and occupy many different molecular states without changing the macroscopic state or the value of the entropy. A single macroscopic state and a single value of the entropy must correspond to many microscopic states of the system. We define the *thermodynamic probability* Ω, to be the number of microscopic states of the system that might be occupied for a given macroscopic state of the system.

Boltzmann defined a *statistical entropy* corresponding to a macroscopic state with given values of the energy, volume, and amount of substance:

$$S_{\mathrm{st}} = k_{\mathrm{B}}\ln(\Omega) + S_0 \quad \text{(definition of statistical entropy)} \tag{26.1-1}$$

where k_{B} is Boltzmann's constant, equal to $1.38066 \times 10^{-23}\ \mathrm{J\,K^{-1}}$. The thermodynamic entropy can have an arbitrary constant added to its value, and the same is true of the statistical entropy. The constant S_0 can be set equal to zero, which corresponds to setting the statistical entropy equal to zero for a system that is known to be in a single microstate. We will see later in this chapter that this definition of the statistical entropy leads to values of the entropy of dilute gases that agree with values of the thermodynamic entropy.

We have already encountered the thermodynamic probability in the discussion of our model system of four harmonic oscillators. For the macroscopic state that we studied, Ω was equal to 35. For a typical macroscopic system, Ω will be much larger.

Exercise 26.1

Calculate the statistical entropy of our model system of four harmonic oscillators for the macrostate discussed in Section 25.1.

EXAMPLE 26.1

Estimate the value of Ω for 1.000 mol of helium at 298.15 K and 1.000 atm, using the value of the third-law entropy, $126\ \mathrm{J\,K^{-1}}$.

Solution

$$\Omega = e^{S/k_{\mathrm{B}}} = \exp\left[\frac{126\ \mathrm{J\,K^{-1}}}{1.38 \times 10^{-23}\ \mathrm{J\,K^{-1}}}\right] = e^{9.13\times10^{24}} = 10^{3.96\times10^{24}}$$

Ten raised to an exponent larger than Avogadro's constant is a *very* large number.

In a dilute gas the individual molecules independently occupy molecule energy levels. Each system microstate corresponds to a distribution, which is a list of the numbers of molecules occupying each molecular energy level. However, a given distribution can correspond to many different system microstates. The total number of possible system microstates is equal to the sum of the numbers of microstates corresponding to each distribution:

$$\Omega = \sum_{\{N\}} W(\{N\}) \tag{26.1-2}$$

where $W(\{N\})$ is the number of system microstates corresponding to the distribution denoted by $\{N\}$. There is one term in the sum for each possible distribution. We now make what seems like a drastic approximation. We replace the entire sum shown in Eq. (26.1-2) by its largest term, W_{mp}, the term corresponding to the *most probable distribution*. In our model system of four oscillators, this replacement would amount to replacing $\Omega = 35$ by $\Omega = 12$. The replacement of Ω by W_{mp} is a much worse approximation for a dilute gas of many molecules, but is a very good approximation for the logarithm of the sum.

This strange situation can be illustrated as follows: Assume that we want to have 12 significant digits when we approximate $\ln(\Omega)$ by $\ln(W_{\text{mp}})$. Assume also that Ω has roughly the value as in Example 26.1, so that $\ln(\Omega) \approx 10^{25}$. We let

$$\Omega = xW_{\text{mp}} \tag{26.1-3a}$$

or

$$\ln(\Omega) = \ln(W_{\text{mp}}) + \ln(x) \tag{26.1-3b}$$

Since $\ln(\Omega)$ is roughly equal to 10^{25}, to have $\ln(\Omega)$ and $\ln(W_{\text{mp}})$ agree to 12 significant digits, $\ln(x)$ must obey

$$\ln(x) \le 10^{13}, \quad \text{or} \quad x \le e^{10^{13}}$$

An error in approximating Ω is permissible that makes it incorrect by a factor of $e^{10^{13}}$. The exponent in this expression is roughly equal to the federal debt of the United States in U.S. dollars, and e raised to that power is beyond imagination. However, this tremendous error in Ω still produces a value of $\ln(\Omega)$ that is correct to 12 significant digits. Such is the strange behavior of very large numbers, due to the fact that the logarithm is a very slowly varying function for large values of its argument. Although we will not prove this fact, the largest term in the sum shown in Eq. (26.1-2) is smaller than the entire sum by roughly the same factor as that shown in Eq. (26.1-3), giving 12 significant digits in approximating $\ln(\Omega)$ by $\ln(W_{\text{mp}})$.[1]

Exercise 26.2

Find the value of $d\ln(x)/dx$

a. for $x = 1$

b. for $x = 1.00 \times 10^5$

c. for $x = 1.00 \times 10^{10^5}$

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[1] One year, the author's physical chemistry class showed up for their final examination wearing identical T-shirts. On the T-shirts were written "The top 10 things I learned in p-chem." One of the statements was "12 is equal to 35, but only to 12 significant digits."

The expression for W for a given distribution in a dilute gas was given in Eq. (25.2-13).

$$W(\{N\}) = \prod_{j=1}^{\infty} \frac{g_j^{N_j}}{N_j!}$$

Replacement of $\ln(\Omega)$ by $\ln(W_{\text{mp}})$ and substitution into Eq. (26.1-1) gives

$$\begin{aligned} S = k_{\text{B}}\ln(W_{\text{mp}}) &= k_{\text{B}}\ln\left(\prod_j \frac{g_j^{N_j}}{N_j!}\right) = k_{\text{B}}\sum_j \left[N_j\ln(g_j) - \ln(N_j!)\right] \\ &\approx k_{\text{B}}\sum_j\left[N_j\ln\left(\frac{g_j}{N_j}\right) + N_j\right] \end{aligned} \tag{26.1-4}$$

where we have used the fact that the logarithm of a product is the sum of the logarithms of the factors and have used Stirling's approximation for $\ln(N_j!)$, shown in Eq. (25.2-21). We now replace g_i/N_j in Eq. (26.1-4) by its expression from Eq. (25.3-22):

$$\begin{aligned} S &= k_{\text{B}}\sum_j\left[N_j\ln\left(\frac{z}{N}e^{\varepsilon_j/k_{\text{B}}T}\right) + N_j\right] \\ &= k_{\text{B}}\sum_j\left[N_j\ln\left(\frac{z}{N}\right) + \frac{N_j\varepsilon_j}{k_{\text{B}}T} + N_j\right] = k_{\text{B}}\left[N\ln\left(\frac{z}{N}\right) + \frac{E}{k_{\text{B}}T} + N\right] \end{aligned}$$

$$S = \frac{U}{T} + Nk_{\text{B}}\ln\left(\frac{z}{N}\right) + Nk_{\text{B}} \tag{26.1-5}$$

where the mechanical energy E is identified with the thermodynamic energy U. Equation (26.1-5) is our desired result: a formula for the entropy of a dilute gas in terms of the partition function. It contains the internal energy U, but we have already obtained a formula for U in Eq. (25.3-26).

The Pressure of a Dilute Gas

Since the molecules of a dilute gas move independently, the pressure of the gas is equal to the sum of the pressures exerted by the individual molecules. If the system is in microstate number k, its pressure is

$$P_k = P_{k,1} + P_{k,2} + P_{k,3} + \cdots + P_{k,N} \tag{26.1-6}$$

where $P_{k,1}$ is the pressure exerted by the first molecule given that the system is in microstate k, and so on. This sum can be written in another way by summing over molecular states instead of over molecules. We number the molecular states 1, 2, 3, . . . :

$$P = N_1P_1 + N_2P_2 + N_3P_3 \cdots = \sum_i P_iN_i \tag{26.1-7}$$

where N_i is the number of molecules in molecular state i, and where P_i is the pressure exerted by a molecule in state i.

To find an expression for P_i, we consider a system consisting of a single molecule in a specified state. From Eq. (4.2-6) we have the thermodynamic relation:

$$P = -\left(\frac{\partial U}{\partial V}\right)_{S,n} \tag{26.1-8}$$

If the single molecule is known to be in molecular state i with energy eigenvalue ε_i, $\Omega = 1$ and $S_{\mathrm{st}} = 0$. Since the statistical entropy is constant and the amount of substance is fixed at one molecule, we write an expression for the pressure due to a molecule in state number i

$$P_i = -\frac{d\varepsilon_i}{dV} \tag{26.1-9}$$

If the molecule is confined in a rectangular box, its translational energy levels depend on the dimensions of the box. We assume that the shape of the box is unimportant and proceed as though the box were a cube so that the translational energy levels depend only on the volume of the system. The rotational, vibrational, and electronic energy levels are independent of the volume of the system.

We substitute the expression for p_i from Eq. (25.3-24) into Eq. (26.1-7). We apply a mathematical trick by which we recognize the summand as a derivative:

$$\begin{aligned} P = \frac{N}{z}\sum_i P_i e^{-\varepsilon_i/k_{\mathrm{B}}T} &= -\frac{N}{z}\sum_i \left(\frac{d\varepsilon_i}{dV}\right) e^{-\varepsilon_i/k_{\mathrm{B}}T} \\ &= \frac{Nk_{\mathrm{B}}T}{z}\sum_i \left(\frac{\partial}{\partial V} e^{-\varepsilon_i/k_{\mathrm{B}}T}\right)_T \end{aligned} \tag{26.1-10}$$

If the sum is uniformly convergent, the order of summing and differentiating can be exchanged to give

$$\begin{aligned} P &= \frac{Nk_{\mathrm{B}}T}{z}\left(\frac{\partial}{\partial V}\sum_i e^{-\varepsilon_i/k_{\mathrm{B}}T}\right)_T = Nk_{\mathrm{B}}T\frac{1}{z}\left(\frac{\partial z}{\partial V}\right)_T \\ &= Nk_{\mathrm{B}}T\left(\frac{\partial \ln(z)}{\partial V}\right)_T \end{aligned} \tag{26.1-11}$$

Uniform convergence means that the series converges with at least a certain rate for all values of the variables in the expression.

The translational partition function is the only factor in the partition function that depends on V.

$$P = Nk_{\mathrm{B}}T\left(\frac{\partial \ln(z)}{\partial V}\right)_T = Nk_{\mathrm{B}}T\left(\frac{\partial \ln(z_{\mathrm{tr}})}{\partial V}\right)_T = Nk_{\mathrm{B}}T\left(\frac{\partial \ln[(2\pi m k_{\mathrm{B}}T/h^2)^{3/2}V]}{\partial V}\right)_T$$

$$\boxed{P = Nk_{\mathrm{B}}T\left(\frac{d\ln(V)}{dV}\right) = \frac{Nk_{\mathrm{B}}T}{V} \quad \text{(any dilute gas)}} \tag{26.1-12}$$

Our dilute gas obeys the ideal gas equation of state.

Exercise 26.3

Verify Eq. (26.1-12) by explicit differentiation.

The Heat Capacity of a Dilute Gas

The heat capacity at constant volume is given by Eq. (2.4-4) for a simple system

$$C_{\mathrm{V}} = \left(\frac{\partial U}{\partial T}\right)_{N,V} = \left(\frac{\partial}{\partial T}\left[Nk_{\mathrm{B}}T^2\left(\frac{\partial \ln(z)}{\partial T}\right)_V\right]\right)_{N,V}$$

$$C_{\mathrm{V}} = 2Nk_{\mathrm{B}}T\left(\frac{\partial \ln(z)}{\partial T}\right)_V + Nk_{\mathrm{B}}T^2\left(\frac{\partial^2 \ln(z)}{\partial T^2}\right)_V \tag{26.1-13}$$

The heat capacity at constant pressure for our dilute gas can be obtained from C_{V}. From Eq. (2.5-9) and Eq. (2.5-1)

$$C_{\mathrm{P}} = \left(\frac{\partial H}{\partial T}\right)_{P,n} = \left(\frac{\partial U}{\partial T}\right)_{P,n} + P\left(\frac{\partial V}{\partial T}\right)_{P,n} \tag{26.1-14}$$

Equation (B-7) of Appendix B is an example of the **variable-change identity**:

$$\left(\frac{\partial U}{\partial T}\right)_{P,n} = \left(\frac{\partial U}{\partial T}\right)_{V,n} + \left(\frac{\partial U}{\partial V}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{P,n} \tag{26.1-15}$$

We substitute this equation into Eq. (26.1-14) and use the fact that $C_{\mathrm{V}} = (\partial U/\partial T)_{V,n}$ to write

$$C_{\mathrm{P}} = C_{\mathrm{V}} + \left[\left(\frac{\partial U}{\partial V}\right)_{T,n} + P\right]\left(\frac{\partial V}{\partial T}\right)_{P,n} \tag{26.1-16}$$

From Eq. (26.1-12) a dilute gas obeys the ideal gas equation of state so that

$$\left(\frac{\partial V}{\partial T}\right)_{P,n} = \frac{nR}{P} \quad \text{(dilute gas)} \tag{26.1-17}$$

We assume that our dilute gas shares another property of an ideal gas:

$$(\partial U/\partial V)_{T,n} = 0 \quad \text{(ideal gas)} \tag{26.1-18}$$

so that

$$C_{\mathrm{P}} = C_{\mathrm{V}} + nR = C_{\mathrm{V}} + Nk_{\mathrm{B}} \tag{26.1-19}$$

The Enthalpy of a Dilute Gas

The enthalpy is defined by Eq. (2.5-1):

$$H = U + PV \tag{26.1-20}$$

Since our dilute gas obeys the ideal gas equation of state,

$$H = U + PV = Nk_{\mathrm{B}}T^2\left(\frac{\partial \ln(z)}{\partial T}\right)_V + Nk_{\mathrm{B}}T \tag{26.1-21}$$

The Helmholtz Energy of a Dilute Gas

Using the formula for the entropy, we can obtain a formula for the Helmholtz energy:

$$A = U - TS = U - T\left[\frac{U}{T} + Nk_{\mathrm{B}} + Nk_{\mathrm{B}}\ln\left(\frac{z}{N}\right)\right]$$

$$\boxed{A = -Nk_{\mathrm{B}}T\ln\left(\frac{z}{N}\right) - Nk_{\mathrm{B}}T} \qquad (26.1\text{-}22)$$

The Chemical Potential of a Dilute Gas

In statistical mechanics, it is customary to define the chemical potential as a derivative with respect to the number of molecules, not with respect to the amount in moles:

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} \qquad (26.1\text{-}23)$$

This chemical potential is equal to the thermodynamic chemical potential divided by Avogadro's constant. The number of molecules is an integer, so we use a quotient of finite differences to approximate the derivative in Eq. (26.1-23):

$$\mu = \frac{A_N - A_{N-1}}{1} = A_N - A_{N-1} \qquad (26.1\text{-}24)$$

where the subscripts indicate the number of molecules in the system.

$$\begin{aligned}\mu &= -Nk_{\mathrm{B}}T\ln(z/N) - Nk_{\mathrm{B}}T - \left[-(N-1)k_{\mathrm{B}}T\ln\left(\frac{z}{N-1}\right) - (N-1)k_{\mathrm{B}}T\right]\\ &= -Nk_{\mathrm{B}}T\ln(z) + Nk_{\mathrm{B}}T\ln(N) - Nk_{\mathrm{B}}T + (N-1)k_{\mathrm{B}}T\ln(z)\\ &\quad -(N-1)k_{\mathrm{B}}T\ln(N-1) + Nk_{\mathrm{B}}T - k_{\mathrm{B}}T\\ &= -k_{\mathrm{B}}T\ln(z) + Nk_{\mathrm{B}}T\ln\left(\frac{N}{N-1}\right) + k_{\mathrm{B}}T\ln(N-1) - k_{\mathrm{B}}T \qquad (26.1\text{-}25)\end{aligned}$$

Since N is a large number, the second term of the right-hand side of the final version of this equation can be approximated:

$$\begin{aligned}Nk_{\mathrm{B}}T\ln\left(\frac{N}{N-1}\right) &= -Nk_{\mathrm{B}}T\ln\left(\frac{N-1}{N}\right) = -Nk_{\mathrm{B}}T\ln\left(1-\frac{1}{N}\right)\\ &\approx -Nk_{\mathrm{B}}T\left(-\frac{1}{N}\right) = k_{\mathrm{B}}T \qquad (26.1\text{-}26)\end{aligned}$$

Two terms cancel. Since N is a large number (near 10^{24} in most systems), $\ln(N-1)$ can be replaced by $\ln(N)$ without serious error, so that

$$\boxed{\mu = -k_{\mathrm{B}}T\ln\left(\frac{z}{N}\right)} \qquad (26.1\text{-}27)$$

EXAMPLE 26.2

Show that $\ln(N-1)$ differs from $\ln(N)$ by a term that is proportional to $1/N$.

Solution

$$\ln(N-1) = \ln(N) + \ln\left(1 - \frac{1}{N}\right)$$

The Taylor series that represents $\ln(1-x)$ is

$$\begin{aligned}\ln(1-x) &= \ln(1) + \frac{1}{1!}\left(\frac{d\ln(1-x)}{dx}\right)_{x=0} x + O(x^2)\\ &= 0 - x + O(x^2)\end{aligned}$$

where $O(x^2)$ stands for terms that have powers of x at least as great as x^2.

$$\ln(N-1) = \ln(N) - \frac{1}{N}$$

Exercise 26.4

Equation (26.1-27) can also be obtained by pretending that N can take on any real value and performing the differentiation in Eq. (26.1-23). Carry out this differentiation.

The Gibbs Energy of a Dilute Gas

The Gibbs energy is defined by

$$G = A + PV \tag{26.1-28}$$

so that

$$G = -Nk_BT\ln\left(\frac{z}{N}\right) - Nk_BT + Nk_BT$$

$$\boxed{G = -Nk_BT\ln\left(\frac{z}{N}\right)} \tag{26.1-29}$$

Note that

$$G = N\mu \tag{26.1-30}$$

This is a version of Euler's theorem, which is discussed in Part I of this textbook.

PROBLEMS

Section 26.1: The Statistical Thermodynamics of a Dilute Gas

26.1 Consider the two isotopic substances $^{17}O_2$ and $^{16}O^{18}O$. Round off the atomic masses in amu to the nearest integer. Answer the following questions without detailed calculation:

a. How will the translational partition functions of the two molecules compare at equal volumes and equal temperatures?

b. How will the rotational partition functions of the two molecules compare at equal volumes and equal temperatures?

c. How will the vibrational partition functions of the two molecules compare at 300 K?

d. How will the energies of 1.000 mol of each substance compare at 1.000 bar (100,000 Pa) and 300 K?

e. How will the entropies of 1.000 mol of each substance compare at 1.000 bar and 300 K?

26.2 **a.** Find the molar entropy of helium at 323.15 K and 1.000 bar (100,000 Pa).

b. Using the value from part a, estimate the value of Ω for 1.000 mol of helium at 323.15 K and 1.000 bar (100,000 Pa). Find the ratio of this value to the value of Example 26.1 and comment on this ratio.

26.3 Using the thermodynamic relation

$$\mu = \left(\frac{\partial G}{\partial N}\right)_{T,P}$$

derive the formula for the chemical potential of a dilute gas. You must express the molecular partition function in terms of T and P.

26.4 Calculate the Helmholtz energy of 1.000 mol of Cl_2 gas at 298.15 K and 1.000 bar pressure.

26.5 Calculate the molar entropy of water vapor at 100°C and 1.000 bar. The bond distances are equal to 95.8 pm and the bond angle is equal to 104.45°. The vibrational frequencies are $4.7817 \times 10^{13}\ \mathrm{s}^{-1}$, $1.0947 \times 10^{14}\ \mathrm{s}^{-1}$, and $1.1260 \times 10^{14}\ \mathrm{s}^{-1}$.

26.6 Calculate the value of $\mu - \varepsilon_0$ for water vapor at 100°C and 1.000 bar, where ε_0 is the ground-state energy of the molecule.

26.7 Calculate the molar heat capacity at constant pressure for carbon dioxide at 298.15 K.

26.2 Working Equations for the Thermodynamic Functions of a Dilute Gas

In the previous section we obtained general formulas for the thermodynamic variables of a dilute gas in terms of the logarithm of the molecular partition function. In this section we write working formulas for the different contributions to the thermodynamic functions. If the partition function is factored as in Eq. (25.4-6), the logarithm is a sum of terms:

$$\ln(z) = \ln(z_{\mathrm{tr}}) + \ln(z_{\mathrm{rot}}) + \ln(z_{\mathrm{vib}}) + \ln(z_{\mathrm{elec}}) \quad \text{(atoms)} \tag{26.2-1a}$$

$$\ln(z) = \ln(z_{\mathrm{tr}}) + \ln(z_{\mathrm{rot}}) + \ln(z_{\mathrm{vib}}) + \ln(z_{\mathrm{el}}) \quad \text{(molecules)} \tag{26.2-1b}$$

The Internal Energy of a Dilute Gas

Since the logarithm of the partition function is a sum of terms, the internal energy of a dilute gas is a sum of contributions. For a monatomic substance

$$U = U_{\mathrm{tr}} + U_{\mathrm{el}} \tag{26.2-2a}$$

For a molecular substance

$$U = U_{\mathrm{tr}} + U_{\mathrm{el}} + U_{\mathrm{rot}} + U_{\mathrm{vib}} \tag{26.2-2b}$$

The Translational Energy of a Dilute Gas

The translational contribution to the energy is the same for all dilute gases:

$$
\begin{aligned}
U_{\mathrm{tr}} &= Nk_{\mathrm{B}}T^2\left(\frac{\partial \ln(z_{\mathrm{tr}})}{\partial T}\right)_V = Nk_{\mathrm{B}}T^2\left(\frac{\partial}{\partial T}\ln\left(\frac{2\pi m k_{\mathrm{B}}T}{h^2}\right)^{3/2}V\right)_V \\
&= \frac{3}{2}Nk_{\mathrm{B}}T^2\frac{d}{dT}\ln(T)
\end{aligned}
$$

$$\boxed{U_{\mathrm{tr}} = \frac{3}{2}Nk_{\mathrm{B}}T} \tag{26.2-3}$$

The Electronic Energy of a Dilute Gas

The electronic contribution to the energy is obtained by manual summation:

$$
\begin{aligned}
U_{\mathrm{el}} &= Nk_{\mathrm{B}}T^2\left(\frac{d\ln(z_{\mathrm{el}})}{dT}\right) \\
U_{\mathrm{el}} &= Nk_{\mathrm{B}}T^2\frac{d}{dT}\left[\ln(g_0e^{-\varepsilon_0/k_{\mathrm{B}}T} + g_1e^{-\varepsilon_1/k_{\mathrm{B}}T} + \cdots\right] \\
&= Nk_{\mathrm{B}}T\frac{1}{z_{\mathrm{el}}}\left[g_0\frac{\varepsilon_0}{k_BT}e^{-\varepsilon_0/k_{\mathrm{B}}T} + g_1\frac{\varepsilon_1}{k_{\mathrm{B}}T}e^{-\varepsilon_1/k_{\mathrm{B}}T} + \cdots\right] \\
&= \frac{N}{z_{\mathrm{el}}}[g_0\varepsilon_0e^{-\varepsilon_0/k_{\mathrm{B}}T} + g_1\varepsilon_1e^{-\varepsilon_1/k_{\mathrm{B}}T} + \cdots\,]
\end{aligned}
\tag{26.2-4}
$$

In most atoms and molecules, the ground electronic level is nondegenerate and the first excited level is sufficiently high in energy that at room temperature the second and further terms in the sum can be neglected. In this case the electronic partition function is very nearly equal to $g_0e^{-\varepsilon_0/k_{\mathrm{B}}T}$ and

$$U_{\mathrm{el}} \approx N\varepsilon_0\begin{pmatrix}\text{molecules with high}\\ \text{first excited level}\end{pmatrix} \tag{26.2-5a}$$

If the ground-state electronic energy ε_0 is chosen to equal zero, then

$$U_{\mathrm{el}} \approx 0\begin{pmatrix}\text{molecules with high}\\ \text{first excited level}\\ \text{and } \varepsilon_0 = 0\end{pmatrix} \tag{26.2-5b}$$

Some substances such as NO have an excited level that is near the ground level, so that Eq. (26.2-5) does not apply, as will be illustrated in the following example.

EXAMPLE 26.3

Find the electronic contribution to the thermodynamic energy of 1.000 mol of gaseous NO at 1.000 atm and 298.15 K. The ground electronic level is a $^2\Pi_{1/2}$ term. The first excited level is a $^2\Pi_{3/2}$ term with an energy 2.380×10^{-21} J above the ground level. Both levels have a degeneracy equal to 2.

Solution

$$z_{\mathrm{el}} \approx 2 + 2e^{-\varepsilon_1/k_{\mathrm{B}}T} = 2 + 2\exp\left(\frac{-2.380 \times 10^{-21}\,\mathrm{J}}{(1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}})(298.15\,\mathrm{K})}\right)$$

$$\approx 2 + 2e^{-0.57815} = 3.1219$$

$$U_{m,\mathrm{el}} \approx \frac{N_{\mathrm{Av}}}{z_{\mathrm{el}}}\left(0 + g_1\varepsilon_1 e^{-\varepsilon_1/k_{\mathrm{B}}T}\right)$$

$$\approx \frac{6.02214 \times 10^{23}\,\mathrm{mol^{-1}}}{3.1219}\left(0 + 2(2.38 \times 10^{-21}\,\mathrm{J})e^{-0.57815}\right)$$

$$\approx 515.1\,\mathrm{J\,mol^{-1}}$$

The Rotational Energy of a Dilute Gas

For a diatomic substance or a polyatomic substance with linear molecules the rotational energy is given by

$$U_{\mathrm{rot}} = Nk_{\mathrm{B}}T^2\left(\frac{d\ln(z_{\mathrm{rot}})}{dT}\right)_V = Nk_{\mathrm{B}}T^2\left(\frac{d\ln(8\pi^2 Ik_{\mathrm{B}}T/\sigma h^2}{dT}\right)$$

$$= Nk_{\mathrm{B}}T^2\frac{d\ln(\mathrm{constant})}{dT} + Nk_{\mathrm{B}}T^2\frac{d\ln(\mathrm{T})}{dT} = Nk_{\mathrm{B}}T^2\frac{1}{T}$$

$$U_{\mathrm{rot}} = Nk_{\mathrm{B}}T = nRT \quad \text{(diatomic or linear molecules)} \tag{26.2-6}$$

For a polyatomic substance with nonlinear molecules, z_{rot} is proportional to $T^{3/2}$ so that

$$U_{\mathrm{rot}} = \frac{3}{2}Nk_{\mathrm{B}}T = \frac{3}{2}nRT \quad \text{(nonlinear molecules)} \tag{26.2-7}$$

Exercise 26.5

Show by differentiation that Eq. (26.2-7) is correct.

The Vibrational Energy of a Dilute Gas

If the zero-point vibrational energy is excluded from the vibrational energy, the vibrational energy of a dilute diatomic gas is given by

$$U_{\mathrm{vib}} = Nk_{\mathrm{B}}T^2\left(\frac{d\ln(z_{\mathrm{vib}})}{dT}\right)_V = Nk_{\mathrm{B}}T^2\,\frac{d}{dT}\left[\ln\left(\frac{1}{1 - e^{-h\nu/k_{\mathrm{B}}T}}\right)\right]$$

$$U_{\mathrm{vib}} = \frac{Nhc\tilde{\nu}_e}{e^{hc\tilde{\nu}_e/k_{\mathrm{B}}T} - 1} \quad \text{(diatomic substance)} \tag{26.2-8}$$

Exercise 26.6

a. Carry out the steps of algebra to obtain Eq. (26.2-8).

b. Find the expression for the vibrational energy if the zero-point energy is included in the vibrational energy, giving the vibrational partition function of Eq. (25.4-20).

For a polyatomic substance, the vibrational energy contains one term for each normal mode:

$$U_{\mathrm{vib}} = Nk_{\mathrm{B}}T^2\left(\frac{\partial \ln(z_{\mathrm{vib}})}{\partial T}\right)_V = \sum_{i=1}^{3n-5(6)} Nk_{\mathrm{B}}T^2\frac{d}{dT}\left[\ln\left(\frac{1}{1-e^{-h\nu_i/k_{\mathrm{B}}T}}\right)\right]$$

$$U_{\mathrm{vib}} = \sum_{i=1}^{3n-5(6)} \frac{Nh\nu_i}{e^{h\nu_i/k_{\mathrm{B}}T}-1} = \sum_{i=1}^{3n-5(6)} \frac{Nhc\tilde{\nu}_i}{e^{hc\tilde{\nu}_i/k_{\mathrm{B}}T}-1} \quad \begin{pmatrix}\text{polyatomic}\\ \text{substances}\end{pmatrix} \tag{26.2-9}$$

The upper limit on the sum equals $3n-5$ for linear polyatomic molecules and equals $3n-6$ for nonlinear polyatomic molecules.

EXAMPLE 26.4

The vibrational frequency of CO is equal to $6.5048 \times 10^{13}\ \mathrm{cm}^{-1}$.

a. Find the value of the vibrational partition function at 298.15 K.

b. Find the vibrational contribution to the molar energy at 298.15 K.

Solution

We set the zero of vibrational energy at the lowest vibrational state. We let

$$x = \frac{h\nu}{k_{\mathrm{B}}T} = \frac{(6.6261 \times 10^{-34}\,\mathrm{J\ s})(6.5048 \times 10^{13}\ \mathrm{s}^{-1})}{(1.3807 \times 10^{-23}\,\mathrm{J\ K}^{-1})(298.15\,\mathrm{K})} = 10.47$$

a. $z_{\mathrm{vib}} = \frac{1}{1-e^{-x}} = 1.0000284$

b. $U_{\mathrm{vib}} = \frac{Nh\nu}{e^x-1}$

$$= \frac{(6.022 \times 10^{23}\ \mathrm{mol}^{-1})(6.6261 \times 10^{-34}\ \mathrm{J\ s})(6.5048 \times 10^{13}\mathrm{s}^{-1})}{e^{10.47}-1}$$

$$= 0.737\,\mathrm{J\ mol}^{-1}$$

The closeness of the partition function to unity and the small value of the vibrational energy show that the ground vibrational state is the only significantly occupied vibrational state.

Exercise 26.7

a. Repeat the calculation of Example 26.4 with the zero-point energy included in the vibrational energy, so that the vibrational partition function is given by Eq. (25.4-20).

b. Find the value of the vibrational partition function and the vibrational energy for 1.000 mol of gaseous iodine at 500 K with the zero of energy taken at the zero-point energy.

c. Find the value of the vibrational partition function and the vibrational energy for 1.000 mol of gaseous iodine at 500 K with the zero of energy taken at the minimum of the vibrational potential energy.

The Heat Capacity of a Dilute Gas

The heat capacity at constant volume is given by Eq. (26.1-13), but it is easier to differentiate the formulas for the internal energy.

$$C_{\mathrm{V,tr}} = \left(\frac{\partial U_{\mathrm{tr}}}{\partial T}\right)_{V,N} = \frac{3}{2}Nk_{\mathrm{B}} = \frac{3}{2}n\mathrm{R} \tag{26.2-10a}$$

$$C_{\mathrm{V,el}} = \left(\frac{\partial U_{\mathrm{el}}}{\partial T}\right)_{N} \approx 0 \quad \text{(most substances)} \tag{26.2-10b}$$

$$C_{\mathrm{V,rot}} = \left(\frac{\partial U_{\mathrm{rot}}}{\partial T}\right)_{N} = Nk_{\mathrm{B}} = n\mathrm{R} \quad \left(\begin{array}{c}\text{diatomic or linear}\\ \text{polyatomic}\\ \text{substances}\end{array}\right) \tag{26.2-10c}$$

$$C_{\mathrm{V,rot}} = \left(\frac{\partial U_{\mathrm{rot}}}{\partial T}\right)_{N} = \frac{3}{2}Nk_{\mathrm{B}} = \frac{3}{2}n\mathrm{R} \quad \left(\begin{array}{c}\text{nonlinear}\\ \text{polyatomic}\\ \text{substances}\end{array}\right) \tag{26.2-10d}$$

$$\begin{aligned} C_{\mathrm{V,vib}} &= \frac{d}{dT}\left(\frac{Nh\nu}{e^{h\nu/k_{\mathrm{B}}T}-1}\right) = \frac{Nh\nu}{(e^{h\nu/k_{\mathrm{B}}T}-1)^2}e^{h\nu/k_{\mathrm{B}}T}\left(\frac{h\nu}{k_{\mathrm{B}}T^2}\right) \\ &= Nk_{\mathrm{B}}\left(\frac{h\nu}{k_{\mathrm{B}}T}\right)^2\frac{e^{h\nu/k_{\mathrm{B}}T}}{(e^{h\nu/k_{\mathrm{B}}T}-1)^2} = Nk_{\mathrm{B}}\left(\frac{h\nu}{k_{\mathrm{B}}T}\right)^2\frac{e^{h\nu/k_{\mathrm{B}}T}}{(e^{h\nu/k_{\mathrm{B}}T}-1)^2} \end{aligned}$$

$$C_{\mathrm{V,vib}} = Nk_{\mathrm{B}}\left(\frac{hc\tilde{\nu}}{k_{\mathrm{B}}T}\right)^2\frac{e^{hc\tilde{\nu}/k_{\mathrm{B}}T}}{(e^{hc\tilde{\nu}/k_{\mathrm{B}}T}-1)^2} \quad \left(\begin{array}{c}\text{diatomic}\\ \text{substances}\end{array}\right) \tag{26.2-10e}$$

$$C_{\mathrm{V,vib}} = Nk_{\mathrm{B}}\sum_{i=1}^{3n-5(6)}\left(\frac{hc\tilde{\nu}_i}{k_{\mathrm{B}}T}\right)^2\frac{e^{hc\tilde{\nu}_i/k_{\mathrm{B}}T}}{(e^{hc\tilde{\nu}_i/k_{\mathrm{B}}T}-1)^2} \quad \left(\begin{array}{c}\text{polyatomic}\\ \text{substances}\end{array}\right) \tag{26.2-10f}$$

The heat capacity at constant pressure is given by Eq. (26.1-19). We add the term Nk_{B} to the translational contribution. The other contributions to C_{P} are the same as the contributions to C_{V}.

$$C_{\mathrm{P,tr}} = C_{\mathrm{V,tr}} + Nk_{\mathrm{B}} = \frac{5}{2}Nk_{\mathrm{B}} = \frac{5}{2}nR \tag{26.2-10g}$$

EXAMPLE 26.5

Calculate C_V and C_P for 1.000 mol of $^{35}Cl_2$ at 298.15 K.

Solution

From Table A.22 in Appendix A, $\tilde{\nu}_e = 559.7\ \mathrm{cm^{-1}}$. The rotational constant is not needed.

$$C_{V,m,\mathrm{tr}} = \frac{3N_{\mathrm{Av}}k_B}{2} = \frac{3R}{2} = \frac{3(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})}{2} = 12.472\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

$$C_{V,m,\mathrm{rot}} = N_{\mathrm{Av}}k_B = R = 8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

$$\text{Let } x = \frac{h\nu}{k_BT} = \frac{hc\tilde{\nu}_e}{k_BT}$$

$$= \frac{(6.6261\times10^{-34}\ \mathrm{J\,s})(2.9979\times10^{10}\ \mathrm{cm\,s^{-1}})(559.7\ \mathrm{cm^{-1}})}{(1.3807\times10^{-23}\ \mathrm{J\,K^{-1}})(298.15\ \mathrm{K})} = 2.701$$

$$C_{V,m,\mathrm{vib}} = Rx^2\frac{e^x}{(e^x-1)^2} = R(2.701)^2\frac{e^{2.7009}}{(e^{2.701}-1)^2} = 4.680\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

$$C_{V,m,\mathrm{el}} \approx 0$$

$$C_{V,m} = C_{V,m,\mathrm{tr}} + C_{V,m,\mathrm{rot}} + C_{V,m,\mathrm{vib}} + C_{V,m,\mathrm{el}}$$

$$= 12.472\ \mathrm{J\,K^{-1}\,mol^{-1}} + 8.3145\ \mathrm{J\,mol^{-1}} + 4.68\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

$$= 25.466\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

$$C_{P,m} = C_{V,m} + R = 25.466\ \mathrm{J\,K^{-1}\,mol^{-1}} + 8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

$$= 33.781\ \mathrm{J\,K^{-1}\,mol^{-1}}$$

This compares with the experimental, value 33.949 $\mathrm{J\,K^{-1}\,mol^{-1}}$. The discrepancy is presumably due to the use of the harmonic oscillator–rigid rotor approximation.

EXAMPLE 26.6

Derive a formula for the electronic contribution to the heat capacity for a system like NO for which two electronic states must be included.

Solution

Take the energy of the ground electronic state as zero:

$$z_{\mathrm{el}} = g_0 + g_1e^{-\varepsilon_1/k_BT}$$

$$\varepsilon_{\mathrm{el}} = \frac{1}{z_{\mathrm{el}}}g_1\varepsilon_1e^{-\varepsilon_1/k_BT}$$

$$C_{V,\text{el}} = N\frac{d\varepsilon_{\text{el}}}{dT} = -\frac{N}{z_{\text{el}}^2}\frac{dz_{\text{el}}}{dT}g_1\varepsilon_1 e^{-\varepsilon_1/k_\text{B}T} + \frac{N}{z_{\text{el}}}g_1\frac{\varepsilon_1^2}{k_\text{B}T^2}e^{-\varepsilon_1/k_\text{B}T}$$

$$= -\frac{N}{z_{\text{el}}{}^2}\frac{1}{k_\text{B}T^2}\left(g_1\varepsilon_1 e^{-\varepsilon_1/k_\text{B}T}\right)^2 + \frac{N}{z_{\text{el}}}g_1\frac{\varepsilon_1^2}{k_\text{B}T^2}e^{-\varepsilon_1/k_\text{B}T}$$

$$= \frac{N}{z_{\text{el}}}e^{-\varepsilon_1/k_\text{B}T}\left(\frac{g_1\varepsilon_1^2}{k_\text{B}T^2}\right)\left(1 - \frac{g_1 e^{-\varepsilon_1/k_\text{B}T}}{z_{\text{el}}}\right)$$

Exercise 26.8

Evaluate the electronic contribution to the molar heat capacity of NO at 298.15 K. The ground electronic level is a $^2\Pi_{1/2}$ term. The first excited level is a $^2\Pi_{3/2}$ term with an energy 2.380×10^{-21} J above the ground level. Both levels have a degeneracy equal to 2.

The Entropy of a Dilute Gas

The entropy is also a sum of contributions.

$$S = S_{\text{tr}} + S_{\text{rot}} + S_{\text{vib}} + S_{\text{el}} \tag{26.2-11}$$

From Eq. (26.1-5)

$$S_{\text{tr}} = \frac{U_{\text{tr}}}{T} + Nk_\text{B}\ln\left(\frac{\mathcal{Z}_{\text{tr}}}{N}\right) + Nk_\text{B} \tag{26.2-12a}$$

$$S_{\text{rot}} = \frac{U_{\text{rot}}}{T} + Nk_\text{B}\ln(\mathcal{Z}_{\text{rot}}) \tag{26.2-12b}$$

$$S_{\text{vib}} = \frac{U_{\text{vib}}}{T} + Nk_\text{B}\ln(\mathcal{Z}_{\text{vib}}) \tag{26.2-12c}$$

$$S_{\text{el}} = \frac{U_{\text{el}}}{T} + Nk_\text{B}\ln(\mathcal{Z}_{\text{el}}) \tag{26.2-12d}$$

There is only one additive term, Nk_B, and there is only one divisor, N, in Eq. (26.1-5), and these are placed with the translational contribution to the entropy.

The translational molar energy is $3R/2$ and the additive term is equal to R, so that the translational contribution to the molar entropy of a dilute gas is

$$S_{\text{m,tr}} = \frac{5R}{2} + R\ln\left(\frac{z_{\text{tr}}}{N_{\text{Av}}}\right) \tag{26.2-13}$$

where N_{Av} is Avogadro's constant. Using Eq. (25.3-21) and the ideal gas equation of state, we write

$$\frac{z_{\text{tr}}}{N_{\text{Av}}} = \left(\frac{2\pi mk_\text{B}T}{h^3}\right)^{3/2}\frac{V}{N_{\text{Av}}} = \left(\frac{2\pi mk_\text{B}T}{h^3}\right)^{3/2}\frac{k_\text{B}T}{P} = \frac{(2\pi m)^{3/2}(k_\text{B}T)^{5/2}}{h^3P}$$

$$= \frac{(2\pi M/N_{\text{Av}})^{3/2}(k_\text{B}T)^{5/2}}{h^3P^\circ}\left(\frac{P^\circ}{P}\right) \tag{26.2-14}$$

where M is the molar mass of the gas. The symbol $P°$ represents the *standard-state pressure*, which is defined to equal exactly 100,000 Pa = 1.000 bar. Substituting in the values of the constants we obtain the *Sackur–Tetrode equation* for the translational contribution to the entropy of any dilute gas:

$$S_{\mathrm{m}} = S_{\mathrm{m,tr}} = R\left[9.2100 + \frac{3}{2}\ln\left(\frac{M}{1\,\mathrm{kg\,mol}^{-1}}\right) + \frac{5}{2}\ln\left(\frac{T}{1\,K}\right) - \ln\left(\frac{P}{P°}\right)\right] \tag{26.2-15}$$

where the divisors 1 kg mol^{-1} and 1 K are inserted to make the arguments of the logarithms dimensionless. For a monatomic gas without significant electronic excitation, the translational contribution is the only contribution to the entropy.

EXAMPLE 26.7

Calculate the molar entropy of helium gas at 1.000 bar pressure and 298.15 K.

Solution

At this temperature there is no significant electronic excitation and the ground electronic state is a $^1S_0$ term, so $z_{\mathrm{el}} = 1$ and $z = z_{\mathrm{tr}}$. The molar mass of helium is equal to $M = 0.0040026\,\mathrm{kg\,mol}^{-1}$, so that from the Sackur–Tetrode equation

$$\begin{aligned} S^{\circ}_{\mathrm{m,tr}} &= (8.3145\,\mathrm{J\,K}^{-1}\,\mathrm{mol}^{-1})\left(9.2100 + \frac{3}{2}\ln(0.0040026) + \frac{5}{2}\ln(298.15) + \ln(1)\right) \\ &= 126.23\,\mathrm{J\,K}^{-1}\,\mathrm{mol}^{-1} \end{aligned}$$

The third-law entropy value of the standard-state entropy of He gas is 126.152 J K^{-1} mol^{-1}. This degree of agreement lends credence to our identification of the statistical entropy with the thermodynamic entropy.

Exercise 26.9

The value of the energy in the ground state has been assigned the value zero in the calculation of Example 26.7. Show that the value of the entropy of a dilute gas is unchanged if the zero of energy is changed.

EXAMPLE 26.8

Calculate the partition function and the molar energy, enthalpy, and entropy and constant-pressure heat capacity 1.000 mol of $^{35}\mathrm{Cl}_2$ at 298.15 K and the standard-state pressure $P°$. Assume that the uncorrected harmonic oscillator–rigid rotor energy levels can be used.

Data: $\tilde{\nu}_e = 559.7\ \mathrm{cm}^{-1}$

$\tilde{B}_e = 0.2440\ \mathrm{cm}^{-1}$

$M = 0.0699375\,\mathrm{kg\,mol}^{-1}$

$m = 1.16134 \times 10^{-25}\,\mathrm{kg}$

$V = 0.02479\,\mathrm{m}^3$(the molar volume of an ideal gas at $P°$)

Solution

$$
\begin{aligned}
z_{\mathrm{tr}} &= \left(\frac{2\pi m k_{\mathrm{B}} T}{h^2}\right)^{3/2} V \\
&= \left(\frac{2\pi(1.16134 \times 10^{-25}\ \mathrm{kg})(1.3807 \times 10^{-23}\ \mathrm{J\ K^{-1}})(298.15\ \mathrm{K})}{(6.6261 \times 10^{-34}\ \mathrm{J\ s})^2}\right)^{3/2} (0.02479\ \mathrm{m^3}) \\
&= 1.4028 \times 10^{31}
\end{aligned}
$$

$$
\frac{z_{\mathrm{tr}}}{N} = \frac{1.4028 \times 10^{31}}{6.022 \times 10^{23}} = 2.329 \times 10^{7}
$$

The rotational partition function was already calculated in Example 25.7:

$$
z_{\mathrm{rot}} = 424.7
$$

The vibrational partition function was already calculated in Example 25.8:

$$
\begin{aligned}
z_{\mathrm{vib}} &= 1.072 \\
z_{\mathrm{el}} &\approx 1.000 \\
z &= z_{\mathrm{tr}} z_{\mathrm{rot}} z_{\mathrm{vib}} z_{\mathrm{el}} = (1.4028 \times 10^{31})(424.7)(1.072)(1.000) = 6.3867 \times 10^{33} \\
\frac{z}{N} &= \frac{6.3867 \times 10^{33}}{6.02214 \times 10^{23}} = 1.0605 \times 10^{10} \\
U^{\circ}_{\mathrm{m,tr}} &= \frac{3}{2} RT = (1.500\ \mathrm{mol})(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K}) = 3718.45\ \mathrm{J\ mol^{-1}} \\
U^{\circ}_{\mathrm{m,rot}} &= RT = (1.000\ \mathrm{mol})(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K}) = 2478.97\ \mathrm{J\ mol^{-1}} \\
U^{\circ}_{\mathrm{m,vib}} &= \frac{N_{\mathrm{Av}} h\nu}{e^{h\nu/k_{\mathrm{B}}T} - 1} = \frac{N_{\mathrm{Av}} hc\tilde{\nu}}{e^{hc\tilde{\nu}/k_{\mathrm{B}}T} - 1} = 481.92\ \mathrm{J\ mol^{-1}} \\
U^{\circ}_{\mathrm{m,el}} &\approx 0 \\
U^{\circ}_{\mathrm{m}} &= 3718.45\ \mathrm{J\ mol^{-1}} + 2478.97\ \mathrm{J\ mol^{-1}} + 481.92\ \mathrm{J\ mol^{-1}} \\
&= 6679.34.42\ \mathrm{J\ mol^{-1}} \\
&= 6.67934\ \mathrm{kJ\ mol^{-1}} \\
H^{\circ}_{\mathrm{m}} &= U^{\circ}_{\mathrm{m}} + PV_{\mathrm{m}} = U^{\circ}_{\mathrm{m}} + RT = 6679.34\ \mathrm{J\ mol^{-1}} + 2478.97\ \mathrm{J\ mol^{-1}} \\
&= 9158.31\ \mathrm{J\ mol^{-1}} = 9.15831\ \mathrm{kJ\ mol^{-1}}
\end{aligned}
$$

These values are relative to the ground-state energy. The experimental value of $\mathrm{H}^{\circ}_{\mathrm{m}}$ is $9.181\ \mathrm{kJ\ mol^{-1}}$ relative to this zero of energy.

$$
\begin{aligned}
S^{\circ}_{\mathrm{m,tr}} &= (8.3145\ \mathrm{J\ K^{-1} mol^{-1}})\left(9.2100 + \frac{5}{2}\ln(298.15) + \frac{3}{2}\ln(0.0699375) + \ln(1)\right) \\
&= 161.831\ \mathrm{J\ K^{-1}\ mol^{-1}} \\
S^{\circ}_{\mathrm{m,rot}} &= \frac{U_{\mathrm{m,\,rot}}}{T} + R\ln(z_{\mathrm{rot}}) = R + R\ln(z_{\mathrm{rot}}) \\
&= 8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}} + (8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})\ln(424.7) = 58.627\ \mathrm{J\ K^{-1}\ mol^{-1}}
\end{aligned}
$$

$$
\begin{aligned}
S^{\circ}_{\text{m,vib}} &= \frac{U_{m,\text{vib}}}{T} + R\ln(z_{\text{vib}}) \\
&= \frac{481.92\ \text{J mol}^{-1}}{298.15\ \text{K}} + (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\ln(1.072) = 2.194\ \text{J K}^{-1}\ \text{mol}^{-1} \\
S^{\circ}_{\text{m,el}} &= \frac{U^{\circ}_{m,\text{el}}}{T} + R\ln(z_{\text{el}}) \approx 0 + 0 = 0 \\
S^{\circ}_{\text{m}} &= 161.831\ \text{J K}^{-1}\ \text{mol}^{-1} + 58.627\ \text{J K}^{-1}\ \text{mol}^{-1} + 2.194\ \text{J K}^{-1}\ \text{mol}^{-1} \\
&= 222.652\ \text{J K}^{-1}\ \text{mol}^{-1}
\end{aligned}
$$

The experimental value is 223.079 J K^{-1} mol^{-1}.

$$
\begin{aligned}
C^{\circ}_{\text{V,m,tr}} &= \frac{3}{2}R = 12.4718\ \text{J K}^{-1}\ \text{mol}^{-1} \\
C^{\circ}_{\text{V,m,rot}} &= R = 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1} \\
C^{\circ}_{\text{V,m,vib}} &= R\left(\frac{h\nu}{k_{\text{B}}T}\right)^2 \frac{e^{h\nu/k_{\text{B}}T}}{(e^{h\nu/k_{\text{B}}T}-1)^2} = Rx^2\frac{e^x}{(e^x-1)^2} = 4.680\ \text{J K}^{-1}\ \text{mol}^{-1} \\
C^{\circ}_{\text{V,mel}} &\approx 0 \\
C^{\circ}_{\text{V,m}} &= 25.466\ \text{J K}^{-1}\ \text{mol}^{-1} \\
C^{\circ}_{\text{P,m}} &= 25.466\ \text{J K}^{-1}\ \text{mol}^{-1} + 8.3145\ \text{J K}^{-1}\ \text{mol}^{-1} = 33.780\ \text{J K}^{-1}\ \text{mol}^{-1}
\end{aligned}
$$

The experimental value is 33.949 J K^{-1} mol^{-1} at this temperature. The discrepancies between our values and the experimental values are presumably due to the inadequacy of the harmonic oscillator–rigid rotor energy level expression.

The Helmholtz Energy of a Dilute Gas

The contributions to the Helmholtz energy are given by the formulas

$$A_{\text{tr}} = -Nk_{\text{B}}T\ln\left(\frac{\mathcal{Z}_{\text{tr}}}{N}\right) - Nk_{\text{B}}T \tag{26.2-16a}$$

$$A_{\text{rot}} = -Nk_{\text{B}}T\ln(\mathcal{Z}_{\text{rot}}) \tag{26.2-16b}$$

$$A_{\text{vib}} = -Nk_{\text{B}}\ln(\mathcal{Z}_{\text{vib}}) \tag{26.2-16c}$$

$$A_{\text{elec}} = -Nk_{\text{B}}\ln(\mathcal{Z}_{\text{elec}}) \tag{26.2-16d}$$

where we place the divisor N and the term $Nk_{\text{B}}T$ with the translational contribution.

EXAMPLE 26.9

Find the vibrational contributions to the thermodynamic energy, Helmholtz energy, and entropy of 1.000 mole of water vapor at 1.00 atm and 100°C. There are three vibrational normal modes, with frequencies $1.0947 \times 10^{14}\ \text{s}^{-1}$, $4.7817 \times 10^{13}\ \text{s}^{-1}$, and $1.1260 \times 10^{14}\ \text{s}^{-1}$.

Solution

The vibrational contribution is independent of the pressure. Let $x_i = h\nu_i/k_\mathrm{B}T$, so that at 373.15 K, $x_1 = 14.079$, $x_2 = 6.1498$, and $x_3 = 14.482$.

$$U_\mathrm{vib} = \sum_{i=1}^{3} \frac{Nh\nu_i}{e^{h\nu_i/k_\mathrm{B}T} - 1} = Nh\sum_{i=1}^{3} \frac{\nu_i}{e^{x_i} - 1}$$

$$= (1.000\,\mathrm{mol})(6.022 \times 10^{23}\,\mathrm{mol}^{-1})(6.6261 \times 10^{-34}\,\mathrm{J\,s})$$

$$\times \left[\frac{1.0947 \times 10^{14}\,\mathrm{s}^{-1}}{e^{14.079} - 1} + \frac{4.7817 \times 10^{13}\,\mathrm{s}^{-1}}{e^{6.1498} - 1} + \frac{1.1260 \times 10^{14}\,\mathrm{s}^{-1}}{e^{14.482} - 1}\right]$$

$$= 40.86\,\mathrm{J}$$

$$A_\mathrm{vib} = Nk_\mathrm{B}T\ln\left(z_\mathrm{vib}\right)$$

$$= nRT\ln\left[\left(\frac{1}{1 - e^{-14.079}}\right)\left(\frac{1}{1 - e^{-6.1498}}\right)\left(\frac{1}{1 - e^{-14.482}}\right)\right]$$

$$= (1.000\,\mathrm{mol})(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(373.15\,\mathrm{K})(2.137 \times 10^{-3})$$

$$= 6.632\,\mathrm{J}$$

$$S_\mathrm{vib} = \frac{U - A}{T} = \frac{40.86\,\mathrm{J} - 6.63\,\mathrm{J}}{373.15\,\mathrm{K}} = 0.0917\,\mathrm{J\,K^{-1}}$$

In this example, vibrational frequencies have been used. Most tables of values give frequencies divided by the speed of light, usually expressed in cm^{-1} and denoted by $\tilde{\nu}$. Multiply these values by the speed of light to get the frequencies.

The Chemical Potential of a Dilute Gas

The four contributions to the chemical potential are given by the formulas

$$\mu_\mathrm{tr} = -k_\mathrm{B}T\ln(z_\mathrm{tr}/N) \tag{26.2-17a}$$

$$\mu_\mathrm{rot} = -k_\mathrm{B}T\ln(z_\mathrm{rot}) \tag{26.2-17b}$$

$$\mu_\mathrm{vib} = -k_\mathrm{B}T\ln(z_\mathrm{vib}) \tag{26.2-17c}$$

$$\mu_\mathrm{el} = -k_\mathrm{B}T\ln(z_\mathrm{el}) \tag{26.2-17d}$$

As usual, the divisor N is placed with the translational contribution. The formulas for the Gibbs energy can be obtained by multiplying those for the chemical potential by N, the number of molecules in the system.

EXAMPLE 26.10

Calculate the chemical potential and the Gibbs energy of 1.000 mol of $^{35}Cl_2$ at 298.15 K and 1.000 atm.

Solution

We take the energy of the ground electronic state as zero. From Example 25.7, $z_{\text{rot}} = 424.7$, and from Example 25.8, $z_{\text{vib}} = 1.0720$. Since the ground electronic state is nondegenerate and since all excited states must lie high in energy, $z_{\text{el}} \approx 1$, and the electronic contributions to μ and G are approximately equal to zero.

$$\begin{aligned}\frac{z_{\text{tr}}}{N} &= \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\frac{V}{N} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\frac{k_B T}{P} = \left(\frac{2\pi M}{N_{Av} h^2}\right)^{3/2}\frac{(k_B T)^{5/2}}{P}\\ &= \left(\frac{2\pi(0.0699377\ \text{kg mol}^{-1})}{(6.02214 \times 10^{23}\ \text{mol}^{-1})(6.6261 \times 10^{-34}\ \text{J s})^2}\right)^{3/2}\frac{[(1.3807 \times 10^{-23}\ \text{J K}^{-1})(298.15\ \text{K})]^{5/2}}{101325\ \text{Pa}}\\ &= 2.299 \times 10^7\end{aligned}$$

$$\begin{aligned}\mu_{\text{tr}} &= -k_B T\ln(2.299 \times 10^7) = -6.978 \times 10^{-20}\ \text{J}\\ \mu_{\text{rot}} &= -k_B T\ln(424.7) = -2.491 \times 10^{-20}\ \text{J}\\ \mu_{\text{vib}} &= -k_B T\ln(1.072) = -2.86 \times 10^{-22}\ \text{J}\\ \mu_{\text{el}} &\approx 0\\ \mu &= -5.35 \times 10^{-20}\ \text{J}\\ G &= N\mu = (1.000\ \text{mol})(6.02214 \times 10^{-23}\ \text{mol}^{-1})(-5.35 \times 10^{-20}\ \text{J})\\ &= -3.22 \times 10^4\ \text{J}\end{aligned}$$

PROBLEMS

Section 26.2: Working Equations for the Thermodynamic Functions of a Dilute Gas

26.8 Assuming the harmonic oscillator–rigid rotor approximation, and taking the energy of the electronic ground state to be zero:

a. Find the translational contribution to the energy of 1.000 mol of F_2 at 1.000 bar and 298.15 K.

b. Find the rotational contribution to the energy of 1.000 mol of F_2 at 1.000 bar and 298.15 K.

c. Find the electronic contribution to the entropy of 1.000 mol of F_2 at 1.000 bar and 298.15 K.

d. Find the vibrational factor in the partition function of F_2 gas at 1.000 bar and 298.15 K.

26.9 Calculate the standard-state molar entropy of argon at 298.15 K. Compare your result with the experimental value, 154.845 J K^{-1} mol^{-1}. Compare your result with the value for helium at the same temperature and comment on the difference.

26.10 **a.** Calculate the value of each factor in the molecular partition function of $^{16}O_2$ gas at 500.0 K and a pressure of $P° = 1.000$ bar.

b. Calculate the standard-state molar thermodynamic energy, U_m°, for O_2 at 500.0 K. Give the values of the translational, rotational, vibrational, and electronic contributions.

c. Calculate the standard-state molar thermodynamic entropy, S_m°, of O_2 at 500.0 K. Give the values of the translational, rotational, vibrational, and electronic contributions.

26.11 Calculate the values of H_m°, U_m°, A_m°, G_m°, S_m°, and $C_{V,m}^\circ$ for krypton gas at 298.15 K.

26.12 Calculate the standard-state molar entropy of CO at 298.15 K.

26.13 Estimate the difference in the rotational contribution to the entropy of 1.000 mol of $^{14}N^{15}N$ and 1.000 mol of $^{14}N_2$ at 298.15 K. Ignore the difference in the masses.

26.14 Calculate the standard-state energy, entropy, and Gibbs energy of 1.000 mol of xenon gas at 298.15 K.

26.15 Calculate the molar entropy of water vapor at 25.0°C and 1.000 bar. The bond distances are equal to 95.8 pm and the bond angle is equal to 104.45°. The vibrational frequencies are $4.7817 \times 10^{13}\ \mathrm{s}^{-1}$, $1.0947 \times 10^{14}\ \mathrm{s}^{-1}$, and $1.1260 \times 10^{14}\ \mathrm{s}^{-1}$.

26.16 Calculate the translational, rotational, and vibrational contributions to $C_{V,\mathrm{m}}$ of SO_2 gas at 298.15 K and 1.000 bar. The vibrational frequencies are in Figure 22.6.

26.17 Calculate the standard-state enthalpy (relative to the value at 0 K) of argon gas at 298.15 K and at 500.0 K.

26.18 Using data in Example 25.10, make a graph of the electronic contribution to the molar energy of NO and a graph of the electronic contribution to the molar heat capacity of NO between 0 K and 500 K. The behavior of this electronic heat capacity as a function of temperature is known as the *Schottky effect*.

26.3 Chemical Equilibrium in Dilute Gases

In previous chapters we have written a chemical reaction equation in the form

$$0 = \sum_{a=1}^{s} \nu_a \mathscr{F}_a \tag{26.3-1}$$

where s represents the number of substances involved in the reaction and $\mathscr{F}_a$ represents the chemical formula of substance a. In Eq. (7.1-10), we established that at equilibrium

$$\boxed{\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \sum_{a=1}^{s} \nu_a \mu_a(\mathrm{eq}) = 0} \tag{26.3-2}$$

Equation (26.1-27) for the chemical potential corresponds to an unspecified choice of the zero of energy and gives a different value for a different choice of the zero of energy. We must use a consistent zero of energy for all substances. We write the molecular partition function as in Eq. (25.3-28):

$$z = \sum_i e^{-\varepsilon_i/k_\mathrm{B}T} = \sum_i e^{-(\varepsilon_i - \varepsilon_0 + \varepsilon_0)k_\mathrm{B}T} = e^{-\varepsilon_0/k_\mathrm{B}T} \sum_i e^{-(\varepsilon_i - \varepsilon_0)k_\mathrm{B}T} \tag{26.3-3}$$

where ε_0 is the energy eigenvalue of the molecule's ground state relative to a fixed zero of energy. We denote the sum in the second version of Eq. (26.3-3) by z', so that

$$z = e^{-\varepsilon_0/k_\mathrm{B}T} z' \tag{26.3-4}$$

The partition function z' is the partition function relative to the ground-state energy of the molecule. It is independent of the choice of the zero of energy since it contains only energy differences. Equation (26.1-27) for the chemical potential now becomes

$$\begin{aligned} \mu &= -k_\mathrm{B}T\ln\left(\frac{z}{N}\right) = -k_\mathrm{B}T\left[\frac{-\varepsilon_0}{k_\mathrm{B}T} + \ln\left(\frac{z'}{N}\right)\right] \\ &= \varepsilon_0 - k_\mathrm{B}T\ln\left(\frac{z'}{N}\right) \end{aligned} \tag{26.3-5}$$

In a dilute gas mixture, each substance behaves as though the other substances were absent, so we can use our formulas for each one of the gases in the mixture. When a version of Eq. (26.3-5) for each substance is substituted into Eq. (26.3-2) we obtain the following equation for a reacting dilute gas mixture at equilibrium

$$0 = \sum_{a=1}^{s} \nu_a \left[\varepsilon_{0a} - k_B T \ln\left(\frac{z'_a}{N_a} \right) \right] \tag{26.3-6}$$

where all of the ε_0 values must be taken with respect to the same zero of energy. We define $\Delta\varepsilon_0$ as the difference in the energies of the ground states of the product and reactant molecules:

$$\Delta\varepsilon_0 = \sum_{a=1}^{s} \nu_a \varepsilon_{0a} \tag{26.3-7}$$

This quantity is equal to the energy change when ν_a molecules of substance a appear if a is a product, and $|\nu_a|$ molecules of substance a are consumed if a is a reactant, with all molecules in their ground states.

The sum of logarithms is the logarithm of a product. Use of the identity

$$y \ln(x) = \ln(x^y) \tag{26.3-8}$$

and division by $k_B T$ gives

$$0 = \frac{\Delta\varepsilon_0}{k_B T} - \ln\left[\prod_{a=1}^{s} \left(\frac{z'_a}{N_a} \right)^{\nu_a} \right] \tag{26.3-9}$$

This equation can be manipulated into an equation containing the equilibrium constant. The molecular partition functions are proportional to V, since the translational factor is

$$z_{\mathrm{tr}} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V \tag{26.3-10}$$

and the other factors are independent of V. We define

$$z''_a = \frac{z'_a}{V} \tag{26.3-11}$$

so that z''_a is independent of V. Since dilute gases obey the ideal gas law,

$$\frac{V}{N_a} = \frac{k_B T}{P_a} = \frac{k_B T}{P^\circ} \frac{P^\circ}{P_a} = \frac{V_m^\circ}{N_{\mathrm{Av}}} \frac{P^\circ}{P_a} \tag{26.3-12}$$

where P_a is the partial pressure of substance a, N_{Av} is Avogadro's constant, and V_m° is the volume occupied by 1.000 mol of ideal gas at the standard pressure P° (exactly 1 bar) and temperature T. Equation (26.3-9) can now be written as

$$0 = \frac{\Delta\varepsilon_0}{k_B T} - \ln\left[\prod_{a=1}^{s} \left(\frac{z''_a V_m^\circ}{N_{\mathrm{Av}}} \right)^{\nu_a} \right] + \ln\left[\prod_{a=1}^{s} \left(\frac{P_a}{P^\circ} \right)^{\nu_a} \right] \tag{26.3-13}$$

The last term in this expression is the logarithm of the equilibrium constant in Eq. (7.2-2). We can now write

$$\ln(K) = -\frac{\Delta\varepsilon_0}{k_B T} + \ln\left[\prod_{a=1}^{s} \left(\frac{z''_a V_m^\circ}{N_{\mathrm{Av}}} \right)^{\nu_a} \right] \tag{26.3-14}$$

or

$$K = e^{-\Delta\varepsilon_0/k_BT}\prod_{a=1}^{s}\left(\frac{z_a'^{\circ}}{N_{Av}}\right)^{\nu_a} \tag{26.3-15}$$

where $z_a'^{\circ} = z_a'' V_m^{\circ}$ is the molecular partition function of substance number a with the volume set equal to the standard molar volume at pressure P° and with the zero of energy set equal to the ground-state energy of the molecule.

The result in Eq. (26.3-15) has a physical interpretation that helps in remembering the formula. The partition function is a measure of the availability of states for the molecules of a given substance. If the partition functions of the products are larger than those of the reactants, the equilibrium constant will be larger than unity, corresponding to a larger number of accessible states for the products and a larger probability for the products than for the reactants. Similarly, if there are fewer states available for the products than for the reactants, the equilibrium constant will be smaller than unity.

EXAMPLE 26.11

Calculate the equilibrium constant for the reaction

$$H_2 \rightleftharpoons 2H$$

at 500.0 K. Assume that the vibrational and electronic partition functions of the hydrogen molecule are both approximately equal to 1.000. Assume that the H_2 is an equilibrium mixture of *ortho*- and *para*-hydrogen. If this is the case, the nuclear spin degeneracy will cancel (there is a degeneracy of 4 for the molecule and a degeneracy of 2 for each atom).

Solution

From Eq. (26.3-8),

$$\begin{aligned} z_{\text{rot},H_2} &= \frac{1}{\sigma}\frac{8\pi^2 I_e k_B T}{h^2} = \frac{1}{2}\frac{8\pi^2 \mu r_e^2 k_B T}{h^2} \\ &= \frac{1}{2}\frac{8\pi^2(8.37\times 10^{-28}\text{ kg})(0.741\times 10^{-10}\text{ m})^2(1.3807\times 10^{-23}\text{ J K}^{-1})(500\text{ K})}{(6.6261\times 10^{-34}\text{ J s})^2} \\ &= 2.85 \end{aligned}$$

A better approximation to the rotational partition function could be obtained by explicit summation, but we will use this approximation. The translational partition function of atomic hydrogen is

$$\begin{aligned} \frac{z'_{\text{tr},H^{\circ}}}{N_{Av}} &= \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2}\frac{V_m^{\circ}}{N_{Av}} \\ &= \left(\frac{2\pi(1.674\times 10^{-27}\text{ kg})(1.3807\times 10^{-23}\text{ J K}^{-1})(500\text{ K})}{(6.6261\times 10^{-34}\text{ J s})^2}\right)^{3/2} \\ &\quad\times \frac{0.04157\text{ m}^3\text{ mol}^{-1}}{6.022\times 10^{23}\text{ mol}^{-1}} \\ &= 1.468\times 10^5 \end{aligned}$$

The electronic partition function of atomic hydrogen is approximately equal to 2.00 since the ground level is a doublet. The electronic partition function of molecular hydrogen is approximately equal to 1.000. The translational partition function of the molecule is given by the same expression as that of the atom except for the mass. Its value is

$$\frac{z'_{\mathrm{tr,H}_2^\circ}}{N_{\mathrm{Av}}} = 4.152 \times 10^5$$

The dissociation energy, D_e, is equal to 4.75 eV for the H_2 molecule. The value of $\Delta\varepsilon_0$ is equal to D_0, which is equal to D_e minus the zero-point vibrational energy of the molecule:

$$\begin{aligned}\Delta\varepsilon_0 &= 4.75\,\mathrm{eV} - \frac{1}{2}hc\tilde{\nu}_{\mathrm{e}} = 7.61 \times 10^{-19}\,\mathrm{J} - \frac{1}{2}hc\tilde{\nu}_{\mathrm{e}} \\ &= 7.61 \times 10^{-19}\,\mathrm{J} - \frac{1}{2}(6.6261 \times 10^{-34}\,\mathrm{J\,s})(2.9979 \times 10^{10}\,\mathrm{cm\,s^{-1}})(4401.2\ \mathrm{cm^{-1}}) \\ &= 7.17 \times 10^{-19}\,\mathrm{J}\end{aligned}$$

$$e^{-\Delta\varepsilon_0/k_{\mathrm{B}}T} = \exp\left[\frac{-7.17 \times 10^{-19}\,\mathrm{J}}{(1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}})(500\ \mathrm{K})}\right] = 7.8 \times 10^{-46}$$

$$\begin{aligned}K &= e^{-\Delta\varepsilon_0/k_{\mathrm{B}}T}(z^\circ_{\mathrm{el,H}})^2(z'_{\mathrm{tr,H}^\circ}/N_{\mathrm{Av}})^2(z'_{\mathrm{tr,H2}^\circ}/N_{\mathrm{Av}})^{-1}(z'^{\circ}_{\mathrm{rot,\,H}_2})^{-1} \\ &= \frac{(7.8 \times 10^{-46})(2.00)^2(1.468 \times 10^5)^2}{(4.152 \times 10^5)(2.85)} = 5.7 \times 10^{-41}\end{aligned}$$

We can calculate the thermodynamic value of K by using techniques discussed in Part I of this textbook. The standard-state Gibbs energy change of the reaction is 385.914 kJ mol^{-1} and the thermodynamic value of K is

$$K = e^{-\Delta G^\circ/RT} = \exp\left(\frac{-385914\,\mathrm{J\,mol^{-1}}}{(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(500.0\,\mathrm{K})}\right) = 4.84 \times 10^{-41}$$

Exercise 26.10

Without making detailed calculations, estimate the equilibrium constant for the reaction at 298.15 K:

$$H_2 + D_2 \rightleftharpoons 2HD$$

Assume that the electronic and vibrational partition functions equal unity and that the rotational partition functions cancel except for the symmetry numbers. Also assume that $\Delta\varepsilon_0 \approx 0$.

We can express the equilibrium constant for a dilute gas reaction in terms of molar concentrations. This equilibrium constant is proportional to K and is denoted by K_c.

$$K_c = \prod_{a=1}^{c}\left(\frac{c_a}{c^\circ}\right)^{\nu_a} \tag{26.3-16}$$

where we denote the molar concentration of substance a by c_a, expressed in mol m^{-3}.

$$c_a = \frac{n_a}{V} = \frac{N_a}{N_{\mathrm{Av}}V} \tag{26.3-17}$$

so that

$$\frac{z'_a}{N_a} = \frac{z'_a}{N_{\mathrm{Av}}n_a} = \frac{z'_a}{N_{\mathrm{Av}}Vc_a} = \frac{z'_a}{N_{\mathrm{Av}}Vc^\circ}\frac{c^\circ}{c_a} \tag{26.3-18}$$

where c° is defined to equal to 1 mol m^{-3}. Equation (26.3-9) can be written

$$0 = \frac{\Delta\varepsilon_0}{k_B T} - \ln\left[\prod_{a=1}^{c}\left(\frac{z_a'}{N_{Av} V c^\circ}\right)^{\nu_a}\right] + \ln\left[\prod_{a=1}^{c}\left(\frac{c_a}{c^\circ}\right)^{\nu_a}\right] \tag{26.3-19}$$

so that

$$K_c = \prod_{a=1}^{c}\left(\frac{c_a}{c^\circ}\right)^{\nu_a} = e^{-\Delta\varepsilon_0/k_B T}\prod_{a=1}^{c}\left(\frac{z_a'}{N_{Av} V c^\circ}\right)^{\nu_a}$$

$$= e^{-\Delta\varepsilon_0/k_B T}\prod_{a=1}^{c}\left(\frac{z_a'}{N_{Av} c^\circ}\right)^{\nu_a} \tag{26.3-20}$$

Exercise 26.11

Calculate K_c for the reaction of Example 26.11.

PROBLEMS

Section 26.3: Chemical Equilibrium in Dilute Gases

26.19 Calculate the equilibrium constant for the dissociation of hydrogen at 5000 K.

26.20 Find the value of the equilibrium constant at 298.15 K for the reaction

$$Cl_2(g) \rightleftharpoons 2Cl(g)$$

Assume that the electronic partition functions can be approximated as the degeneracy of the ground levels. The dissociation energy at 0 K is equal to 239.242 kJ mol^{-1}.

26.21 Calculate the value of the equilibrium constant at 900 K for the reaction

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

Carbon dioxide is linear, with bond lengths of 1.161×10^{-10} m. The vibrational frequencies are in Example 25.12. The bond distances in H_2O are equal to 95.8 pm and the bond angle is equal to 104.45°. The value of ΔU_0 for the reaction is equal to 40.33 kJ mol^{-1}.[2] The experimental value of the equilibrium constant is 0.46. Calculate your percent error.

26.22 Calculate the value of the equilibrium constant at 750 K for the reaction

$$H_2 + I_2 \rightleftharpoons 2HI$$

The value of ΔU_0° is equal to -8.461 kJ mol^{-1}.[3]

26.23 Without doing any detailed calculations, estimate the equilibrium constant for each of the following gas-phase reactions; assume that $\Delta\varepsilon_0 \approx 0$. Ignore differences in masses and moments of inertia. Assume that all vibrational partition functions ≈ 1.

a. $NH_3 + D_2O \rightleftharpoons NH_2D + HDO$

b. $^{35}Cl_2 + {}^{37}Cl \rightleftharpoons {}^{35}Cl^{37}Cl + {}^{35}Cl$

26.24 Without doing any detailed calculations, estimate the equilibrium constant for the gas-phase chemical reaction at 298.15 K.

$$^{1}H^{35}Cl + {}^{37}Cl_2 \rightleftharpoons {}^{1}H\,{}^{37}Cl + {}^{35}Cl^{37}Cl$$

State any assumptions. Does your result depend on temperature? Why or why not?

26.25 Without doing any detailed calculations, estimate the equilibrium constant for each of the following gas-phase reactions. Assume that $\Delta\varepsilon_0 \approx 0$. Ignore differences in masses and moments of inertia. Assume that all

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[2] G. Herzberg, *Molecular Spectra and Molecular Structure. Vol. II. Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand Reinhold, New York, 1945, p. 429.

[3] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure. Vol. IV. Constants of Diatomic Molecules,* Van Nostrand Reinhold, New York, 1979, pp. 240, 330, 324.

vibrational partition functions ≈ 1. Do your equilibrium constants depend on temperature? Why or why not?

a. $H_2 + D_2 \rightleftharpoons 2HD$

b. $HF + D \rightleftharpoons DF + H$

26.26 Without doing any detailed calculations, estimate the equilibrium constant for each of the gas-phase reactions. State any assumptions. Do your equilibrium constants depend on temperature? Why or why not?

a. $HF + D_2 \rightleftharpoons DF + HD$

b. $CH_4 + D_2 \rightleftharpoons CH_3D + HD$

26.27 Show that the equilibrium constant for a racemization reaction equals unity.

26.28 The ionization energy of the hydrogen atom is equal to 13.60 eV. Find the equilibrium constant for the dissociation of a hydrogen atom into a proton and an electron at 10000 K.

26.29 Consider a hypothetical *cis–trans* isomerization in the gas phase:

$$C \rightleftharpoons T$$

Assume that the only important differences between the two isomers are that one of the moments of inertia of the *trans* isomer is 8.3% higher than that of the *cis* isomer and that one of the vibrational degrees of freedom has a higher frequency in the *cis* isomer:

$$\nu(trans) = 6.45 \times 10^{13}\ \mathrm{s^{-1}}$$
$$\nu(cis) = 7.54 \times 10^{13}\ \mathrm{s^{-1}}$$

Assume that the ground-state energy of the *cis* isomer is 8.15×10^{-21} J higher than that of the *trans* isomer. Find the value of the equilibrium constant for this reaction at 500.0 K.

26.30 Consider a substance that can exist in two tautomeric forms, A and B. Define a partition function for the combined forms

$$z = z_A + z_B$$

where the same zero of energy (say the ground-state energy of form A) must be used for both forms. Let the energy of the ground state of form B be denoted by $\varepsilon_{0,B}$.

a. In terms of z_A and z_B, what fraction of the molecules will be form B? Form A?

b. In terms of z_A and z_B what is the equilibrium constant for the reaction

$$A \rightleftharpoons B$$

How does this relate to the expression for the equilibrium constant derived as in the chapter?

26.4 The Activated Complex Theory of Bimolecular Chemical Reaction Rates in Dilute Gases

We write the chemical equation for a hypothetical reaction as

$$aA + bB \rightarrow dD + fF \tag{26.4-1}$$

where the capital letters stand for chemical formulas and the lower-case letters represent stoichiometric coefficients. We define the forward rate of the reaction, denoted by r_f:

$$r_f = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = -\frac{1}{d}\frac{d[D]}{dt} = \frac{1}{f}\frac{d[F]}{dt} \quad \text{(definition of } r_f\text{)} \tag{26.4-2}$$

There is a large class of chemical reactions in which the forward reaction rate is proportional to the concentration of each reactant raised to some power:

$$r_f = \frac{1}{a}\frac{d[A]}{dt} = k_f[A]^{\alpha}[B]^{\beta} \tag{26.4-3}$$

Equation (26.4-3) is called a *rate law with definite orders*. The proportionality constant k_f is called the *forward rate constant*. It is not a true constant. It depends on temperature, but is independent of the concentrations. The exponent α is called the *order with respect to substance A* and the exponent β is called the *order with respect to substance B*. The sum of the orders with respect to the different substances is called the *overall order*. If α and β both equal unity, the reaction is said to be first order with respect to substance A, first order with respect to substance B, and second order overall. The orders α and β are not necessarily equal to the stoichiometric coefficients a and b.

Potential Energy Surfaces

A reaction that takes place in a step that cannot be divided into simpler steps is called an *elementary reaction*. An elementary reaction involving two molecules is called a *bimolecular reaction*. Consider a bimolecular elementary gas-phase reaction between a diatomic molecule and an atom:

$$\mathrm{CD} + \mathrm{F} \rightarrow \mathrm{C} + \mathrm{DF} \tag{26.4-4}$$

where the letters are abbreviations for the chemical symbols of the elements. We assume that the Born–Oppenheimer Schrödinger equation for the electrons in the system has been solved for various positions of the three nuclei. As with a bound molecule, the Born–Oppenheimer energy acts as a potential energy for nuclear motion. As the reaction occurs, the C and D nuclei move apart and the D and F nuclei move toward each other. If the three nuclei remain *colinear* (on the same line) the potential energy of the nuclei is a function of two internuclear distances:

$$\mathscr{V} = \mathscr{V}(r_{\mathrm{CD}}, r_{\mathrm{DF}}) \tag{26.4-5}$$

This potential energy can be represented by a surface above a plane in which the distance r_{CD} is plotted on one axis and the distance r_{DF} is plotted on the other axis.

The earliest calculation of a potential energy function for a three-atom reacting system was a semi-empirical calculation for the collinear reaction of a hydrogen atom with a hydrogen molecule.[4] This system has been repeatedly studied ever since.[5] Figure 26.1a shows schematically a view of a three-dimensional graph of the potential energy function for the collinear conformation. Figure 26.1b shows the same information in a different way by giving contours that represent positions of equal potential energy.

There is a trough that runs from the point labeled a at the upper left of the diagram (corresponding to reactants) along a roughly L-shaped path past the point labeled b to the point labeled c at the lower right (corresponding to products). In a region near b at the lower left of the diagram the bottom of the trough rises to a maximum height so that in this region the potential energy surface is shaped like a saddle or a mountain pass. A curve is drawn along the bottom of the trough and over the saddle at point b in Figure 26.1b, and the energy as a function of position along this curve is shown schematically in Figure 26.1c. Motion along the curve in Figure 26.1b corresponds to motion along the axis in Figure 26.1c and represents progress toward completion of the reaction, and we call the distance along this curve the *reaction coordinate* ζ.

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[4] H. Eyring and M. Polanyi, *Z. Phys. Chem.*, **B12**, 279 (1931).

[5] T. J. Park and J. C. Light, *J. Chem. Phys.*, **91**, 974 (1989); see D. G. Truhlar and C. J. Horowitz, *J. Chem. Phys.*, **68**, 2466 (1978) for an accurate potential energy function.

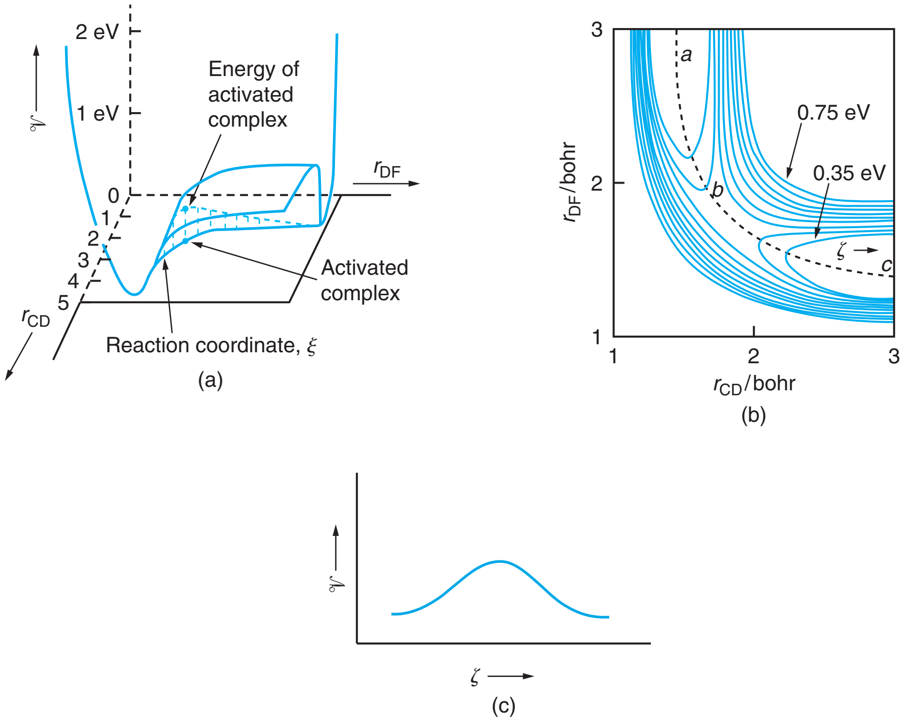

Figure 26.1 Potential Energy Surface of H_3 for Linear Geometry. (a) Perspective view of the surface (schematic). (b) Contours of constant potential energy for H_3. From R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity*, Oxford University Press, New York, 1987, p. 124. (c) Potential energy along the reaction coordinate.

The *activation energy* is the energy that must be added to the reactants to bring them to the state at the saddle point, which is called the *transition state* or the *activated complex*, denoted by $CDF^{\ddagger}$. The height of the maximum in the curve of Figure 26.1c above the energy of the reactants is approximately equal to the activation energy, since except for zero-point vibrational energy it is the minimum excitation energy that is required for the reactants to pass over the maximum to form products. Calculations show that the activation energy for the hydrogen reaction is lowest for the collinear conformation, and many calculations of three-atom reactions include only the collinear geometry. A more complete discussion would take an average over the possible values of the angle of approach, and this has been carried out for some reactions, including the hydrogen reaction.

Trajectory Calculations

Once the potential energy surface is obtained, the reaction can be studied by solving for the nuclear motion along the reaction coordinate. Most nuclei other than hydrogen are sufficiently massive that classical mechanics is thought to be an adequate approximation, but quantum calculations are also carried out. Neither the classical nor quantum equations can be solved in closed form, and the motions are numerically simulated using computer programs. If classical mechanics is used, the calculation is carried out for a number of different trajectories. The fraction of the trajectories that pass over the saddle and the time required for the passage are used to calculate a rate constant.[6]

The Activated Complex Theory (Transition State Theory)

Rather than calculating trajectories, one can use statistical mechanics in an approximate form. The oldest such approximate theory was pioneered in the 1930s by Eyring and Polanyi, and is called the *activated complex theory*, or the *transition-state theory*.[7]

Henry Eyring, 1900–1981, was an American physical chemist who made contributions in various areas of theoretical physical chemistry.

Michael Polanyi, 1891–1976, was a Hungarian-born chemist who was originally trained as a physician, and who later became a professor of social sciences.

We illustrate the activated complex theory for the gas-phase bimolecular reaction of Eq. (26.4-4). We begin with the following assumptions:

1. The activated complex $CDF^{\ddagger}$ can be identified as a distinct chemical species.
2. The concentration of the activated complex can be obtained by assuming that it is in chemical equilibrium with the reactants.
3. The rate of the chemical reaction is equal to the concentration of the activated complex times ν_{passage}, the frequency of passage of an activated complex over the maximum in the potential energy:

$$\text{Rate} = \nu_{\text{passage}}[\text{CDF}^{\ddagger}] \tag{26.4-6}$$

In most reactions there is clearly too little time for the activated complex to come to chemical equilibrium with the reactants, so the second assumption is questionable. In spite of this fact the theory is more successful than one might expect.

The formation of the activated complex corresponds to the chemical equation

$$\text{CD} + \text{F} \rightleftharpoons \text{CDF}^{\ddagger} \tag{26.4-7}$$

and its equilibrium constant is given by Eq. (26.3-20):

$$K_c = \frac{([\text{CDF}^{\ddagger}]/c^{\circ})}{([\text{CD}]/c^{\circ})([F]/c^{\circ})} = e^{-\Delta\varepsilon_0^{\ddagger}/k_{\text{B}}T}\,\frac{(z''_{\text{CDF}}/N_{\text{Av}}c^{\circ})}{(z''_{\text{CD}}/N_{\text{Av}}c^{\circ})(z''_{\text{F}}/N_{\text{Av}}c^{\circ})} \tag{26.4-8}$$

where $\Delta\varepsilon_0^{\ddagger}$ is the energy required to form one activated complex in its ground state from one CD molecule and one F atom in their ground states. It is equal to the height of the maximum in Figure 26.1c above the energy of the reactants, plus the difference in the zero-point vibrational energies.

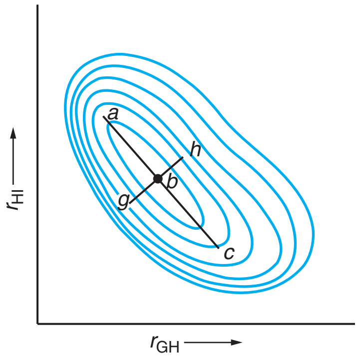

Figure 26.2 A Contour Plot for the Potential Energy of Nuclear Motion for a Stable Triatomic Molecule.

The vibrations of the activated complex resemble those of an ordinary triatomic molecule except for the asymmetric stretch. A stable linear triatomic molecule GHI would have a potential energy surface as shown by the contours of equal potential energy in Figure 26.2, with a relative minimum at point *b* instead of a saddle point. It has four normal modes: two bends, a symmetric stretch, and an asymmetric stretch. Motion along the path labeled *abc* corresponds to the asymmetric stretch, and motion along the path labeled *gbh* corresponds to the symmetric stretch. The activated complex has three vibrational modes: two bends and a symmetric stretch, which is like that of GHI because the saddle in the potential energy surface corresponds to a minimum in the *gbh* direction. The asymmetric stretch of the activated complex corresponds to

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[6] R. N. Porter, *Ann. Rev. Phys. Chem.*, **25**, 317 (1974).

[7] H. Eyring, *J. Chem. Phys.*, **3**, 107 (1935); M. Evans and M. Polanyi, *Trans. Faraday Soc.*, **312**, 875 (1935). See K. J. Laidler and M. C. King, *J. Phys. Chem.*, **87**, 2657 (1983) for a history of the theory.

motion along the reaction coordinate and leads to dissociation to form either products or reactants, since the potential energy is at a maximum instead of a minimum along the reaction coordinate.

We write the partition function of the activated complex in the form

$$z''_{\text{CDF}} = z^{\ddagger''}_{\text{CDF}} z_{\text{rc}} \tag{26.4-9}$$

where z_{rc} is the factor in the partition function corresponding to motion along the reaction coordinate and where $z^{\ddagger''}_{\text{CDF}}$ represents the translational factor, the rotational factor, the electronic factor, and the three vibrational factors.

We adopt a nonrigorous approach to obtain a formula for z_{rc}. We pretend that we can change the potential energy surface so that the asymmetric stretch is like that of a triatomic molecule in Figure 26.2. The partition function for the reaction coordinate is now that for an asymmetric stretch:

$$z_{\text{rc}} = \frac{1}{1 - e^{-h\nu_{\text{as}}/k_{\text{B}}T}} \tag{26.4-10}$$

where ν_{as} is the frequency of oscillation of the asymmetric stretch. We now let the potential energy surface become flatter in the *abc* direction. As its curvature in the direction of the reaction coordinate becomes small, ν_{as} becomes small, and we can use the approximation $e^{-x} \approx 1 - x$, which gives

$$z_{\text{rc}} = \frac{1}{1 - (1 - h\nu_{\text{as}}/k_{\text{B}}T)} = \frac{k_{\text{B}}T}{h\nu_{\text{as}}} \tag{26.4-11}$$

The frequency of the asymmetric stretch, ν_{as}, gives the number of oscillations per second in the direction of the asymmetric stretch, which becomes the direction of the reaction coordinate in this limit. We assume that we can identify ν_{as} with ν_{passage}, and write

$$\nu_{\text{passage}} = \frac{k_{\text{B}}T}{hz_{\text{rc}}} \tag{26.4-12}$$

This process of mentally distorting the potential energy surface is not very satisfactory because the process must be continued until the curvature becomes negative in order to recover the actual surface. There are better ways to derive Eq. (26.4-12) that lead to the same result.[8]

The concentration of the activated complex is given by Eqs. (26.4-8), (26.4-9), and (26.4-12):

$$[\text{CDF}^{\ddagger}] = e^{-\Delta\varepsilon_0^{\ddagger}/k_{\text{B}}T} \frac{z^{\ddagger''}_{\text{CDF}} z_{\text{rc}}}{z''_{\text{CD}} z''_{\text{F}}} N_{\text{Av}}[\text{CD}][\text{F}] \tag{26.4-13}$$

The rate of the reaction is given by

$$\begin{aligned} \text{Rate} = \nu_{\text{passage}}[\text{CDF}^{\ddagger}] &= \frac{k_{\text{B}}T}{hz_{\text{rc}}} e^{-\Delta\varepsilon_0^{\ddagger}/k_{\text{B}}T} \frac{z^{\ddagger''}_{\text{CDF}} z_{\text{rc}}}{z''_{\text{CD}} z_{\text{F}}} N_{\text{Av}}[\text{CD}][\text{F}] \\ &= \frac{k_{\text{B}}T}{h} e^{-\Delta\varepsilon_0^{\ddagger}/k_{\text{B}}T} \frac{z^{\ddagger''}_{\text{CDF}}}{z''_{\text{CD}} z''_{\text{F}}} N_{\text{Av}}[\text{CD}][\text{F}] \end{aligned} \tag{26.4-14}$$

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[8] K. J. Laidler, *Chemical Kinetics*, 3rd ed., HarperCollins, New York, 1987, p. 97ff.

and the rate constant is given by

$$k = \frac{k_{\mathrm{B}}T}{h} e^{-\Delta\varepsilon_0^{\ddagger}/k_{\mathrm{B}}T} \frac{z_{\mathrm{CDF}}^{\ddagger\prime\prime}}{z_{\mathrm{CD}}^{\prime\prime} z_{\mathrm{F}}^{\prime\prime}} N_{\mathrm{Av}} = \frac{RT}{h} e^{-\Delta\varepsilon_0^{\ddagger}/k_{\mathrm{B}}T} \frac{z_{\mathrm{CDF}}^{\ddagger\prime\prime}}{z_{\mathrm{CD}}^{\prime\prime} z_{\mathrm{F}}^{\prime\prime}} \tag{26.4-15}$$

where the concentrations [CD] and [F] are expressed in mol m^{-3}. Since the $z^{\ddagger\prime\prime}$ factors have units of m^{-3}, the rate constant has the units $\mathrm{m}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1}$. An additional factor of 1000 L m^{-3} would give the rate constant the units L $\mathrm{mol}^{-1}\ \mathrm{s}^{-1}$.

Sometimes the expression shown in Eq. (26.4-15) is multiplied by a *transmission coefficient* κ, which represents the fraction of activated complexes that react. The transmission coefficient is commonly used as a correction factor to make the theory agree with experiment. It is probably better to omit this factor and to admit that the theory is approximate and cannot be expected to give exact agreement with experiment.

EXAMPLE 26.12

Calculate the rate constant at 500.0 K for the gas-phase reaction

$$\mathrm{H} + \mathrm{HBr} \rightarrow \mathrm{H_2} + \mathrm{Br}$$

Assume a linear activated complex H $\cdots$ H $\cdots$ Br with the internuclear distances given by[9]

$$r_{\mathrm{H-H}} = 1.50 \times 10^{-10}\ \mathrm{m}$$
$$r_{\mathrm{H-Br}} = 1.42 \times 10^{-10}\ \mathrm{m}$$

and the vibrational frequencies given by

$$\tilde{\nu}_1 = \tilde{\nu}\ (\text{symmetric stretch}) = 2340\ \mathrm{cm}^{-1}$$
$$\tilde{\nu}_2 = \tilde{\nu}\ (\text{bend}) = 460\ \mathrm{cm}^{-1}$$

The value of $\Delta\varepsilon_0^{\ddagger}$ is 8.3×10^{-21} J.

Solution

The rate constant is given by

$$k = \frac{k_{\mathrm{B}}T}{h} e^{-\Delta\varepsilon_0^{\ddagger}/k_{\mathrm{B}}T} \frac{z_{\mathrm{HHBr}}^{\ddagger\prime\prime}}{z_{\mathrm{H}}^{\prime\prime} z_{\mathrm{HBr}}^{\prime\prime}} N_{\mathrm{Av}}$$

We assume that the electronic factors in the partition functions of $\mathrm{HHBr}^{\ddagger}$ and HBr can be approximated by 1.000. The ground state of the hydrogen atom has a degeneracy of 2, so we assume that its electronic factor can be approximated by 2.000. We also assume that the vibrational factor in the HBr partition function can be approximated by 1.000. The partition function of the H atom is

$$z_{\mathrm{H}}^{\prime\prime} = z_{\mathrm{tr,H}}^{\prime\prime} z_{\mathrm{el,H}}^{\prime\prime} = \left(\frac{2\pi m_{\mathrm{H}} k_{\mathrm{B}} T}{h^2}\right)^{3/2} \tag{2}$$

---

[9] K.J. Laidler, *op. cit.*, p. 109 (note 8).

$$= \left(\frac{2\pi(1.674 \times 10^{-27}\,\mathrm{kg})(1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}})(500.0\ \mathrm{K})}{(6.6261 \times 10^{-34}\,\mathrm{J\,s})^2}\right)^{3/2} (2)$$

$$= 2.127 \times 10^{30}\,\mathrm{m^{-3}}(2) = 4.254 \times 10^{30}\,\mathrm{m^{-3}}$$

The partition function of HBr has a translational and a rotational factor:

$$\begin{aligned}
z''_{\mathrm{tr,Br}} &= \left(\frac{2\pi m_{\mathrm{HB}_r} k_{\mathrm{B}} T}{h^2}\right)^{3/2} \\
&= \left(\frac{2\pi(1.327 \times 10^{-25}\,\mathrm{kg})(1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}})(500.0\,\mathrm{K})}{(6.6261 \times 10^{-34}\,\mathrm{J\,s})^2}\right)^{3/2} \\
&= 1.501 \times 10^{33}\,\mathrm{m^{-3}} \\
z_{\mathrm{rot,HBr}} &= \frac{k_{\mathrm{B}}T}{hc\tilde{B}_{\mathrm{e}}} = \frac{(1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}})(500.0\,\mathrm{K})}{(6.6261 \times 10^{-34}\,\mathrm{J\,s})(2.9979 \times 10^{10}\,\mathrm{cm\,s^{-1}})(8.4649\ \mathrm{cm^{-1}})} \\
&= 41.05 \\
z''_{\mathrm{HBr}} &= (1.501 \times 10^{33}\,\mathrm{m^{-3}})(41.05) = 6.161 \times 10^{34}\,\mathrm{m^{-3}}
\end{aligned}$$

The partition function of the activated complex has a translational, a rotational, and a vibrational factor:

$$\begin{aligned}
z^{\ddagger''}_{\mathrm{HHBr}} &= z^{\ddagger'}_{\mathrm{HHBr,tr}} z^{\ddagger'}_{\mathrm{HHBr,rot}} z^{\ddagger'}_{\mathrm{HHBr,vib}} \\
z^{\ddagger''}_{\mathrm{tr,HHBr}} &= \left(\frac{2\pi m_{\mathrm{HHBr}} k_{\mathrm{B}} T}{h^2}\right)^{3/2} \\
&= \left(\frac{2\pi(1.360 \times 10^{-25}\,\mathrm{kg})(1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}})(500.0\,\mathrm{K})}{(6.6261 \times 10^{-34}\,\mathrm{J\,s})^2}\right)^{3/2} \\
&= 1.558 \times 10^{33}\,\mathrm{m^{-3}}
\end{aligned}$$

To obtain the rotational partition function, we require the moment of inertia of the activated complex. The center of mass of three objects is found as in Eq. (D-25) of Appendix D.

$$x_c = \frac{m_1x_1 + m_2x_2 + m_3x_3}{m_1 + m_2 + m_3}$$

If the origin of coordinates is taken at the hydrogen nucleus at the end of the activated complex, we have

$$\begin{aligned}
x_{\mathrm{c}} &= \frac{0 + m_{\mathrm{H}}(150\,\mathrm{pm}) + m_{\mathrm{Br}}(292\,\mathrm{pm})}{m_{\mathrm{H}} + m_{\mathrm{H}} + m_{\mathrm{Br}}} \\
&= \frac{(1.008\,\mathrm{amu})(150\,\mathrm{pm}) + (79.904\,\mathrm{amu})(292\,\mathrm{pm})}{2.016\,\mathrm{amu} + 79.904\,\mathrm{amu}} = 286.7\,\mathrm{pm}
\end{aligned}$$

The moment of inertia is

$$\begin{aligned}
I_{\mathrm{e}} &= m_{\mathrm{H}}(286.7\,\mathrm{pm})^2 + m_{\mathrm{H}}(136.7\,\mathrm{pm})^2 + m_{\mathrm{Br}}(5.3\,\mathrm{pm})^2 \\
&= (1.008\,\mathrm{amu})(286.7\,\mathrm{pm})^2 + (1.008\,\mathrm{amu})(136.7\,\mathrm{pm})^2 + (79.904\,\mathrm{amu})(5.3\,\mathrm{pm})^2 \\
&= (1.039\ \times 10^4\ \mathrm{amu\ pm^2})\left(\frac{0.001\mathrm{kg}}{6.02214 \times 10^{23}\ \mathrm{amu}}\right)\left(\frac{1\mathrm{m}}{10^{12}\,\mathrm{pm}}\right)^2 \\
&= 1.73 \times 10^{-46}\,\mathrm{kg\ m^2}
\end{aligned}$$

$$
\begin{aligned}
z^{\ddagger\prime\prime}_{\mathrm{rot,HHBr}} &= \frac{8\pi^2 I_e k_B T}{h^2} \\
&= \frac{8\pi^2(1.73\times10^{-46}\ \mathrm{kg\,m^2})(1.3807\times10^{-23}\ \mathrm{J\,K^{-1}})(500.0\ \mathrm{K})}{(6.6261\times10^{-34}\ \mathrm{J\,s})^2} \\
&= 214.3
\end{aligned}
$$

Normal mode number 1 is the symmetric stretch:

$$
\begin{aligned}
&= \frac{hc\tilde{\nu}_1}{k_B T} = \frac{(6.6261\times10^{-34}\ \mathrm{J\,s})(2.9979\times10^{10}\ \mathrm{m\,s^{-1}})(2340\ \mathrm{cm^{-1}})}{(1.3807\times10^{-23}\ \mathrm{J\,K^{-1}})(500.0\ \mathrm{K})} \\
&= 6.73
\end{aligned}
$$

Normal mode number 2 is the bend (there are two of these)

$$
\begin{aligned}
&= \frac{hc\tilde{\nu}_2}{k_B T} = \frac{(6.6261\times10^{-34}\ \mathrm{J\,s})(2.9979\times10^{10}\ \mathrm{cm\,s^{-1}})(460\ \mathrm{cm^{-1}})}{(1.3807\times10^{-23}\ \mathrm{J\,K^{-1}})(500.0\ \mathrm{K})} \\
&= 1.32
\end{aligned}
$$

$$
\begin{aligned}
z_{\mathrm{vib,HHBr}} &= \frac{1}{1-e^{-x_1}}\left(\frac{1}{1-e^{-x_2}}\right)^2 \\
&= \frac{1}{1-e^{-6.73}}\left(\frac{1}{1-e^{-1.32}}\right)^2 = (1.0011)(1.3645)^2 = 1.864 \\
z^{\ddagger}_{\mathrm{HHBr}} &= (1.558\times10^{33}\ \mathrm{m^{-3}})(214.3)(1.864) = 6.22\times10^{35}\ \mathrm{m^{-3}} \\
k &= \frac{k_B T}{h} e^{-\Delta\varepsilon_0^{\ddagger}/k_B T}\,\frac{z^{\ddagger\prime\prime}_{\mathrm{HHBr}}}{z''_{\mathrm{H}} z''_{\mathrm{HBr}}} N_{\mathrm{Av}} \\
&= \frac{(1.3807\times10^{-23}\ \mathrm{J\,K^{-1}})(500.0\ \mathrm{K})}{6.6261\times10^{-34}\ \mathrm{J\,s}} \exp\left(\frac{-8.3\times10^{-21}\ \mathrm{J}}{(1.3807\times10^{-23}\ \mathrm{J\,K^{-1}})(500.0\ \mathrm{K})}\right) \\
&\quad\times \frac{6.22\times10^{35}\ \mathrm{m^{-3}}}{(4.254\times10^{30}\ \mathrm{m^{-3}})(6.161\times10^{34}\ \mathrm{m^{-3}})}(6.02214\times10^{23}\ \mathrm{mol^{-1}}) \\
&= 4.475\times10^{6}\ \mathrm{m^3\,mol^{-1}\,s^{-1}} \\
&= 4.475\times10^{9}\ \mathrm{L\,mol^{-1}\,s^{-1}}
\end{aligned}
$$

Exercise 26.12

a. Calculate the rate constant at 500.0 K for the reverse of the reaction in the previous example:

$$H_2 + \mathrm{Br} \to \mathrm{H} + \mathrm{HBr}$$

Assume the same activated complex as in the forward reaction so that $\Delta\varepsilon_0^{\ddagger} = 1.24\times10^{-19}$ J for the reverse reaction.

b. Use the values of the forward and reverse rate constants to calculate the equilibrium constant for the reaction. If you have already studied Part I of this textbook, compare your result with the result of a calculation from thermodynamic data.

Equation (26.4-15) can be written in a "thermodynamic" form, using Eq. (7.1-20):

$$k = \frac{k_B T}{h}\frac{1}{c^{\circ}}K_c^{\ddagger} = \frac{k_B T}{h}\frac{1}{c^{\circ}}e^{-\Delta G^{\ddagger\circ}/RT} \qquad (26.4\text{-}16)$$

where the equilibrium constant $K_c^{\ddagger}$ and the standard-state Gibbs energy change $\Delta G^{\ddagger\circ}$ are for the formation of the activated complex excluding the motion along the reaction coordinate.

Svante Arrhenius, 1859–1927, was a Swedish chemist who won the 1905 Nobel Prize in chemistry for his theory of dissociation and ionization of electrolytes in solution.

There is an empirical formula that represents the temperature dependence of rate constants, due to Arrhenius:

$$k = Ae^{-E_{\mathrm{a}}/RT} \tag{26.4-17}$$

where E_{a} is a parameter called the activation energy. The activation energy E_{a} is sometimes defined as

$$E_{\mathrm{a}} = RT^2 \frac{d\ln(k)}{dT} \tag{26.4-18}$$

Exercise 26.13

Show that Eq. (26.4-18) is compatible with Eq. (26.4-17) if A is constant.

Differentiation of the natural logarithm of k as represented in the first equality of Eq. (26.4-16) gives

$$E_{\mathrm{a}} = RT^2\left(\frac{d\ln(T)}{T} + \frac{d\ln(K_c^{\ddagger})}{dT}\right) \tag{26.4-19}$$

From Eq. (7.6-4)

$$\begin{aligned}\left(\frac{\partial\ln(K)}{\partial T}\right)_P &= -\left(\frac{\partial\Delta G^\circ/RT}{\partial T}\right)_P = \frac{\Delta G^\circ}{RT^2} + \frac{1}{RT}\left(\frac{\partial\Delta G^\circ}{\partial T}\right)_P \\ &= \frac{\Delta G^\circ}{RT^2} + \frac{1}{RT}\Delta S^\circ = \frac{\Delta H^\circ}{RT^2}\end{aligned} \tag{26.4-20}$$

so that

$$E_{\mathrm{a}} = RT + \Delta H^{\circ\ddagger} \tag{26.4-21}$$

Using this relation and the relation $\Delta G = \Delta H - T\Delta S$, which holds for isothermal processes, Eq. (26.4-16) can be rewritten

$$k = \frac{k_{\mathrm{B}}T}{h}\frac{1}{c^\circ}e^{\Delta S^{\ddagger\circ}/R}e^{-\Delta H^{\ddagger\circ}/RT} = \frac{k_{\mathrm{B}}T}{h}\frac{1}{c^\circ}e^{1}e^{\Delta S^{\ddagger\circ}/R}e^{-E_{\mathrm{a}}/RT} \tag{26.4-22}$$

The Arrhenius preexponential factor corresponds to the transition-state preexponential factor

$$A_{\mathrm{ts}} = \frac{k_{\mathrm{B}}T}{h}\frac{1}{c^\circ e}e^{\Delta S^{\ddagger\circ}/R} \tag{26.4-23}$$

The Arrhenius preexponential factor is temperature-independent, but A_{ts} depends on the temperature. However, if we set A_{ts} equal to the Arrhenius preexponential factor we can relate $\Delta S^{\ddagger\circ}$ to the Arrhenius preexponential factor.

EXAMPLE 26.13

The experimental value of the preexponential factor for the reaction

$$H_2 + I_2 \to 2HI$$

is equal to $1.65 \times 10^7\,\mathrm{L\,mol^{-1}\,s^{-1}}$. Find the value of $\Delta S^{\ddagger\circ}$ at 298.15 K.

Solution

From Eq. (26.4-23)

$$\Delta S^{\ddagger\circ} = R\ln\left(\frac{hAc^\circ}{ek_\mathrm{B}T}\right)$$

$$\frac{hAc^\circ}{ek_\mathrm{B}T} = \frac{(6.62 \times 10^{-34}\,\mathrm{J\,s})(1.65 \times 10^7\,\mathrm{L\,mol^{-1}\,s^{-1}})(1\,\mathrm{mol\,L^{-1}})}{(2.71828)(1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}})(298\,\mathrm{K})}$$

$$= 9.77 \times 10^{-7}$$

$$\Delta S^{\ddagger\circ} = (8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})\ln(9.77 \times 10^{-7}) = -115\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

Exercise 26.14

a. Explain why the entropy change of activation for a bimolecular gaseous reaction is generally negative.

b. The collision theory of bimolecular gaseous chemical reactions provides a formula for the preexponential factor:

$$A = N_\mathrm{Av}\pi d_{12}^2\left(\frac{8k_\mathrm{B}\mathrm{T}}{\pi\mu}\right)^{1/2}$$

where d is the collision diameter (the distance between the centers of the particles at collision) and μ is the reduced mass of the two particles:

$$\mu = \frac{m_1m_2}{m_1 + m_2}$$

Estimate the preexponential factor for a typical bimolecular elementary reaction in which two atoms form a diatomic activated complex. Assume typical values of masses and the collision diameter.

PROBLEMS

Section 26.4: The Activated Complex Theory of Bimolecular Chemical Reaction Rates in Dilute Gases

26.31 For the gas-phase reaction

$$CH_3 + CH_4 \to CH_4 + CH_3$$

the Arrhenius preexponential factor equals $5 \times 10^4\,\mathrm{m^3\,mol^{-1}\,s^{-1}}$. Estimate $\Delta S^{\ddagger\circ}$ at 298 K. Explain your value of $\Delta S^{\ddagger\circ}$.

26.32 Moss and Coady[10] give information about approximate potential energy surfaces for several reactions,

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[10] S. J. Moss and C. J. Coady, *J. Chem. Educ.*, **60**, 445 (1983).

calculated with the London–Eyring–Polanyi–Sato (LEPS) method. For the reaction

$$\mathrm{H} + \mathrm{HF} \rightarrow \mathrm{H} + \mathrm{F}_2$$

Their value of $\Delta\varepsilon_0^{\ddagger}$ is 9.0×10^{-21} J, from a barrier height of 9.3×10^{-21} J. They give the following values for the activated complex at 298 K: $z_{\mathrm{rot}}^{\prime\ddagger} = 111.25$, $z_{\mathrm{vib}}^{\prime\ddagger} = (1.00)(1.199)^2$ (for the symmetric stretch and the two degenerate bends). Find the value of the rate constant at 298 K. Compare your value with that from the experimental Arrhenius activation energy, $9\ \mathrm{kJ\ mol^{-1}}$, and the Arrhenius preexponential factor, $6.3 \times 10^7\ \mathrm{m^3\ mol^{-1}\ s^{-1}}$. What is an explanation for the difference between the theoretical and experimental values?

26.33 Calculate the rate constant for the reaction of Example 26.12 at 550.0 K. Determine the Arrhenius activation energy and compare it with the value of $\Delta\varepsilon_0^{\ddagger}$.

26.34 Calculate the forward rate constant at 300 K and at 1000 K for the reaction

$$\mathrm{H} + \mathrm{H}_2 \rightarrow \mathrm{H}_2 + \mathrm{H}$$

using the activated complex theory. Assume a linear activated complex with all vibrational partition functions equal to unity. The intermolecular distance of hydrogen is 0.741×10^{-10} m. For the activated complex take each bond as 0.942×10^{-10} m. Take the value of $\Delta\varepsilon_0^{\ddagger}$ as 6.8×10^{-20} J. What is the value of the equilibrium constant for this reaction? What is the value of the rate constant for the reverse reaction?

26.5 Miscellaneous Topics in Statistical Thermodynamics

We close this chapter with three topics that help in interpreting the statistical mechanics of dilute gases.

A Different Expression for the Probability Distribution

Now that we have the expression for the chemical potential in terms of the molecular partition function, we can write Eq. (26.1-27) in the form

$$\frac{N}{z} = e^{\mu/k_{\mathrm{B}}T} \tag{26.5-1}$$

This equation gives an expression for the Lagrange multiplier, α, in Eq. (25.2-23):

$$\alpha = \mu/k_{\mathrm{B}}T \tag{26.5-2}$$

The equation for the molecular probability distribution for a dilute gas can now be written in the form

$$p_j = \frac{N_j}{N} = g_j e^{\mu/k_{\mathrm{B}}T} e^{-\varepsilon_j/k_{\mathrm{B}}T} = g_j e^{(\mu-\varepsilon_j)/k_{\mathrm{B}}T} \tag{26.5-3}$$

The parameters α and β have the same meaning in all cases. If the dilute occupation approximation cannot be used, Eqs. (25.2-26) and (25.2-29) can be rewritten for noninteracting fermions and bosons:

$$N_j = \frac{g_j e^{(\mu-\varepsilon_j)/k_{\mathrm{B}}T}}{1 + e^{(\mu-\varepsilon_j)/k_{\mathrm{B}}T}} \quad \text{(fermions)} \tag{26.5-4}$$

$$N_j = \frac{g_j e^{(\mu-\varepsilon_j)/k_{\mathrm{B}}T}}{1 - e^{(\mu-\varepsilon_j)/k_{\mathrm{B}}T}} \quad \text{(bosons)} \tag{26.5-5}$$

These equations let us interpret the chemical potential as a kind of benchmark energy. Energies larger than μ are less probable than energies smaller than μ. We will use Eq. (26.5-4) in Chapter 28 when we discuss electrons in an electrical conductor.

The Interpretation of Heat and Work in Statistical Mechanics

From Eq. (4.2-3) we have the relation for reversible changes in a closed simple system

$$dU = TdS - PdV \tag{26.5-6}$$

Since we identify the mechanical energy of the system, E, with its thermodynamic energy, U, we can write a statistical mechanical expression for dU:

$$dU = dE = d\left(\sum_i N_i\varepsilon_i\right) = \sum_i \varepsilon_i dN_i + \sum_i N_i d\varepsilon_i \tag{26.5-7}$$

We have assumed that the molecule energy eigenvalues depend only on the volume of the system, so that

$$dU = \sum_i \varepsilon_i\, dN_i + \sum_i N_i \frac{d\varepsilon_i}{dV} dV \tag{26.5-8}$$

From the expression for the pressure in Eq. (26.1-10) we can write

$$dU = \sum_i \varepsilon_i dN_i - PdV = \sum_i \varepsilon_i dN_i + dw_{\text{rev}} \tag{26.5-9}$$

where we have used the fact that $dw_{\text{rev}} = -PdV$ for a reversible process in a simple system such as a dilute gas.

Comparison with the first law of thermodynamics shows that

$$dq_{\text{rev}} = \sum_i \varepsilon_i dN_i \tag{26.5-10}$$

Heat added to a system corresponds to a change in energy resulting from changes in the numbers of molecules occupying the energy levels. Work done on a dilute gas must be represented by the other term in dE, corresponding to a change in energy resulting from shifts of the molecular energy levels.

More on the Identification of the Statistical Entropy and the Thermodynamic Entropy

We can now shed some additional light on the relation between statistical entropy and thermodynamic entropy, and also on the identification of the parameter β with $1/k_{\text{B}}T$. Using the definition of the statistical entropy in Eq. (26.1-1) and replacing $\ln(\Omega)$ by its largest term, $\ln(W_{\text{mp}})$, we obtain

$$dS_{\text{st}} = k_{\text{B}} d\ln(W_{\text{mp}}) = k_{\text{B}} \sum_i \left(\frac{\partial \ln(W_{\text{mp}})}{\partial N_i}\right) dN_i \tag{26.5-11}$$

From Eq. (25.2-17), we can write

$$\frac{\partial \ln(W_{\mathrm{mp}})}{\partial N_i} = -\alpha + \beta\varepsilon_i \tag{26.5-12}$$

so that

$$dS_{\mathrm{st}} = k\sum_i (-\alpha + \beta\varepsilon_i)\,dN_i = k_{\mathrm{B}}\beta\sum_i \varepsilon_i dN_i = k_{\mathrm{B}}\beta dq_{\mathrm{rev}} \tag{26.5-13}$$

where we have used the fact that since the number of particles is fixed, the dN_i values must sum to zero, and have used Eq. (26.5-10). If the statistical entropy is identified with the thermodynamic entropy, we have an alternative proof that $\beta = 1/(k_{\mathrm{B}}T)$. If $\beta = 1/(k_{\mathrm{B}}T)$ is assumed, then we have a demonstration that the statistical entropy is the same as the thermodynamic entropy except for an additive constant.

Summary of the Chapter

The thermodynamic functions of a dilute gas can be calculated from the molecular partition function of the gas. The necessary formulas are based on the postulates of statistical mechanics and on the definition of the statistical entropy

$$S_{\mathrm{st}} = k_{\mathrm{B}}\ln(\Omega)$$

where Ω is the total number of system mechanical states that might be occupied, given the information that we possess about the state of the system. Working formulas were presented for all of the common equilibrium thermodynamic variables of a dilute gas.

A theoretical expression for the equilibrium constant for a chemical reaction in a dilute gas mixture was obtained:

$$K = e^{-\Delta\varepsilon_0/k_{\mathrm{B}}T}\prod_{j=1}^{s}\left(\frac{z_j'^{\circ}}{N_{\mathrm{Av}}}\right)^{v_j}$$

where z_j' is the molecular partition function of substance number j, given that the volume of the system is equal to the molar volume of a dilute gas at pressure P° and at the temperature of the system.

The statistical mechanical theory of rate constants known as the activated complex theory or the transition state theory is based on the assumption that an activated complex of high potential energy forms during the progress of a reaction, and that this activated complex can be assumed to be at equilibrium with the reactants. Use of the expression for the equilibrium constant in terms of partition functions and an approximate theory for the rate of passage through the transition state gives an expression for the rate constant. For a bimolecular reaction of a diatomic molecule CD and an atom F the rate constant is given by

$$k = \frac{k_{\mathrm{B}}T}{h}e^{-\Delta\varepsilon_0^{\ddagger}/k_{\mathrm{B}}T}\frac{(z_{\mathrm{CDF}}^{\ddagger}/N_{\mathrm{Av}}V)}{(z_{\mathrm{CD}}'/N_{\mathrm{Av}}V)(z_{\mathrm{F}}'/N_{\mathrm{Av}}V)}$$

ADDITIONAL PROBLEMS

26.35 **a.** Find the value of the statistical entropy of the model system of four oscillators in Section 25.1 for the given case that $E = 4h\nu$.

b. Find the value of Ω for the example system of four oscillators if the system energy equals $5h\nu$.

c. Find the value of Ω for the example system of four oscillators if the system energy equals $3h\nu$.

d. Find the value of the statistical entropy of the system corresponding to parts b and c.

e. Consider a combined system made up of two systems, each of which consists of four distinguishable oscillators. The value of Ω for the combined system is equal to $\Omega_a\Omega_b$, where we denote the two subsystems by a and b. Find the statistical entropy of the combined system if each subsystem has an energy of $4h\nu$.

f. Find the statistical entropy of the combined system if one subsystem has an energy of $5h\nu$ and the other has an energy of $3h\nu$. Show that the entropy of the combined system increases if one quantum of energy is transferred from the system with energy equal to $5h\nu$ to the system with an energy of $3h\nu$.

g. Find the temperature of each subsystem prior to the transfer of energy given that $\nu = 2.00 \times 10^{13}\ \mathrm{s}^{-1}$.

26.36 **a.** Choose a diatomic gas and compute its translational, rotational, vibrational, and electronic partition functions at 298.15 K and 1.000 bar, looking up parameters as needed in Table A.2 in Appendix A or in some more complete table.[11] Unless you choose NO or a similar molecule with an unpaired electron, assume that only the ground electronic state needs to be included.

b. Compute the standard-state energy, entropy, Helmholtz energy, Gibbs energy, and heat capacity of your gas at 298.15 K. It might be interesting for members of a class to choose different substances and to make a table of their collective results.

26.37 **a.** Calculate the difference between the Helmholtz energy, A of 1.000 mol of ^{36}Ar and 1.000 mol of ^{40}Ar at 298.15 K and 1.000 bar. The molar masses are 35.9675 g mol^{-1} and 39.9624 g mol^{-1}.

b. Calculate the same difference for U.

c. Calculate the same difference for S.

d. Calculate the entropy of mixing for 0.0040 mol of ^{36}Ar and 99.60 mol of ^{40}Ar, which approximates 100.00 mol of ordinary argon. Explain why this entropy of mixing and similar entropies of isotopic mixing can be ignored in ordinary chemical reactions.

26.38 The ground electronic level of NO is a $^2\Pi_{1/2}$ term. The first excited level is a $^2\Pi_{3/2}$ term with an energy 2.380×10^{-21} J above the ground level. Both these states have degeneracy equal to 2. All other electronic states are more than 7×10^{-19} J above the ground level and can be neglected. The value of the vibrational constant, $\tilde{\nu}_e$, is 1904.20 cm^{-1}, and the value of the rotational constant, $\tilde{B}_e$, is 1.67195 cm^{-1}.

a. Find the electronic factor in the molecular partition function of NO at 500.0 K and 1.000 atm.

b. Find the fraction of NO molecules in the first excited electronic state at 500.0 K.

c. Find the rotational factor in the molecular partition function of NO at 500.0 K and 1.000 atm.

d. Find the translational factor in the molecular partition function of NO at 298.15 K and 1.000 atm.

e. Find the vibrational factor in the molecular partition function of NO at 500.0 K and 1.000 atm.

f. Find the value of A_m° for 1.000 mol of NO at 500.0 K and find the value of each contribution to it. Does the vibrational contribution need to be included?

g. Find the value of U_m° for 1.000 mol of NO at 500.0. Take the energy of the ground electronic state as zero.

26.39 **a.** Using the C−C and C=C bond energies, estimate the activation energy for a *cis trans* isomerization around a C=C bond.

b. Estimate the ratio of the rate of a *cis trans* isomerization at 310.0 K to the rate at 300.0 K.

26.40 The rotational states of *para*-hydrogen are restricted to even values of J (see Chapter 22). The rotational contribution to the heat capacity of *para*-hydrogen exhibits an interesting effect similar to the Schottky effect (see Problem 26.18).[12] Assume that in solid and

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[11] K. P. Huber and G. Herzberg, *op. cit.* (note 3).

[12] R. L. Scott, *J. Chem. Educ.*, **83**, 1071 (2006).

liquid hydrogen the molecules rotate freely. (This seems to be an accurate assumption.)

a. Construct an accurate graph of the molar rotational energy of *para*-hydrogen (restricted to even values of J) from 0 K to 500 K. Sum up the rotational partition function explicitly, including rotational states up to $J = 6$.

b. Construct an accurate graph of the molar rotational heat capacity of *para* -hydrogen from 0 K to 500 K. Explain in physical terms why the heat capacity exhibits a maximum and compare your values with the value of 8.3145 J K^{-1} mol^{-1} from Eq. (26.2-10c).

26.41 Identify the following statements as either true or false. If a statement is true only under special circumstances, label it as false.

a. Statistical thermodynamic calculations for monatomic gases are generally more accurate than those for molecular gases.

b. The identification of statistical entropy and thermodynamic entropy gives agreement with experimental and statistical thermodynamic values for dilute gases.

c. An isomerization reaction must have an equilibrium constant equal to unity.

d. Values of standard-state thermodynamic functions of gases calculated with statistical mechanics are always less reliable than experimental values.

27

Equilibrium Statistical Mechanics. III. Ensembles

PRINCIPAL FACTS AND IDEAS

1. Statistical mechanics can be studied by visualizing an ensemble, which is an imaginary set of many replicas of the physical system.
2. In the microcanonical ensemble, all replicas in the ensemble have the same energy. The treatment of dilute gases in Chapters 25 and 26 is equivalent to using the microcanonical ensemble to represent that system.
3. In the canonical ensemble, all replicas in the ensemble have the same temperature. Use of this ensemble provides an alternative approach to the statistical mechanics of dilute gases, and results in the same formulas for thermodynamic variables for dilute gases as in Chapter 26.
4. Statistical mechanics can be based on classical mechanics instead of on quantum mechanics, and this approach is useful in the discussion of nonideal gases and liquids.

27.1 The Canonical Ensemble

In Chapters 25 and 26 we applied statistical mechanics to dilute gases, based on the probability distribution for states of molecules in a dilute gas with fixed energy, fixed volume, and fixed number of molecules. This chapter presents an alternative approach to statistical mechanics, which is in principle applicable to any kind of a system. It is based on the concept of an *ensemble*, which is an imaginary collection of very many replicas of the real system. Each replica occupies the same macrostate as the real system, but different members of the ensemble occupy different system microstates.

If the equilibrium macrostate of a closed system is specified by fixed values of the thermodynamic energy U, the volume V, and number of molecules N, a *microcanonical ensemble* is used to represent it. The systems of this ensemble have the same values of E (with E equal to U), N, and V but occupy different microstates. Our discussion in Chapters 25 and 26 is equivalent to using the microcanonical ensemble to represent a dilute gas.

The *canonical ensemble* represents a closed system at equilibrium with a macrostate specified by values of T, V, and N. The systems of the canonical ensemble are placed in thermal contact with each other so that each system of the ensemble is in a constant-temperature bath consisting of the other systems of the ensemble, and all have the same temperature. Figure 27.1 schematically depicts a portion of such an ensemble.

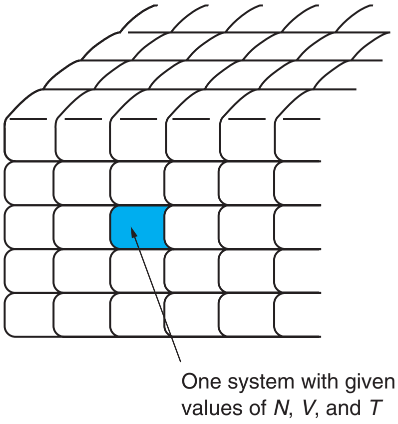

Figure 27.1 A Canonical Ensemble.

The *grand canonical ensemble* represents an open system with a macrostate specified by values of T, V, and μ (the chemical potential) for each substance present. Each system of the ensemble is open to the other systems of the ensemble and can exchange matter and energy with the other systems. Discussions of the grand canonical ensemble can be found in statistical mechanics textbooks, but we will not discuss it.

The Postulates of Statistical Mechanics

The two postulates of equilibrium statistical mechanics introduced in Chapter 25 can now be restated:

Postulate 1. *Observed values of thermodynamic variables in the actual system can be represented by ensemble averages of the corresponding mechanical variables.*

Postulate 2. *In any ensemble, each system microstate corresponding to the same values of* E, V, *and* N *is occupied by an equal number of systems.*

The Canonical Probability Distribution

Imagine that the Schrödinger equation of the real system has been solved, and that we have a list of its very many system energy eigenfunctions and energy eigenvalues, each corresponding to the same volume and same number of molecules. The fact that we cannot actually carry out this solution is unimportant until we attempt to carry out calculations. The energy eigenfunctions are numbered Ψ_1, Ψ_2, Ψ_3, and so on, with energy eigenvalues E_1, E_2, E_3, and so on. Although there are infinitely many such states, we imagine that the ensemble contains so many systems that each of these system states is occupied by some members of the ensemble. Let n_1 be the number of systems in the ensemble that are in system state 1, n_2 be the number of systems in system state 2, and so on. Since the systems are macroscopic in size, they are distinguishable and there is no exclusion principle.

Let the fraction of systems in system microstate k be denoted by

$$p_k = \frac{n_k}{n} \tag{27.1-1}$$

where n is the total number of systems in the ensemble. Since by the second postulate every state corresponding to the same energy is assumed to be equally represented in the ensemble, we assume that p_k depends only on the energy eigenvalue E_k corresponding to the state k:

$$p_k = p(E_k) \tag{27.1-2}$$

We also make the important assumption that p is the same function of E for all different kinds of systems. In order to determine what kind of a mathematical function p is, we consider a system that is made up of two parts, which we call subsystem I and subsystem II. Each part is closed and at constant volume, but the two parts are in thermal contact with each other (as well as with the rest of the ensemble) so that both are at the same temperature. We assume that the two subsystems occupy mechanical states independently of each other and that the system energy is a sum of the subsystem energies:

$$E_k = E_{\mathrm{I},k} + E_{\mathrm{II},k} \tag{27.1-3}$$

The subscript I, k represents the state of subsystem I corresponding to system state k, and II, k represents the corresponding state of subsystem II.

A canonical ensemble that represents the system contains many replicas of the system, each made up of two subsystems. The fraction of the replicas of subsystem I in the ensemble that occupy state I, k is

$$p_{\mathrm{I},k} = p(E_{\mathrm{I},k}) \tag{27.1-4a}$$

and the fraction of the replicas of subsystem II in state II, k is

$$p_{\mathrm{II},k} = p(E_{\mathrm{II},k}) \tag{27.1-4b}$$

Furthermore, the probability that the combined system is in state k is

$$p_k = p(E_k) \tag{27.1-4c}$$

where by our hypothesis p represents the same mathematical function of its argument for the combined system and for each subsystem.

Probability theory asserts that the joint probability of two independent occurrences is equal to the product of the probabilities of the two occurrences. Therefore

$$p(E_k) = p(E_{\mathrm{I},k} + E_{\mathrm{II},k}) = p(E_{\mathrm{I},k})p(E_{\mathrm{II},k}) \tag{27.1-5}$$

The exponential function is the only function that has this property. We write p in the form

$$p(E) = Ae^{-\beta E} \tag{27.1-6}$$

where A and β are parameters that do not depend on E. To prevent the probability from increasing indefinitely for large energy, we must require that $\beta > 0$. Equation (27.1-6) is not restricted to dilute gases or any other particular kind of system, nor is it restricted to a system made up of two separate subsystems.

Exercise 27.1

Choose several different functions of E such as $\sin(E), \cos(E), E, E^2$, and so on, and show that they do not satisfy Eq. (27.1-5). Show that the function of Eq. (27.1-6) does satisfy this relation.

We can derive Eq. (27.1-6). Let x and y represent the two subsystem energies, so that

$$p(x+y) = p(z) = p(x)p(y) \tag{27.1-7}$$

where $x + y = z$. By the chain rule (see Appendix B),

$$\frac{dp}{dx} = \frac{dp}{dz}\frac{\partial z}{\partial x} = \frac{dp}{dx}p(y) \tag{27.1-8a}$$

$$\frac{dp}{dy} = \frac{dp}{dz}\frac{\partial z}{\partial y} = \frac{dp}{dy}p(x) \tag{27.1-8b}$$

Since $z = x + y, \partial z/\partial y = \partial z/\partial x = 1$, and we can write

$$\frac{dp}{dx}p(y) = \frac{dp}{dy}p(x) \tag{27.1-9}$$

We divide by $p(x)p(y)$:

$$\frac{1}{p(x)}\frac{dp}{dx} = \frac{1}{p(y)}\frac{dp}{dy} \tag{27.1-10}$$

We have separated the variables x and y. A function of x that equals a function of y for all values of the independent variables x and y must be a constant function of x, since y can be held fixed while x varies. We let the constant functions equal $-\beta$, so that

$$\frac{1}{p(x)}\frac{dp}{dx} = -\beta = \text{constant} \tag{27.1-11}$$

We multiply by dx and do an indefinite integration

$$\frac{1}{p(x)}\frac{dp}{dx}dx = \frac{1}{p}dp = d[\ln(p)] = -\beta dx \tag{27.1-12}$$

$$\ln(p) = -\beta x + \ln(A) \tag{27.1-13}$$

where $\ln(A)$ is a constant of integration. We take antilogarithms:

$$p = Ae^{-\beta x} \tag{27.1-14}$$

which is the same as Eq. (27.1-6), with x replaced by E.

The Canonical Partition Function

We now need to eliminate the parameters A and β from the distribution shown in Eq. (27.1-14). The total number of systems in the ensemble is fixed, so that

$$\sum_k n_k = n \tag{27.1-15}$$

and

$$\sum_k p_k = \frac{\sum_k n_k}{n} = 1 = A\sum_k e^{-\beta E_k} \tag{27.1-16}$$

which is equivalent to

$$\boxed{\frac{1}{A} = \sum_k e^{-\beta E_k} = \mathcal{Z} \quad \text{(definition of } \mathcal{Z})} \tag{27.1-17}$$

Equation (27.1-17) defines the sum $\mathcal{Z}$, which is called the *canonical partition function*. In German, a partition function is called a *Zustandsumme* (sum over states), a name that better represents the sum and is our motivation for using $\mathcal{Z}$ for its symbol. The canonical probability distribution can now be written as

$$p_k = \frac{1}{\mathcal{Z}}e^{-\beta E_k} \tag{27.1-18}$$

The ensemble average energy can be written

$$\langle E\rangle = U = \sum_{k=1}^{\infty} E_k p_k = \frac{1}{\mathcal{Z}}\sum_k E_k e^{-\beta E_k} \tag{27.1-19}$$

where we use the symbol $\langle\cdots\rangle$ for an ensemble average value. The sum is over all of the infinitely many system microstates, but we will omit the limits on our sums. This equation can be rewritten using a mathematical trick that we applied in Chapter 25:

$$\begin{aligned}\langle E\rangle &= -\frac{1}{\mathcal{Z}}\sum_k\left(\frac{\partial e^{-\beta E_k}}{\partial\beta}\right)_{V,N} = \frac{1}{\mathcal{Z}}\left(\frac{\partial}{\partial\beta}\sum_k e^{-\beta E_k}\right)_{V,N}\\ &= -\frac{1}{\mathcal{Z}}\left(\frac{\partial\mathcal{Z}}{\partial\beta}\right)_{V,N} = -\left(\frac{\partial\ln(\mathcal{Z})}{\partial\beta}\right)_{V,N}\end{aligned} \tag{27.1-20}$$

where we have interchanged the order of summing and differentiating. This is permissible if the sum is uniformly convergent, which we assume to be the case. A sum is convergent if it approaches more and more closely to a finite value as more and more terms are taken. It is uniformly convergent if it converges with at least a certain rate for all cases. We must keep V and N constant in the differentiation in order to keep the energy eigenvalues fixed, because the energy eigenvalues depend on V and N.

We can write an equation for the pressure, using some information from thermodynamics. Let P_k be the pressure of the system if it is in system microstate k. The statistical entropy was defined in Eq. (26.1-1). If the system is known to be in microstate number k, Ω equals 1 and the statistical entropy is equal to a constant. We assert that if the statistical entropy is constant we can use Eq. (26.1-8), which applies to constant thermodynamic entropy:

$$P_k = -\left(\frac{\partial U}{\partial V}\right)_{S,N} = -\left(\frac{\partial E_k}{\partial V}\right)_N \quad \text{(system in microstate } k) \tag{27.1-21}$$

where we assume that the energy eigenvalue E_k depends only on V and N. The ensemble average pressure becomes

$$\langle P\rangle = \sum_k P_k p_k = -\frac{1}{\mathcal{Z}}\sum_k\left(\frac{\partial E_k}{\partial V}\right)_N e^{-\beta E_k} = \frac{1}{\beta}\left(\frac{\partial\ln(\mathcal{Z})}{\partial V}\right)_{\beta,N} \tag{27.1-22}$$

where we used the mathematical trick applied in Eq. (27.1-20).

In order to investigate the parameter β, we assert that β has the same properties for any system and consider a dilute gas with N molecules. In a dilute gas the molecules are independent of each other and the system energy is a sum of the energies of the molecules:

$$E_i = \varepsilon_{1i} + \varepsilon_{2i} + \varepsilon_{3i} + \varepsilon_{4i} + \cdots + \varepsilon_{Ni} \tag{27.1-23}$$

where the subscript $1i$ stands for the quantum numbers of molecule number 1 that correspond to system state number i, and so on. The canonical partition function of a dilute gas is given by a sum over all of these quantum numbers:

$$\mathcal{Z} = \sum_{1i}\sum_{2i}\sum_{3i}\cdots\sum_{Ni}\exp[-\beta(\varepsilon_{1i} + \varepsilon_{2i} + \varepsilon_{3i} + \cdots + \varepsilon_{Ni})] \tag{27.1-24}$$

If each of the sums were independent of the others every molecule state would occur in every sum, and the multiple sum could be factored:

$$\mathcal{Z} = \sum_{1i} e^{-\beta\varepsilon_{1i}} \sum_{2i} e^{-\beta\varepsilon_{2i}} \sum_{3i} e^{-\beta\varepsilon_{3i}} \cdots \sum_{Ni} e^{-\beta\varepsilon_{Ni}} \quad \begin{pmatrix}\text{independent}\\ \text{sums}\end{pmatrix} \tag{27.1-25}$$

Identical molecules are indistinguishable from each other and the sums are not independent of each other, so that Eq. (27.1-25) is not usable. There are two reasons for this. First, if the molecules are fermions, any term in which two or more molecules are in the same state must be deleted from the sums. If the volume of the gas is very large and if the gas is dilute, the total number of molecular states available to be occupied can be much larger than the number of molecules in the system. We call this the case of *dilute occupation* of molecule states, and have assumed this case to apply in Chapters 25 and 26. In this case the forbidden sets of quantum numbers for a system of fermions occur in only a small fraction of the terms of the sum, and these terms can be left in the sum without serious error. This approximation also removes the difference between fermion and boson molecules.

The second reason that we cannot use Eq. (27.1-25) is that we must take account of the indistinguishability of the particles, whether they are fermions or bosons. If the molecules were distinguishable from each other we could assign a set of N molecules to N states in $N!$ ways, where $N!$ represents N factorial, equal to $(N)(N-1)(N-2)\cdots(3)(2)(1)$, the product of all integers starting with N and ranging down to 1. Summing independently over all values of the molecule quantum numbers denoted by $1i$, $2i$, etc., includes $N!$ terms that represent the same system state. We can make correction for the overcounting of states by dividing by $N!$:

$$\mathcal{Z} = \frac{1}{N!}\sum_{1i} e^{-\beta\varepsilon_{1i}} \sum_{2i} e^{-\beta\varepsilon_{2i}} \sum_{3i} e^{-\beta\varepsilon_{3i}} \cdots \sum_{Ni} e^{-\beta\varepsilon_{Ni}} \tag{27.1-26}$$

Since every sum is over the same set of molecule states, these sums over molecule states are identical:

$$\boxed{\mathcal{Z} = \frac{z^N}{N!} \quad \text{(gas of noninteracting molecules)}} \tag{27.1-27}$$

where z is a sum over molecule states, the *molecular partition function*:

$$\boxed{z = \sum_{k} e^{-\beta\varepsilon_k} \quad \begin{pmatrix}\text{definition of } z,\\ \text{the molecular partition function}\end{pmatrix}} \tag{27.1-28}$$

where we now denote a molecule state by the single index k. This molecular partition function is the same as the molecular partition function defined in Chapter 25.

For a monatomic gas without electronic excitation Eq. (25.3-18) gives the formula for the molecular partition function:

$$z = z_{\mathrm{tr}} = \left(\frac{2\pi m}{h^2\beta}\right)^{3/2} V \tag{27.1-29}$$

From Eq. (27.1-22), the ensemble average pressure of a monatomic dilute gas is

$$\langle P\rangle = \frac{1}{\beta}\left(\frac{\partial \ln(\mathcal{Z})}{\partial V}\right)_{\beta,N} = \frac{N}{\beta}\left(\frac{\partial \ln(z)}{\partial V}\right)_{\beta,N} = \frac{N}{\beta}\frac{d\ln(V)}{dV} = \frac{N}{\beta V} \tag{27.1-30}$$

We assume that our dilute gas obeys the ideal gas equation of state so that

$$\langle P\rangle = \frac{nRT}{V} = \frac{Nk_{\mathrm{B}}T}{V} \tag{27.1-31}$$

where k_{B} is Boltzmann's constant, equal to $1.3807 \times 10^{-23}\ \mathrm{J\,K^{-1}}$, and where T is the absolute temperature. This requires that

$$\beta = \frac{1}{k_{\mathrm{B}}T} \tag{27.1-32}$$

The molecular partition function of a dilute monatomic gas without electron excitation becomes the same function as in Eq. (25.3-21):

$$z = z_{\mathrm{tr}} = \left(\frac{2\pi m k_{\mathrm{B}}T}{h^2}\right)^{3/2} V \quad \text{(dilute monatomic gas)} \tag{27.1-33}$$

The canonical probability distribution becomes

$$p_i = \frac{1}{\mathcal{Z}} e^{-E_i/k_{\mathrm{B}}T} \tag{27.1-34}$$

and the canonical partition function becomes

$$\mathcal{Z} = \sum_i e^{-E_i/k_{\mathrm{B}}T} \tag{27.1-35}$$

Although we have established only that $\beta = 1/(k_{\mathrm{B}}T)$ for a dilute gas, we assert that β cannot have a different meaning for different systems and that Eqs. (27.1-34) and (27.1-35) are valid for any kind of a system.

Since the probability of any system microstate is proportional to $e^{-E_i/k_{\mathrm{B}}T}$, the canonical partition function is a measure of the total number of system microstates effectively available to the system, relative to a probability of 1 for a state of zero energy. The canonical partition function has a very large value for a macroscopic system.

EXAMPLE 27.1

Estimate the natural logarithm of the canonical partition function for 1.000 mol of helium gas in a volume of 25.0 L at 298.15 K.

Solution

$$\ln(\mathcal{Z}) = N\ln(z) - \ln(N!)$$

$$z = \left(\frac{2\pi(6.65 \times 10^{-27}\ \text{kg})(1.3807 \times 10^{-23}\ \text{J K}^{-1})}{(6.6261 \times 10^{-34}\ \text{J s})^2}\right)^{3/2} (0.0250\ \text{m}^3)$$
$$= 1.938 \times 10^{29}$$

We use Stirling's approximation for $\ln(N!)$:

$$\begin{aligned}\ln(\mathcal{Z}) &= N\ln(z) - \ln(N!) \approx N\ln(z) - N\ln(N) + N \\ &\approx -(6.022 \times 10^{23})\ln(1.938 \times 10^{29}) \\ &\quad -(6.022 \times 10^{23})\ln(6.022 \times 10^{23}) + 6.023 \times 10^{23} \\ &\approx -4.06 \times 10^{25} - 3.297 \times 10^{25} + 6.023 \times 10^{23} \approx 8.24 \times 10^{24}\end{aligned}$$

This is a large number, and *e* raised to this power is unimaginably large.

PROBLEMS

Section 27.1: The Canonical Ensemble

27.1 From the value of the molecular partition function in Example 25.1, calculate the value of the canonical partition function for 1.000 mol of argon confined in a volume of 25.0 L (0.0250 m^3) at 298.15 K.

27.2 Calculate the natural logarithm of the canonical partition function of 1.000 mol of O_2 gas at 298.15 K and a pressure of 1.000 atm.

27.3 Derive a formula for the canonical partition function when a different zero of energy is used.

27.4 Calculate the natural logarithm of the canonical partition function of 1.000 mol of Cl_2 gas at 298.15 K and a pressure of 1.000 bar. Use the value of the molecular partition function from Chapter 25, and use Stirling's approximation for $\ln(N_{\text{Av}}!)$.

27.5 **a.** Estimate the value of the canonical partition function for 1.000 mol of neon gas in a volume of 25.0 L at 298.15 K. Use Stirling's approximation for $N!$.

b. Estimate the probability of a single microstate of this system with an energy of $3RT/2 = 3718$ J at a temperature of 298.15 K.

27.2 Thermodynamic Functions in the Canonical Ensemble

We can now write the formula for the energy in Eq. (27.1-20) in terms of the temperature:

$$\langle E \rangle = -\left(\frac{\partial \ln(\mathcal{Z})}{\partial \beta}\right)_{V,N} = -\left(\frac{\partial \ln(\mathcal{Z})}{\partial T}\right)_{V,N}\left(\frac{dT}{d\beta}\right) = -\left(\frac{\partial \ln(\mathcal{Z})}{\partial T}\right)_{V,N}(-k_B T^2)$$

$$\langle E \rangle = U = k_B T^2 \left(\frac{\partial \ln(\mathcal{Z})}{\partial T}\right)_{V,N} \quad \text{(general system)} \tag{27.2-1}$$

where we have applied the chain rule (see Appendix B). We can also write Eq. (27.1-22) for the pressure in terms of the temperature:

$$\langle P\rangle = k_{\mathrm{B}}T\left(\frac{\partial \ln(\mathcal{Z})}{\partial V}\right)_T \quad \text{(general system)} \tag{27.2-2}$$

In order to obtain formulas for other thermodynamic variables, we must have a formula for the entropy. We begin with the thermodynamic relation in Eq. (4.2-3), which holds for reversible changes in any closed system:

$$dU = TdS - PdV \tag{27.2-3}$$

We divide this equation by T and write it in a different form:

$$dS = \frac{1}{T}dU + \frac{P}{T}dV = d\left(\frac{U}{T}\right) + \frac{U}{T^2}dT + \frac{P}{T}dV \tag{27.2-4}$$

Using Eqs. (27.2-1) and (27.2-2) for U and P, we obtain

$$dS = d\left(\frac{U}{T}\right) + k_{\mathrm{B}}\left(\frac{\partial \ln(\mathcal{Z})}{\partial T}\right)_V dT + k_{\mathrm{B}}\left(\frac{\partial \ln(\mathcal{Z})}{\partial V}\right)_T dV \tag{27.2-5}$$

For a closed system (fixed N), $\mathcal{Z}$ is a function of T and V. Therefore

$$dS = d\left(\frac{U}{T}\right) + k_{\mathrm{B}}d\ln(\mathcal{Z}) \quad \text{(closed system)} \tag{27.2-6}$$

An indefinite integration leads to

$$S = \frac{U}{T} + k_{\mathrm{B}}\ln(\mathcal{Z}) + S_0 \tag{27.2-7}$$

where S_0 is a constant of integration that we can set equal to zero whenever it is convenient. An alternative derivation of Eq. (27.2-7) is found in Problem 27.6.

We can now write formulas for the other thermodynamic functions of a general system in terms of the canonical partition function.

$$A = U - TS = -k_{\mathrm{B}}T\ln(\mathcal{Z}) \tag{27.2-8a}$$

$$C_{\mathrm{V}} = \left(\frac{\partial U}{\partial T}\right)_{V,N} = k_{\mathrm{B}}T^2\left(\frac{\partial^2 \ln(\mathcal{Z})}{\partial T^2}\right)_{V,N} + 2k_{\mathrm{B}}T\left(\frac{\partial \ln(\mathcal{Z})}{\partial T}\right)_{V,N} \tag{27.2-8b}$$

$$G = A + PV = k_{\mathrm{B}}T\ln(\mathcal{Z}) + Vk_{\mathrm{B}}T\left(\frac{\partial \ln(\mathcal{Z})}{\partial V}\right)_{T,N} \tag{27.2-8c}$$

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} = -k_{\mathrm{B}}T\ln\left(\frac{\mathcal{Z}_N}{\mathcal{Z}_{N-1}}\right) \tag{27.2-8d}$$

We have used the statistical thermodynamics definition of the chemical potential as a derivative with respect to the number of molecules instead of the amount in moles. We have replaced this derivative by a quotient of finite differences as in Eq. (26.1-24), and have attached a subscript to the canonical partition function to indicate the number of particles in the system.

$$H = U + PV = k_B T^2 \left(\frac{\partial \ln(\mathcal{Z})}{\partial T}\right)_{V,N} + V k_B T \left(\frac{\partial \ln(\mathcal{Z})}{\partial V}\right)_{T,N} \tag{27.2-8e}$$

PROBLEMS

Section 27.2: Thermodynamic Functions in the Canonical Ensemble

27.6 A definition of the statistical entropy that can be used for the canonical ensemble is:

$$S_{\mathrm{st}} = -k_B \sum_k p_k \ln(p_k) + S_0$$

where the sum is over all microstates of the system.

a. Apply this definition to the case that all of the p_k values are equal to $1/\Omega$ (as is the case in the microcanonical ensemble) and recover the same formula as in Eq. (26.1-1).

b. Apply this definition to the probability distribution of the canonical ensemble and recover the same formula for the entropy as in Eq. (27.2-7).

27.3 The Dilute Gas in the Canonical Ensemble

The formulas for the thermodynamic functions in the previous section apply to any kind of system. They can be applied to a dilute gas by using Eq. (27.1-27) to express the canonical partition function in terms of the molecular partition function.

$$\langle E \rangle = N k_B T^2 \left(\frac{\partial \ln(z^N/N!)}{\partial T}\right)_{V,N} = N k_B T^2 \left(\frac{\partial \ln(z)}{\partial T}\right)_V \quad \text{(dilute gas)} \tag{27.3-1}$$

Equation (27.3-1) is identical with Eq. (25.3-26). For a dilute gas the pressure is

$$\begin{aligned} P = k_B T \left(\frac{\partial \ln(\mathcal{Z})}{\partial V}\right)_{T,N} &= k_B T \left(\frac{\partial \ln(z^N)}{\partial V}\right)_{T,N} - k_B T \left(\frac{\partial \ln(N!)}{\partial V}\right)_{T,N} \\ &= N k_B T \left(\frac{\partial \ln(z)}{\partial V}\right)_T - 0 = N k_B T \left(\frac{\partial \ln(z)}{\partial V}\right)_T \end{aligned} \tag{27.3-2}$$

This equation is identical with Eq. (26.1-11). The formulas for the other thermodynamic functions can be derived in the same way, and are identical with those in Chapter 26.

Exercise 27.2

Show that the formulas in Eq. (27.2-8) lead to the same formulas for the thermodynamic functions of a dilute gas in terms of the molecular partition function as in Section 26.1.

It is remarkable that the thermodynamic functions for a dilute gas are given by the same formulas for a canonical ensemble, in which the replica systems have various energies, and for a microcanonical ensemble, in which all of the replica systems have the same energy. In the canonical ensemble the probability of a system state of energy E is proportional to $e^{-E/k_\mathrm{B}T}$. At ordinary temperatures, $k_\mathrm{B}T$ is a very small quantity of energy compared with E, the energy of an entire macroscopic system. Therefore except for the very lowest-energy states, $e^{-E/k_\mathrm{B}T}$ is a very small and very rapidly decreasing function of E. The probability of a system energy level is also proportional to the degeneracy of the level:

$$p_E \propto \Omega(E)\, e^{-E/k_\mathrm{B}T} \tag{27.3-3}$$

where $\Omega(E)$ is the number of system microstates corresponding to energy E. In Section 26.2 we estimated a value of Ω and found it to be a very large number (see Example 26.1). Furthermore, Ω increases very rapidly as a function of E. Figure 27.2a schematically shows the probability distribution of states, $e^{-E/k_\mathrm{B}T}$, and Figure 27.2b schematically shows $\Omega(E)$. Unfortunately, the extremely small size of $e^{-E/k_\mathrm{B}T}$ and the extremely large size of $\Omega(E)$ cannot be shown accurately. The large factor is rising so

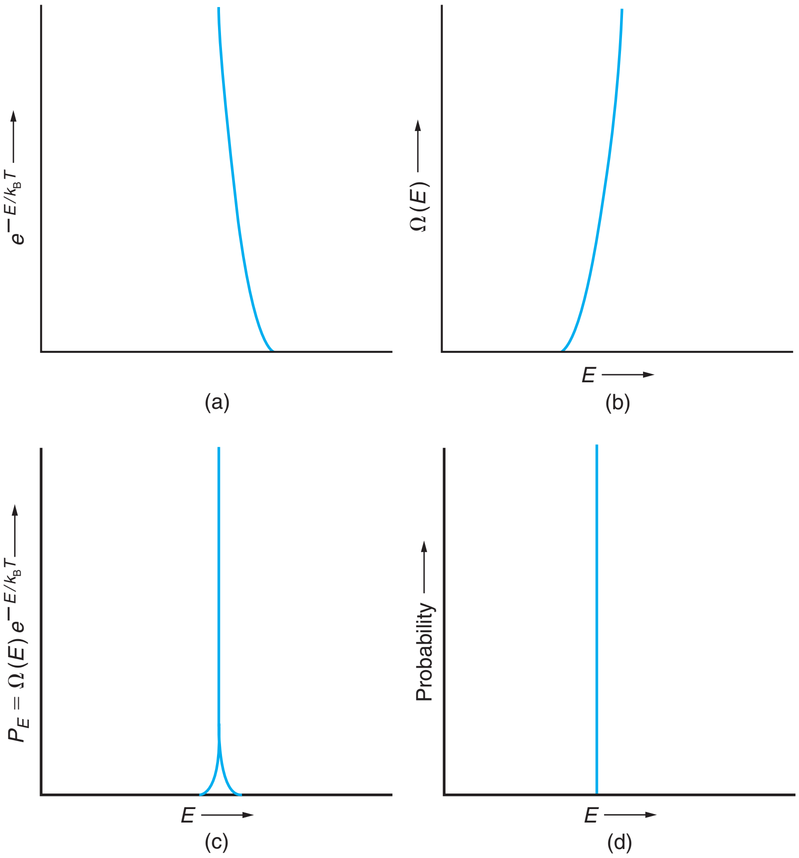

Figure 27.2 The Probability of System States and Levels. (a) Probability distribution of system states in the canonical ensemble as a function of energy (schematic). (b) The degeneracy of system energy levels as a function of energy (schematic). (c) The canonical probability of system energy levels as a function of energy (schematic). (d) The microcanonical probability of system energy levels as a function of energy (schematic).

steeply and the small factor is falling so rapidly that there is a small range of values of E where the product of the two factors is much larger than for other values of E, as shown in Figure 27.2c. For a system of N molecules it turns out that the width of the canonical energy probability distribution p_E is proportional to $\sqrt{N}$, whereas the energy itself is proportional to N. For large values of N the width of the distribution in E becomes very small compared to the value of E. The energy probability distribution of the microcanonical ensemble is nonzero for only a single energy, as depicted Figure 27.2d. The canonical distribution is so narrow that this distribution is virtually indistinguishable from it. This is related to the reason that the results of the canonical and microcanonical ensembles coincide.

The narrowness of the canonical energy probability distribution is also related to the very interesting question: Why is a macroscopic variable such as U given as a smooth mathematical function of other thermodynamic variables such as T, V, and N? We are not prepared to give a complete answer to this question, but comment that the thermodynamic functions are assumed to be equal to ensemble average values. Average quantities in very large populations tend to behave regularly and predictably, even if the properties of each member of the population do not. This regular behavior is related to the fact that the ensemble average energy is a smooth single-valued mathematical function of T, V, and N.

Applications of the canonical ensemble to quantum mechanical systems other than dilute gases are beyond the scope of this book, and we omit them. These applications are discussed in some of the statistical mechanics books listed at the end of this volume. We will make some comments on the application of the canonical ensemble to systems obeying classical mechanics in the next section.

PROBLEMS

Section 27.3: The Dilute Gas in the Canonical Ensemble

27.7 Show that the canonical ensemble formulas lead to

$$U = \frac{3}{2}nRT$$

for a monatomic dilute gas without electronic excitation.

27.8 Show that in the canonical ensemble the energy of a dilute gas would be the same if the molecules were distinguishable from each other.

27.9 **a.** Find the ensemble average energy of 1.000 mol of argon gas at 298.15 K and 1.000 bar.

b. Find the value of the canonical partition function for this system.

c. Find the probability of a single microstate of the system with energy equal to the ensemble average energy. Comment on the magnitude of your answer.

27.10 **a.** The experimental value of the standard-state (1.000 bar) third-law molar entropy of O_2 gas at 298.15 K is 205.146 J K^{-1} mol^{-1}. Using this value and the statistical mechanical value for the energy, calculate the experimental value of the Helmholtz energy of 1.000 mol of oxygen gas at 298.15 K and 1.000 bar. Take the energy of supercooled oxygen gas at 0 K to equal zero.

b. Find the value of the canonical partition function for this system from the result of part a.

c. Find the value of the molecular partition function from the result of part b.

27.11 The experimental value of $H^\circ_m(298.15\text{ K}) - H^\circ_m(0\text{ K})$ for neon is 6.197 kJ mol^{-1} and the experimental value of $S^\circ_m(298.15\text{ K})$ is 146.327 J K^{-1} mol^{-1}.

a. Find the value of G°_m and A°_m for neon at 298.15 K.

b. Find the value of the canonical partition function of neon at 298.15 K and 1.000 bar from the value of A°_m.

27.12 Calculate the value of the molecular partition function of oxygen gas at 298.15 K if 1.000 mol of the gas is confined at a pressure of 1.000 bar. Compare your result with the result of Problem 27.10.

27.13 **a.** Show that $\langle (E - \langle E\rangle)^2\rangle = \langle E^2\rangle - \langle E\rangle^2$

b. Show that $C_V = (1/k_BT)\langle (E - \langle E\rangle)^2\rangle$ so that C_V is always positive.

c. Show that as $T \to 0$, $\langle E^2\rangle = \langle E\rangle^2$ so that $C_V \to 0$ as $T \to 0$.

27.4 Classical Statistical Mechanics

We now give a brief introduction to equilibrium statistical mechanics based on classical mechanics. Classical mechanics is a good approximation for the translational motion of atoms and molecules near room temperature, and appears to be a usable approximation for the rotational motion of most molecules near room temperature. It works very poorly for vibrations, and fails completely for electronic motion. However, we have seen that in many systems the vibrational and electronic energies are numerically unimportant, and classical statistical mechanics can be used with good results in these systems.

Our rather modest goal is to obtain some general formulas and to show how classical and quantum statistical mechanics are related to each other. We will make some elementary comments on the application to nonideal gases and liquids. More detailed discussions are found in the statistical mechanics textbooks listed at the end of this book. Many research articles in classical statistical mechanics appear in journals such as *The Journal of Chemical Physics*, *The Journal of Physical Chemistry*, *The Physical Review*, and *Physica*.

Phase Space

We first consider a system containing a single monatomic substance such as neon or argon. Ignoring electronic motion, the classical state of an atom can be specified by its location and velocity, given by three coordinates and three velocity components. We can also use momentum components instead of velocity components. In Cartesian coordinates the x component of the momentum is denoted by p_x and is equal to mv_x. The y and z components are similar.

The coordinates correspond to a point in ordinary 3-dimensional space, and the momentum components correspond to the location of a point in a three-dimensional momentum space (a mathematical space with p_x plotted on one axis, p_y on another axis, and p_z plotted on a third axis). These two 3-dimensional spaces combine to constitute a 6-dimensional mathematical space and the state of the particle is specified by a single point in this space. A mathematical space with axes that represent time-dependent variables is called a *phase space*. In addition to the 6-dimensional phase space of a single atom we define a $6N$-dimensional phase space for N atoms, corresponding to $3N$ coordinates and $3N$ momentum components.

The Classical Canonical Ensemble

We assume that our real system is closed and maintained at constant temperature, and represent the system by a canonical ensemble of replicas of the system, all in thermal contact with their neighboring systems. We plot all of the phase points for the many systems of the ensemble in a single $6N$-dimensional phase space so that there is a swarm of very many phase points in this phase space, one point for each system in the ensemble. This swarm of points moves about in phase space in a way that is analogous to the flow of a compressible fluid in ordinary space and is governed by an equation called the Liouville equation,[1] which is valid both for an equilibrium system and a nonequilibrium system.

We consider only the equilibrium case so that the distribution of these points' phase space is time-independent. In quantum statistical mechanics, we had a discrete list of possible states. In classical statistical mechanics, we have coordinates and momentum components that can range continuously. We denote the probability distribution (probability density) for the ensemble by f and define the probability that the phase point of a randomly selected system of the ensemble will lie in the $6N$-dimensional volume element $d^3\mathbf{r}_1 d^3\mathbf{p}_1 d^3\mathbf{r}_2 d^3\mathbf{p}_2 \cdots d^3\mathbf{r}_N d^3\mathbf{p}_N$ to be

$$\begin{aligned}\text{Probability} &= f(\mathbf{r}_1, \mathbf{p}_1, \mathbf{r}_2, \mathbf{p}_2, \ldots \mathbf{r}_N, \mathbf{p}_N) d^3\mathbf{r}_1 d^3\mathbf{p}_1 d^3\mathbf{r}_2 d^3\mathbf{p}_2 \cdots d^3\mathbf{r}_N d^3\mathbf{p}_N \\ &= f(q, p)\,dq\,dp \qquad (27.4\text{-}1)\end{aligned}$$

where $d^3\mathbf{r}_1$ stands for $dx_1 dy_1 dz_1$, $d^3\mathbf{p}_1$ stands for $dp_{x1} dp_{y1} dp_{z1}$, and so forth, where q stands for all of the coordinates, p stands for all of the momentum components, and where $dqdp$ stands for the entire volume element $d^3\mathbf{r}_1 d^3\mathbf{p}_1 d^3\mathbf{r}_2 d^3\mathbf{p}_2 \cdots d^3\mathbf{r}_N d^3\mathbf{p}_N$.

Classical mechanical formulas must agree with those obtained by taking the limit of quantum mechanical formulas as masses and energies become large (the *correspondence limit*). This limit does not affect the formula representing the equilibrium canonical probability density, so it must therefore be the same function of the energy as that of quantum statistical mechanics. For a one-component monatomic gas or liquid of N molecules without electronic excitation but with intermolecular forces, the classical energy (*classical Hamiltonian function* $\mathscr{H}$) is expressed in terms of momentum components and coordinates:

$$\mathscr{H} = \mathscr{H}(p, q) = \mathscr{K} + \mathscr{V} = \frac{1}{2m}\sum_{i=1}^{N}(p_{xi}^2 + p_{yi}^2 + p_{zi}^2) + \mathscr{V}(q) \qquad (27.4\text{-}2)$$

where $\mathscr{K}$ is the kinetic energy and $\mathscr{V}$ is the potential energy of the system.

By analogy with Eq. (27.1-34), the normalized canonical probability density is

$$f = f(p, q) = f(\mathscr{H}) = \frac{1}{\mathcal{Z}_{\text{cl}}} e^{-\mathscr{H}(p,q)/k_{\text{B}}T} \qquad (27.4\text{-}3)$$

where $\mathcal{Z}_{\text{cl}}$ is called the *classical canonical partition function* or the classical *phase integral*:

$$\begin{aligned}\mathcal{Z}_{\text{cl}} &= \int\int \cdots \int e^{-\mathscr{H}(p,q)/k_{\text{B}}T} d^3\mathbf{r}_1 d^3\mathbf{r}_2 d^3\mathbf{r}_3 \ldots d^3\mathbf{r}_N d^3\mathbf{p}_1 d^3\mathbf{p}_2 \ldots d^3\mathbf{p}_N \\ &= \int e^{-\mathscr{H}(p,q)/k_{\text{B}}T} dq\,dp \qquad (27.4\text{-}4)\end{aligned}$$

If the system is in a container, the coordinate integrations in this formula range over all values of the coordinates inside the container, and the momentum integrations range from negative infinity to positive infinity. Since our theory is nonrelativistic, there is no limitation on the speeds of the particles.

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[1] D. A. McQuarrie, *Statistical Mechanics*, Harper & Row, New York, 1976, p. 119ff.

The integral over the momentum components factors into a product of integrals, one for each momentum component, such as

$$\int_{-\infty}^{\infty} \exp\left(\frac{-p_{x1}^2}{2mk_\mathrm{B}T}\right) dp_{x1} = (2\pi m k_\mathrm{B} T)^{1/2} \tag{27.4-5}$$

where we have looked up the integral in Appendix C. Every momentum component gives the same result after integration, so that

$$\mathcal{Z}_\mathrm{cl} = (2\pi m k_\mathrm{B} T)^{3N/2} \int e^{-\mathcal{V}(q)/k_\mathrm{B}T} dq = (2\pi m k_\mathrm{B} T)^{3N/2} \zeta \tag{27.4-6}$$

The integral ζ is called the *configuration integral*

$$\zeta = \int e^{-\mathcal{V}(q)/k_\mathrm{B}T} dq \tag{27.4-7}$$

This is a $3N$-fold integral over all of the coordinates.

Exercise 27.3

Carry out the derivation of the classical canonical probability density by considering a system made up of two subsystems.

Dilute Gases in the Classical Canonical Ensemble

The equations we have written apply to any system of atoms without electronic excitation, whether the system is a solid, liquid, or gas. If the system consists of a single particle in a rectangular box with its lower left rear corner at the origin and with dimensions a, b, and c in the x, y, and z directions, the configuration integral would be

$$\zeta = \int_0^c \int_0^b \int_0^a e^{-\mathcal{V}(x,y,z)/k_\mathrm{B}T} dx dy dz \quad \begin{pmatrix}\text{system of a single particle} \\ \text{in a rectangular box}\end{pmatrix} \tag{27.4-8}$$

If there are no forces on the particle inside the box, its potential energy is equal to a constant, which we can set equal to zero:

$$\zeta = \int_0^c \int_0^b \int_0^a e^0 dx dy dz = abc = V \quad \begin{pmatrix}\text{single particle} \\ \text{in a box with} \\ \text{zero potential energy}\end{pmatrix} \tag{27.4-9}$$

If the system is a dilute gas of N atoms we can ignore the intermolecular interactions and each particle moves as though alone in the box. If we set the constant potential energy equal to zero the configuration integral is a product of N integrals like that of Eq. (27.4-9):

$$\zeta = \int e^0 d^3\mathbf{r}_1 d^3\mathbf{r}_2 \ldots d^3\mathbf{r}_N = V^N \quad \begin{pmatrix}\text{dilute monatomic gas} \\ \text{with zero potential energy}\end{pmatrix} \tag{27.4-10}$$

The classical canonical partition function is

$$\mathcal{Z}_\mathrm{cl} = (2\pi m k_\mathrm{B} T)^{3N/2} V^N = z_\mathrm{cl}^N \quad \begin{pmatrix}\text{dilute monatomic gas} \\ \text{with zero potential energy}\end{pmatrix} \tag{27.4-11}$$

where z_{cl} is the *molecular phase integral* or the *classical molecular partition function*:

$$z_{\mathrm{cl}} = (2\pi m k_{\mathrm{B}} T)^{3/2} V \quad \left(\begin{array}{c}\text{dilute monatomic gas}\\ \text{with zero potential energy}\end{array}\right) \tag{27.4-12}$$

This is the entire classical molecular partition function for a monatomic gas without electronic excitation.

The classical molecular partition function for dilute diatomic and polyatomic gases without electronic excitation contains three factors. The translational factor is the same as given by the formula in Eq. (27.4-12), since the translational motion of a molecule is the same as that of an atom:

$$z_{\mathrm{tr,cl}} = (2\pi m k_{\mathrm{B}} T)^{3/2} V \quad \left(\begin{array}{c}\text{any dilute gas without}\\ \text{electronic excitation}\end{array}\right) \tag{27.4-13}$$

The derivation of the rotational factor in the classical molecular partition function of a diatomic molecule is a little more complicated, and is carried out in the following example:

EXAMPLE 27.2

To obtain the rotational factor in the classical molecular partition function of a diatomic or linear polyatomic gas, we must find the conjugate coordinates and momenta as discussed in Appendix E. We consider a rigid rotor. In spherical polar coordinates with $r = r_{\mathrm{e}}$ (fixed) and with $\mathcal{V} = 0$ (fixed) the Lagrangian is

$$\mathcal{L} = \frac{1}{2} m r_{\mathrm{e}}^2 \dot{\theta}^2 + \frac{1}{2} m r_{\mathrm{e}}^2 \sin^2(\theta) \dot{\phi}^2$$

The conjugate momenta to θ and ϕ are obtained through Eq. (E-20) of Appendix E:

$$p_\theta = \frac{\partial \mathcal{L}}{\partial \dot{\theta}} = m r_{\mathrm{e}}^2 \dot{\theta}^2$$

$$p_\phi = \frac{\partial \mathcal{L}}{\partial \dot{\phi}} = m r_{\mathrm{e}}^2 \sin^2(\theta) \dot{\phi}^2$$

The classical Hamiltonian is

$$\mathcal{H} = \frac{p_\theta^2}{2 m r_{\mathrm{e}}^2} + \frac{p_\phi^2}{2 m r_{\mathrm{e}}^2 \sin^2(\theta)}$$

The classical rotational partition function is obtained by integrating over all values of the conjugate momenta, over θ from 0 to π, and over ϕ from 0 to 2π. Note that since we are integrating in phase space, no Jacobian is necessary.

$$\begin{aligned} z_{\mathrm{rot,cl}} &= \int_0^\pi \int_0^{2\pi} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp\left(\frac{p_\theta^2}{2 m r_{\mathrm{e}}^2 k_{\mathrm{B}} T} + \frac{p_\phi^2}{2 m r_{\mathrm{e}}^2 \sin^2(\theta) k_{\mathrm{B}} T} \right) dp_\phi dp_\theta d\phi d\theta \\ &= \int_0^\pi \int_0^{2\pi} \sqrt{2 m r_{\mathrm{e}}^2 k_{\mathrm{B}} T} \sqrt{\pi} \sqrt{2 m r_{\mathrm{e}}^2 \sin^2(\theta) k_{\mathrm{B}} T} \sqrt{\pi} d\phi d\theta \\ &= \sqrt{2 m r_{\mathrm{e}}^2 k_{\mathrm{B}} T} \sqrt{\pi} \sqrt{2 m r_{\mathrm{e}}^2 k_{\mathrm{B}} T} \sqrt{\pi} \int_0^\pi \int_0^{2\pi} \sin^2(\theta) d\phi d\theta \\ &= 2\pi m r_{\mathrm{e}}^2 k_{\mathrm{B}} T 4\pi = 8\pi^2 m r_{\mathrm{e}}^2 k_{\mathrm{B}} T = 8\pi^2 I_{\mathrm{e}} k_{\mathrm{B}} T \end{aligned}$$

The result of this example is

$$z_{\text{rot,cl}} = 8\pi^2 I_e k_B T \quad \big(\text{diatomic or linear polyatomic substance}\big) \tag{27.4-14}$$

where I_e is the moment of inertia of the molecule. The derivation of the rotational factor in the classical partition function for a nonlinear polyatomic substance is even more complicated, and we simply present the result:

$$z_{\text{rot,cl}} = \sqrt{\pi}(8\pi^2 k_B T)^{3/2}(I_A I_B I_C)^{1/2} \quad \big(\text{nonlinear polyatomic substance}\big) \tag{27.4-15}$$

where I_A, I_B, and I_C are the principal moments of inertia as defined in Chapter 22.

We represent the vibration of a diatomic molecule by a harmonic oscillator with mass μ (the reduced mass of the molecule) and frequency ν. The classical vibrational partition function for a harmonic oscillator is

$$\begin{aligned} z_{\text{vib,cl}} &= \int_{-\infty}^{\infty} \exp\left[-\frac{p^2/2\mu}{k_B T}\right] dp \int_{-\infty}^{\infty} \exp\left[-\frac{kx^2/2}{k_B T}\right] dx \\ &= (2\pi\mu k_B T)^{1/2}(2\pi k_B T/k)^{1/2} \\ &= (2\pi k_B T)\sqrt{\frac{\mu}{k}} = \frac{k_B T}{\nu} \quad \text{(dilute diatomic gas)} \end{aligned} \tag{27.4-16}$$

where μ is the reduced mass, k is the force constant, and ν is the frequency of the oscillator, from Eq. (14.2-24). We have used infinite limits for the integrations since the harmonic oscillator is not limited to a finite range of oscillation. For a polyatomic substance, there is one factor like that of Eq. (27.4-16) for each normal mode:

$$z_{\text{vib,cl}} = \prod_{i=1}^{3n-5(6)} \frac{k_B T}{\nu_i} \quad \text{(dilute polyatomic gas)} \tag{27.4-17}$$

where the limit on the product indicates $3n - 5$ normal modes for a linear molecule and $3n - 6$ normal modes for a nonlinear molecule. We will not attempt to discuss electronic motion classically, but assume that electronic excitation can be ignored.

For diatomic and polyatomic dilute gases without electronic excitation we have the same relation as for monatomic gases:

$$\mathcal{Z}_{\text{cl}} = z_{\text{cl}}^N \tag{27.4-18}$$

where

$$z_{\text{cl}} = z_{\text{tr,cl}} z_{\text{rot,cl}} z_{\text{vib,cl}} \quad \big(\text{any dilute gas without eletronic excitation}\big) \tag{27.4-19}$$

Comparison of the Classical and Quantum Partition Functions

The translational factor of the classical molecular partition function is proportional to the quantum mechanical translational factor:

$$z_{\text{tr,qm}} = \left(\frac{2\pi m k_B T}{h^2}\right)^{3/2} V = \frac{z_{\text{tr,cl}}}{h^3} \tag{27.4-20}$$

where h is Planck's constant. For a dilute monatomic gas without electronic excitation, the quantum canonical partition function is related to the classical function as follows:

$$\mathcal{Z}_{\text{qm}} = \frac{z_{\text{qm}}^N}{N!} = \frac{\left(\dfrac{2\pi m k_{\text{B}} T}{h^2}\right)^{3N/2} V^N}{N!} = \frac{\mathcal{Z}_{\text{cl}}}{h^{3N} N!} = \frac{1}{N!}\left(\frac{z_{\text{cl}}}{h^3}\right)^N \tag{27.4-21}$$

The divisor $N!$ occurs because of the indistinguishability of the particles, which is not recognized in classical mechanics. The divisors of Planck's constant indicate a relationship between a volume in phase space and a quantum state. We illustrate this relationship in the two-dimensional phase space of a particle in a one-dimensional box. Figure 27.3 shows several trajectories in this phase space. The first trajectory is for the motion of a classical particle that happens to have an energy equal to ε_1, the energy eigenvalue of a quantum mechanical particle of the same mass in the same box. The trajectory has two parts, one for motion from left to right, and one for the motion from right to left. The second trajectory is for the motion of a classical particle with energy equal to ε_2, and so on.

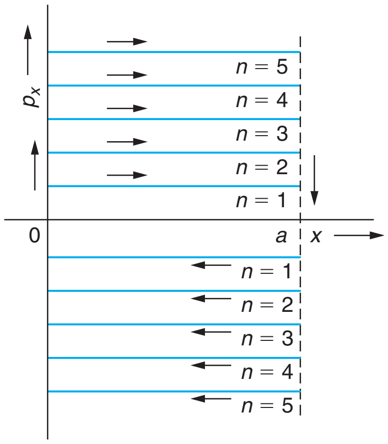

Figure 27.3 Several Trajectories in a Two-Dimensional Phase Space for a Particle in a Hard One-Dimensional Box.

We now show that the area between any two adjacent trajectories is equal to Planck's constant. For n', a given value of the quantum number, the energy is

$$\varepsilon_{\text{cl}} = \frac{p^2}{2m} = \varepsilon_{\text{qm}} = \varepsilon_{n'} = \frac{h^2 n'^2}{8ma^2} \tag{27.4-22}$$

Solving for $|p|$, we obtain

$$|p| = \frac{hn'}{2a} \tag{27.4-23}$$

The area between the trajectory for n' and that for $n' + 1$ is

$$\text{Area} = \left(\frac{h(n'+1)}{2a} - \frac{hn'}{2a}\right)(2a) = h \tag{27.4-24}$$

We multiply by $2a$ instead of by a because the trajectory has two parts, one for positive p and one for negative p. The relation of Eq. (27.4-24) is an example of a general relation. For a 2-dimensional phase space, an area equal to h corresponds to one quantum state. For a 6-dimensional phase space, a volume equal to h^3 corresponds to one quantum state and for a $6N$-dimensional phase space a volume equal to h^{3N} corresponds to one quantum state.

The quantum rotational partition function for a diatomic or linear polyatomic molecule is equal to the classical version divided by h^2 and also divided by the symmetry number σ, equal to 1 for a heteronuclear diatomic molecule and equal to 2 for a homonuclear diatomic molecule.

$$z_{\text{rot,qm}} = \frac{8\pi^2 I_{\text{e}} k_{\text{B}} T}{\sigma h} = \frac{z_{\text{rot,cl}}}{\sigma h^2} \quad \left(\begin{matrix}\text{dilute diatomic or}\\ \text{linear polyatomic gas}\end{matrix}\right) \tag{27.4-25}$$

The division by the symmetry number corrects for the indistinguishability of the nuclei of a homonuclear molecule, which is not recognized in classical mechanics. The divisor of h^2 comes from the relationship of a quantum state with a volume in the 4-dimensional phase space of θ, ϕ, and their conjugate momenta, similar to the relationship between a quantum state and an area of h in a 2-dimensional phase space.

The quantum rotational partition function of a nonlinear polyatomic gas is related to the classical version as follows:

$$z_{\text{rot,qm}} = \frac{\sqrt{\pi}}{\sigma}\left(\frac{8\pi^2 k_B T}{h^2}\right)^{3/2}(I_A I_B I_C)^{1/2} = \frac{z_{\text{rot,cl}}}{\sigma h^3} \quad \left(\begin{array}{c}\text{dilute nonlinear}\\ \text{polyatomic gas}\end{array}\right) \tag{27.4-26}$$

The division by h^3 corresponds to the relation of a quantum state to the phase space of the three angular coordinates of a nonlinear object. The division by the symmetry number σ again relates to the indistinguishability of the nuclei.

The fact that the classical translational and rotational partition functions are related to the quantum mechanical partition functions in this simple way arises from the fact that the spacing between energy levels is relatively small compared with the energy eigenvalues. Because of this we were able to replace sums by integrals in deriving the quantum partition functions in Chapter 25, thus effectively removing the effects of energy quantization.

The relationship between the classical and quantum partition functions is not so simple for the vibrational factor. If we divide the classical vibrational factor for a diatomic molecule by Planck's constant, we obtain

$$\frac{z_{\text{vib,cl}}}{h} = \frac{k_B T}{h\nu} \quad \text{(diatomic molecule)} \tag{27.4-27}$$

which does not match the quantum vibrational partition function of Eq. (25.4-18). However, if we consider the quantum vibrational partition function for large values of T, we obtain

$$\begin{aligned} z_{\text{vib,qm}} &= \frac{e^{-h\nu/2k_B T}}{1 - e^{-h\nu/k_B T}} \approx \frac{1}{1 - (1 - h\nu/k_B T)} \\ &\approx \frac{k_B T}{h\nu} \quad \text{(for large values of } T\text{)} \end{aligned} \tag{27.4-28}$$

Division of the classical vibrational partition function by Planck's constant gives this result, and it would appear that we have a result that is compatible with the correspondence principle. However, the limit of large temperature is physically unreasonable, since it corresponds to large values of the vibrational quantum number that would cause almost any molecule to dissociate.

EXAMPLE 27.3

a. Evaluate the quantum mechanical vibrational partition function for Cl_2 at 298.15 K and at 1000.0 K.

b. Compare your result in part a with $k_B T/h\nu$ for the two temperatures.

Solution

a. From Example 25.8, z_{vib} at 298.15 K is equal to 1.0720. At 1000.0 K, let $x = h\nu/k_B T$:

$$x = \frac{(6.6261 \times 10^{-34}\ \text{J s})(1.6780 \times 10^{13}\ \text{s}^{-1})}{(1.3807 \times 10^{-23}\ \text{J K}^{-1})(1000.0\ \text{K})} = 0.8053$$

$$z_{\text{vib}} = \frac{1}{1 - e^{-x}} = \frac{1}{1 - e^{-0.8053}} = 1.8082$$

b. At 298.15 K

$$\frac{k_BT}{h\nu} = \frac{(1.3807 \times 10^{-23}\ \mathrm{J\ K^{-1}})(298.15\ \mathrm{K})}{(6.6261 \times 10^{-34}\ \mathrm{J\ s})(1.6780 \times 10^{13}\ \mathrm{s^{-1}})} = 0.3702$$

At 1000.0 K

$$\frac{k_BT}{h\nu} = \frac{(1.3807 \times 10^{-23}\ \mathrm{J\ K^{-1}})(1000.0\ \mathrm{K})}{(6.6261 \times 10^{-34}\ \mathrm{J\ s})(1.6780 \times 10^{13}\ \mathrm{s^{-1}})} = 1.2418$$

At 298.15 K, $\dfrac{z_{\mathrm{vib}}}{k_BT/h\nu} = 2.896$. At 1000.0 K, $\dfrac{z_{\mathrm{vib}}}{k_BT/h\nu} = 1.4561$.

Exercise 27.4

Repeat the calculation of the previous example for Br_2.

The classical vibrational partition function divided by Planck's constant will almost never be an adequate approximation to the quantum vibrational partition function. The electronic partition function also cannot be related to a classical version. We define a composite partition functions as follows for a monatomic substance:

$$z = \frac{z_{\mathrm{tr,cl}}}{h^3} z_{\mathrm{qm,el}} \quad \text{(dilute monatomic gas)} \tag{27.4-29}$$

For a diatomic or linear polyatomic dilute gas we define the composite partition function:

$$z = \frac{z_{\mathrm{tr,cl}}}{h^3} \frac{z_{\mathrm{rot,cl}}}{\sigma h^2} z_{\mathrm{vib,qm}} z_{\mathrm{el,qm}} \quad \left(\begin{array}{c}\text{dilute diatomic or}\\ \text{linear polyatomic gas}\end{array}\right) \tag{27.4-30}$$

For a nonlinear polyatomic dilute gas we define the composite partition function

$$z = \frac{z_{\mathrm{tr,cl}}}{h^3} \frac{z_{\mathrm{rot,cl}}}{\sigma h^3} z_{\mathrm{vib,qm}} z_{\mathrm{el,qm}} \quad \left(\text{dilute nonlinear polyatomic gas}\right) \tag{27.4-31}$$

The composite partition functions are identical with the quantum versions of Chapter 25. This illustrates the fact that classical statistical mechanics does not provide any advantage in treating a dilute gas.

PROBLEMS

Section 27.4: Classical Statistical Mechanics

27.14

a. Sketch a diagram in a two-dimensional phase space for a harmonic oscillator that is analogous to Figure 27.3 for a particle in a hard box. Show the trajectories for energies equal to the $v = 0$, $v = 1$, and $v = 2$ quantum states.

b. Calculate the area between any two such trajectories.

27.15 Construct a representation of the trajectory in a 2-dimensional phase space for an object of mass 1.000 kg falling vertically in a vacuum near the surface of the earth.

27.16 **a.** A phase space can represent a coordinate and its conjugate momentum even if the coordinate is not a Cartesian coordinate. Refer to Appendix E and see what the conjugate momentum is for the angle ϕ in plane polar coordinates. The coordinate axis in the phase space for this coordinate extends only from 0 to 2π in the coordinate direction, since it represents the angle ϕ. Draw an accurate trajectory in this phase space for a particle of mass 1.000 kg orbiting in a plane at a fixed distance of 1.000 m from a fixed center, such that it makes one revolution every 1.000 second and has a constant speed.

b. Draw an accurate trajectory in the 2-dimensional phase space of the coordinate ρ, representing the distance from the fixed origin, for the same motion.

27.5 Thermodynamic Functions in the Classical Canonical Ensemble

We now obtain equations for the thermodynamic functions of a system represented by a classical canonical ensemble. We first write general equations and then specialize them for dilute gases.

The Energy

The ensemble average energy of a general system is

$$U = \langle E \rangle = \frac{1}{\mathcal{Z}_{\text{cl}}} \int \mathscr{H}(p,q) e^{-\mathscr{H}(p,q)/k_{\text{B}}T} dpdq \tag{27.5-1}$$

where p and q are abbreviations for the coordinates and momentum components of all particles in the system. We use a mathematical trick similar to the one used in Eq. (27.1-20), writing the integrand as a derivative and exchanging the order of integration and differentiating:

$$U = \frac{1}{\mathcal{Z}_{\text{cl}}} k_{\text{B}} T^2 \int \left(\frac{\partial}{\partial T} [e^{-\mathscr{H}(p,q)/k_{\text{B}}T}] \right) dpdq = k_{\text{B}} T^2 \left(\frac{\partial \ln(\mathcal{Z}_{\text{cl}})}{\partial T} \right)_V \tag{27.5-2}$$

The volume V is held constant in the differentiation, since the potential energy depends on the volume of the system. Equation (27.5-1) is the same as Eq. (27.2-1) except for replacement of the quantum-mechanical canonical partition function by the classical phase integral. There is a problem with this equation. The classical canonical partition is not dimensionless, which is required for the argument of a logarithm. We discuss this problem later.

The Entropy

For a classical system, the definition of the statistical entropy in Eq. (26.1-1) cannot be used because we cannot count states in the same way as with a quantum system. The classical definition of the statistical entropy is analogous to that in Problem 27.6.

$$S_{\text{st}} = -k_{\text{B}} \int f(p,q) \ln[f(p,q)] dpdq \tag{27.5-3}$$

where the integration is over the values of all coordinates and momenta. Use of Eq. (27.4-3) gives

$$S = -k_{\text{B}} \int f(p,q) \left[-\frac{E}{k_{\text{B}}T} - \ln(\mathcal{Z}_{\text{cl}}) \right] dpdq = \frac{U}{T} + k_{\text{B}} \ln(\mathcal{Z}_{\text{cl}}) \tag{27.5-4}$$

where we assume that the probability distribution is normalized:

$$\int f(p,q)dpdq = 1 \tag{27.5-5}$$

The Other Thermodynamic Functions

Once we have expressions for U and S, we can obtain formulas for the other thermodynamic functions. The Helmholtz energy is given by

$$A = U - TS = -k_B T \ln(\mathcal{Z}_{cl}) \tag{27.5-6}$$

and the pressure is given by the thermodynamic relation in Eq. (26.1-8)

$$P = -\left(\frac{\partial A}{\partial V}\right)_{T,n} = k_B T \left(\frac{\partial \ln(\mathcal{Z}_{cl})}{\partial V}\right)_{T,N} \tag{27.5-7}$$

Expressions for the enthalpy, the Gibbs energy, the heat capacity, and the chemical potential can be obtained from these formulas.

Exercise 27.5

Write formulas for H, G, C_V, and μ for the classical canonical ensemble. Compare your formulas with those in Eq. (27.2-8).

The Thermodynamic Functions of a Dilute Gas

We have obtained formulas for the thermodynamic functions of a general system in terms of the classical canonical partition function.

The Energy of a Dilute Gas

If the system is a dilute gas we can express the energy in terms of the classical molecular partition function, using Eq. (27.4-18):

$$U = \langle E \rangle = N\langle \varepsilon \rangle = Nk_B T^2 \left(\frac{\partial \ln(z_{cl})}{\partial T}\right)_V \tag{27.5-8}$$

Using the formula for z_{cl} in Eq. (27.4-12), the energy of a monatomic dilute gas is

$$U = \frac{3Nk_B T}{2} \quad \left(\begin{array}{c}\text{monatomic dilute gas}\\ \text{without electronic excitation}\end{array}\right) \tag{27.5-9}$$

The indistinguishability of the molecules and the relation between quantum states and phase space volume do not affect the energy expression.

The classical *theorem of equipartition of energy* states that if a molecular variable occurs in the classical energy in a quadratic form (to the second power) the contribution to the ensemble average system energy corresponding to that variable is equal to $Nk_B T/2$. Equation (27.5-9) conforms to this theorem. We can verify this theorem as follows: Let u represent some variable such as a coordinate or a momentum component, and assume that the contribution of this variable to the energy of one molecule is

$$\varepsilon = au^2 \tag{27.5-10}$$

where a is a constant and where u can take on any real values. The average energy contribution is

$$U = \langle E\rangle = N\langle\varepsilon\rangle = N\frac{\displaystyle\int_{-\infty}^{\infty} au^2 e^{-au^2/k_\mathrm{B}T}\,du}{\displaystyle\int_{-\infty}^{\infty} e^{-au^2/k_\mathrm{B}T}\,du} \tag{27.5-11}$$

When the integrals are evaluated from a table such as that of Appendix C, we obtain

$$\boxed{U = \frac{Na\pi^{1/2}(k_\mathrm{B}T/a)^{3/2}/2}{(\pi k_\mathrm{B}T/a)^{1/2}} = \frac{Nk_\mathrm{B}T}{2}} \tag{27.5-12}$$

This result is independent of the constant a and corresponds to equipartition of energy.

Exercise 27.6

Look up the integrals and verify Eq. (27.5-12).

The energy of a dilute diatomic or polyatomic gas is a sum of contributions. If we ignore the vibrational and electronic contributions,

$$U = Nk_\mathrm{B}T^2\left(\frac{\partial \ln(z_\mathrm{cl})}{\partial T}\right)_V = Nk_\mathrm{B}T^2\left(\frac{\partial \ln(z_\mathrm{cl,tr})}{\partial T}\right)_V + Nk_\mathrm{B}T^2\left(\frac{\partial \ln(z_\mathrm{cl,rot})}{\partial T}\right)_V = U_\mathrm{tr} + U_\mathrm{rot} \tag{27.5-13}$$

The translational energy is the same as that of a monatomic gas:

$$U_\mathrm{tr} = \frac{3}{2}Nk_\mathrm{B}T \tag{27.5-14}$$

The rotational energy is independent of the moment of inertia:

$$U_\mathrm{rot} = Nk_\mathrm{B}T \quad \text{(diatomic or linear polyatomic substance)} \tag{27.5-15}$$

$$U_\mathrm{rot} = \frac{3}{2}Nk_\mathrm{B}T \quad \text{(nonlinear polyatomic substance)} \tag{27.5-16}$$

These contributions conform to the equipartition of energy and also agree with the quantum statistical mechanics results.

According to equipartition of energy the vibration of a diatomic molecule should make a contribution of $Nk_\mathrm{B}T$ to the energy, since there is one coordinate and one momentum component and both enter quadratically in the energy expression. However, this is a very poor approximation.

Exercise 27.7

a. Show that the vibrational energy given by Eq. (26.2-8) approaches the equipartition value of $Nk_BT = nRT$ for large values of T. However, remember that this equation is not valid for large values of T since the molecule would dissociate for large values of the vibrational energy.

b. Calculate the vibrational energy of 1.000 mol of Br_2 at 298.15 K and at 1000.0 K. Compare your result with RT for each temperature.

c. Repeat the calculation of part b for H_2.

The Entropy of a Dilute Gas

We apply Eq. (27.5-4) to a dilute gas:

$$S = \frac{U}{T} + k_B\ln(\mathcal{Z}_{cl}) = \frac{U}{T} + k_B\ln(z_{cl}^N) = \frac{U}{T} + Nk_B\ln(z_{cl}) \tag{27.5-17}$$

As previously stated, the classical molecular partition function has units of $\mathrm{kg\,m^2\,s^{-1}}$ raised to some power, so a divisor with units must be included to make the argument of the logarithm dimensionless. If a divisor of $1\,\mathrm{kg\,m^2\,s^{-1}}$ is used, values are obtained for the entropy and the Helmholtz energy that differ from the experimental values. However, when the classical canonical translational partition function is divided by $h^{3N}N!$ and Stirling's approximation is used for $\ln(N!)$, the same formulas are obtained as Chapter 26. For a dilute monatomic gas the corrected classical formula is

$$S = \frac{U}{T} + Nk_B\ln\left(\frac{z_{cl}}{Nh^3}\right) + Nk_B = \frac{U}{T} + Nk_B\ln\left(\frac{z_{qm}}{N}\right) + Nk_B \tag{27.5-18}$$

which is the same as Eq. (26.1-5).

Equation (27.5-18) also holds for the translational contribution to the entropy of molecular substances. For a diatomic substance the rotational contribution to the entropy with a unit divisor would be

$$S_{rot,cl} = \frac{U_{rot}}{T} + Nk_B\ln(z_{rot,cl}) \tag{27.5-19}$$

With a divisor of σh^2, where σ is the symmetry number,

$$S_{rot} = \frac{U_{rot}}{T} + Nk_B\ln\left(\frac{z_{rot,cl}}{\sigma h^2}\right) = \frac{U_{rot}}{T} + Nk_B\ln(z_{rot,qm}) \tag{27.5-20}$$

which is also identical to the formula from quantum statistical mechanics. A similar formula holds for polyatomic dilute gases, with division by σh^3 instead of by σh^2.

EXAMPLE 27.4

a. Calculate the rotational contribution to the entropy of 1.000 mol of Cl_2 gas at 298.15 K, using the formula of Eq. (27.5-19).

b. Repeat the calculation of part a using the corrected formula of Eq. (27.5-20).

c. Show that the difference between the result of part a and part b would be the same for any temperature.

Solution

a. From Eq. (27.4-14)

$$z_{\text{rot,cl}} = 8\pi^2 I_e k_B T$$

The moment of inertia of the Cl_2 molecule was calculated in Example 25.7 and is equal to 1.147×10^{-45} kg m^2.

$$\begin{aligned}
z_{\text{rot,cl}} &= 8\pi^2(1.147 \times 10^{-45}\,\text{kg m}^2)(1.3807 \times 10^{-23}\,\text{J K}^{-1})(298.15\,\text{K}) \\
&= 3.728 \times 10^{-64}\,\text{kg}^2\,\text{m}^4\,\text{s}^{-2} \\
S_{\text{rot,cl}} &= \frac{U_{\text{rot}}}{T} + Nk_B \ln(z_{\text{rot,cl}}) = n[R + R\ln(z_{\text{rot,cl}})] \\
&= (1.000\,\text{mol})[8.31455 + (8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\ln(3.728 \times 10^{-64})] \\
&= -1206\,\text{J K}^{-1}
\end{aligned}$$

where we have divided by argument of the logarithm by 1 kg^2 m^4 s^{-2} to make it dimensionless. This result is obviously not useful, showing the deficiency of classical statistical thermodynamics, which ignores the relationship between quantum states and volumes in phase space as well as the indistinguishability of the nuclei.

b. The quantum mechanical partition function of Cl_2 has already been calculated in Example 25.7 and is equal to 424.7.

$$\begin{aligned}
S_{\text{rot}} &= n[R + R\ln(z_{\text{rot}}) = (1.000\,\text{mol})(8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})[1 + \ln(424.7)] \\
&= 58.63\,\text{J K}^{-1}
\end{aligned}$$

c. The difference between these two values is

$$\begin{aligned}
\text{Difference} &= -nR\ln(\sigma h^2) \\
&= -(1.000\,\text{mol})8.3145\,\text{J K}^{-1}\,\text{mol}^{-1})\ln([2][6.6261 \times 10^{-34}\,\text{J s}]^2) \\
&= -1264\,\text{J K}^{-1}
\end{aligned}$$

which is the difference between the results of parts a and b, and is temperature-independent.

After division of the classical vibrational partition function by Planck's constant, the expression for the vibrational contribution to the entropy of a diatomic substance is

$$S_{\text{vib}} = \frac{U_{\text{vib,cl}}}{T} + Nk_B \ln\left(\frac{z_{\text{vib,cl}}}{h}\right) = Nk_B - Nk_B \ln\left(\frac{k_B T}{h\nu}\right) \tag{27.5-21}$$

where we have used the classical equipartition of energy result for $U_{\text{vib,cl}}$.

EXAMPLE 27.5

Calculate the vibrational contribution to the entropy of 1.000 mol of Cl_2 at 298.15 K, using Eq. (27.5-21). The vibrational frequency is 1.6780×10^{13} s^{-1}. Compare your result with that of Example 26.8, which is 2.194 J^{-1} K^{-1}.

Solution

$$\frac{k_\mathrm{B}T}{h\nu} = \frac{(1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}})(298.15\,\mathrm{k})}{(6.6261 \times 10^{-34}\,\mathrm{J\,s})(1.6780 \times 10^{13}\,\mathrm{s^{-1}})} = 0.37023$$

The vibrational energy is given by equipartition of energy, so that

$$\begin{aligned}S_{\mathrm{vib,cl}} &= (1.000\,\mathrm{mol})N_{\mathrm{Av}}k_\mathrm{B} + (1.000\,\mathrm{mol})N_{\mathrm{Av}}\,k_\mathrm{B}\ln(0.37020)\\ &= (1.000\,\mathrm{mol})(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(1 + \ln[0.37020])\\ &= 0.05298\,\mathrm{J\,K^{-1}}\end{aligned}$$

This result compares poorly with the quantum statistical result, 2.194 J K^{-1}.

Exercise 27.8

Repeat the calculation of Example 27.5 for I_2 at 1000.0 K.

The classical translational and rotational contributions to thermodynamic functions must be corrected by choosing the correct divisors. This yields the same results as in quantum statistical mechanics. The classical formulas for vibration are numerically inadequate, even with the correct divisors, and we do not attempt to use classical statistical mechanics for electronic motion. There is nothing to be gained by using classical statistical mechanics for a dilute gas.

PROBLEMS

Section 27.5: Thermodynamic Functions in the Classical Canonical Ensemble

27.17 Calculate the vibrational contribution to the molar heat capacity of CO at 500.0 K, using classical statistical mechanics. Compare your result with that obtained by using Eq. (26.2-10e). Find the minimum temperature at which the two results agree within 5%, and the minimum temperature at which they agree within 1%. Do you think that either one of these equations gives realistic results at these temperatures? Why or why not?

27.18 Calculate the vibrational contribution to the molar heat capacity of H_2 at 500.0 K, using classical statistical mechanics. Compare your result with that obtained with Eq. (26.2-10e). Find the minimum temperature at which the two results agree within 5% and the minimum temperature at which they agree within 1%. Do you think that either one of these equations gives realistic results at these temperatures? Why or why not?

27.19 **a.** Assuming no electronic contribution, calculate the entropy of 1.000 mol of argon gas at $T = 298.15$ K and $V = 0.02479$ m^3 using Eq. (27.5-17) with a unit divisor. This volume corresponds to the thermodynamic standard state of $P = 100{,}000$ Pa.

b. Recalculate the entropy of part b using Eq. (27.5-18).

c. Compare your results of parts b and c with the experimental standard-state value, 154.849 J K^{-1} mol^{-1}.

d. Show that the same difference between the results of parts b and c would result for a different temperature and a different volume.

27.6 The Classical Statistical Mechanics of Dense Gases and Liquids

Although the classical statistical mechanics of dilute gases provides no advantage over quantum statistical mechanics, its application to liquids and dense gases is more productive than the application of quantum statistical mechanics to these systems. Unfortunately, a full discussion of this application is beyond the scope of this book, and we present only a few basic facts and formulas.

We consider a model monatomic substance that has a *pairwise intermolecular potential energy*:

$$\mathscr{V} = \sum_{i=1}^{N-1} \sum_{i=j+1}^{N} u(r_{ij}) \tag{27.6-1}$$

where $u(r_{ij})$ is the potential energy of particles i and j (the pair potential function) and r_{ij} is the distance between the centers of molecules i and j. This is a good approximation for dense gases. In liquids there can be contributions to the potential energy that involve three particles at a time, but it is still a fair approximation for liquids. The limits on the sums are chosen so that each pair of particles appears only once in the double sum.

The general equations for the canonical partition function and its application to thermodynamics functions are valid. From Eq. (27.4-6)

$$\mathcal{Z}_{\text{cl}} = (2\pi m k_{\text{B}} T)^{3N/2} \int \exp\left[-\sum_{j=1}^{N-1} \sum_{i=j+1}^{N} \frac{u(r_{ij})}{k_{\text{B}} T} \right] dq = (2\pi m k_{\text{B}} T)^{3N/2} \zeta \tag{27.6-2}$$

where ζ is the configuration integral. Mayer showed that the configuration integral can be expressed as a series of powers and logarithms of the density of the gas or liquid. The leading term is that for a dilute gas, and the coefficients of the other terms are integrals called *cluster* integrals.[2]

Joseph E. Mayer was an American physical chemist who made various contributions to statistical mechanics. He met his future wife, Maria Goeppert (1906–1972) in Göttingen, Germany, when he was a postdoctoral researcher. They moved to the United States in 1930 and worked at the Johns Hopkins University, Columbia University, the University of Chicago, and the University of California at San Diego. Mrs. Goeppert Mayer worked without pay until 1959, when they moved to UCSD. She received the 1963 Nobel Prize in physics for her work on the shell model of the nucleus, which she had carried out while working without pay.

The potential energy of our model fluid is given by

$$\langle \mathcal{V} \rangle = \frac{1}{\zeta} \int \left[\sum_{b=1}^{N-1} \sum_{a=b+1}^{N} u(r_{\text{ab}}) \right] \exp\left[-\sum_{j=1}^{N-1} \sum_{i=j+1}^{N} \frac{u(r_{ij})}{k_{\text{B}} T} \right] d^3\mathbf{r}_1 \ldots d^3\mathbf{r}_N \tag{27.6-3}$$

After the integration, all of the terms in the a and b sums are identical, so that

$$\begin{aligned} \langle \mathcal{V} \rangle &= \frac{N(N-1)}{\zeta} \int u(r_{12}) \exp\left[-\sum_{j=1}^{N-1} \sum_{i=j+1}^{N} \frac{u(r_{ij})}{k_{\text{B}} T} \right] d^3\mathbf{r}_1 \ldots d^3\mathbf{r}_N \\ &= N(N-1) \int u(r_{12})\ f^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d^3\mathbf{r}_1 d^3\mathbf{r}_2 \end{aligned} \tag{27.6-4}$$

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[2] J. E. Mayer and M. G. Mayer, *Statistical Mechanics*, Wiley, New York, 1940. See T. Hill, *Statistical Thermodynamics*, Addison-Wesley, Reading, MA., 1960, p. 261ff for a readable discussion.

where $f^{(2)}(r_1, r_2)$ is the two-body *reduced coordinate distribution function*

$$f^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\zeta}\int \exp\left[-\sum_{j=1}^{N-1}\sum_{i=j+1}^{N}\frac{u(r_{ij})}{k_\mathrm{B}T}\right]d^3\mathbf{r}_3 \dots d^3\mathbf{r}_N \tag{27.6-5}$$

The one-body reduced coordinate distribution function is defined similarly:

$$f^{(1)}(\mathbf{r}_1) = \frac{1}{\zeta}\int \exp\left[-\sum_{j=1}^{N-1}\sum_{i=j+1}^{N}\frac{u(r_{ij})}{k_\mathrm{B}T}\right]d^3\mathbf{r}_2 d^3\mathbf{r}_3 \dots d^3\mathbf{r}_N \tag{27.6-6}$$

Mayer showed that the two-body reduced coordinate distribution function can be expressed as a series of powers and logarithms of the density, with a second type of cluster integrals as coefficients.[3]

The radial distribution function, or pair correlation function, $g(r)$, is defined by

$$g(r_{12}) = \frac{f^{(2)}(1,2)}{f^{(1)}(1)\,f^{(1)}(2)} \tag{27.6-7}$$

The radial distribution function, $g(r)$, is the probability of finding a second molecule at a location at a distance r from a given molecule divided by the probability of finding a molecule far from the given molecule. For a system of particles without intermolecular forces, it is equal to unity for all values of r. For a dense gas or a liquid with intermolecular forces, it is equal to zero for $r = 0$ and goes through one or more maxima and minima and approaches unity for large values of r.[4]

The pressure can be expressed in terms of the radial distribution function[5]

$$P = \frac{Nk_\mathrm{B}T}{V}\left[1 - \frac{N}{6Vk_\mathrm{B}T}\int r\left(\frac{du}{dr}\right)g(r)d^3\mathbf{r}\right] \tag{27.6-8}$$

Exercise 27.9

Show that Eq. (27.6-8) gives the correct pressure of an ideal gas, for which $u(r) = 0$.

The pressure of a nonideal gas can also be described by the *virial equation of state*, which is a power series in the reciprocal of the molar volume, V_m:

$$\frac{PV_\mathrm{m}}{RT} = B_1 + \frac{B_2}{V_\mathrm{m}} + \frac{B_3}{V_\mathrm{m}^2} + \frac{B_4}{V_\mathrm{m}^3} + \cdots \tag{27.6-9}$$

where the first virial coefficient, B_1, is equal to unity. The virial coefficients can be expressed as sums of cluster integrals of a third type.[6] The second virial coefficient, B_2, is given by

$$B_2 = -\frac{N_\mathrm{AV}}{2}\int_0^\infty [e^{-u(r)/k_\mathrm{B}T} - 1]4\pi r^2 dr \tag{27.6-10}$$

where r is the distance between the particles and N_Av is Avogadro's constant.

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[3] J. E. Mayer and M. G. Mayer, *op. cit.* (note 2).

[4] The radial distribution function unfortunately has the same name as the probability density for finding an electron at a specified distance from the nucleus in an atom, defined in Chapter 17.

[5] P. A. Egelstaff, *An Introduction to the Liquid State*, Academic Press, New York, 1967, p. 20.

[6] J. E. Mayer and M. G. Mayer, *op. cit.* (note 2).

EXAMPLE 27.6

Obtain a formula for the second virial coefficient of a hard-sphere gas with molecular diameter d.

Solution

The pair potential function is

$$u(r) = \begin{cases} \infty & \text{if } r < d \\ 0 & \text{if } r > d \end{cases}$$

so that

$$[e^{-u(r)/k_B T} - 1] = \begin{cases} -1 & \text{if } r < d \\ 0 & \text{if } r > d \end{cases}$$

The virial coefficient of the hard-sphere gas is equal to a constant

$$B_2 = -\frac{N_{AV}}{2} \int_0^d [-1] 4\pi r^2 dr = \frac{2\pi N_{Av} d^3}{3} \qquad (27.6\text{-}11)$$

Exercise 27.10

The effective hard-sphere diameter of argon at 273 K is equal to 3.65×10^{-10} m. Using this value for d in the formula of Eq. (27.6-11), calculate B_2 for argon at this temperature. Compare your result with the experimental value at 273 K, -2.15×10^{-5} m^3 mol^{-1}. How do you explain the difference?

Exercise 27.11

a. Obtain a formula for the second virial coefficient of a "square-well" gas, for which

$$u(r) = \begin{cases} \infty & \text{if } r < d \\ -u_0 & \text{if } d < r < c \\ 0 & \text{if } r > c \end{cases}$$

where u_0 is a positive constant. Explain why this virial coefficient depends on temperature while that of a hard-sphere gas does not.

b. Take the following parameters for a square-well representation of the argon intermolecular potential: $d = 3.162 \times 10^{-10}$ m, $c = 5.850 \times 10^{-10}$ m, and $u_0 = 9.58 \times 10^{-22}$ J. Find the value of the second virial coefficient of argon at 0°C. Compare it with the experimental value, -2.15×10^{-5} m^3 mol^{-1}.

The second virial coefficient of a hard-sphere gas is positive, illustrating the fact that repulsive forces correspond to a raising of the pressure of the gas over that of an ideal gas at the same molar volume and temperature. The second virial coefficient of the square-well gas has a constant positive part that is identical with that of the hard-sphere gas, and a temperature-dependent negative part due to the attractive part of the potential, illustrating the fact that attractive forces contribute to lowering the pressure of the gas at fixed volume and temperature.

A great deal of research has been carried out on the classical statistical mechanics of liquids and dense gases, both for equilibrium and for nonequilibrium states. The interested reader is invited to consult some of the statistical mechanics textbooks listed at the end of this book, as well as such journals as the *Journal of Chemical Physics*, the *Physical Review*, and the *Journal of Physical Chemistry*.

PROBLEMS

Section 27.6: The Classical Statistical Mechanics of Dense Gases and Liquids

27.20 Using the parameters in Exercise 27.11 for the square-well representation of the potential energy function of argon, calculate the second virial coefficient of argon at 50°C and at 150°C. Compare with the experimental values, $-1.12 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}$ at 50°C and $0.11 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}$ at 150°C.

27.21 The effective hard-sphere diameter of helium atoms at 293 K is 2.17×10^{-10} m. Use the formula of Eq. (27.6-11) to calculate the second virial coefficient of helium at 293 K. The experimental value of this coefficient is nearly temperature-independent, equal to $1.17 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}$ at −100°C and equal to $1.10 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}$ at 150°C.

Summary of the Chapter

Statistical mechanics can be studied through use of an ensemble, which is an imaginary collection of many replicas of the physical system. All of the systems in the ensemble are in the same macroscopic state as the physical system, but members of the ensemble occupy all possible microscopic states compatible with the macroscopic state. The canonical ensemble represents a system with known values of T, V, and n, and each system of the ensemble is in a constant-temperature bath consisting of the other systems of the ensemble. The probability distribution for the canonical ensemble is

$$p_i = p(E_i) = \frac{1}{\mathcal{Z}} e^{-E_i/k_\mathrm{B}T}$$

where k_B is Boltzmann's constant, T is the absolute temperature, and $\mathcal{Z}$ is the canonical partition function, which is a sum over system states:

$$\mathcal{Z} = \sum_i e^{-E_i/k_\mathrm{B}T}$$

In the case that the system is a dilute gas,

$$\mathcal{Z} = \frac{z^n}{N!}$$

where z is the same molecular partition function as in Chapters 25 and 26. We obtained formulas for all of the equilibrium thermodynamic functions of a general system, and found that for a dilute gas, the formulas obtained were the same as those in Chapters 25 and 26.

Statistical mechanics can also be based on classical mechanics, and a brief introduction to this subject was included in the chapter, based on the canonical ensemble. Since classical states are specified by values of coordinates and momentum components, the probability distribution for classical statistical mechanics is a probability density in phase space, which has both coordinates and momentum components on its axes. This probability density was obtained, and formulas for thermodynamic variables were obtained in terms of a classical partition function. For a dilute gas, corrections for particle indistinguishability and the relation between volume in phase space and quantum states must be made in order to recover the same formulas as were obtained with the quantum canonical ensemble, but no advantage over quantum statistical mechanics is obtained. A brief introduction to the classical statistical mechanics of dense gases and liquids was presented.

ADDITIONAL PROBLEMS

27.22 In Chapter 9 of this textbook, a crude equation of state for a hard-sphere gas was written:

$$P(V_\mathrm{m} - b) = PV_\mathrm{m}(1 - b/V_\mathrm{m}) = RT$$

where

$$b = N_\mathrm{Av}\frac{2}{3}\pi d^3$$

and where N_Av is Avogadro's constant, V_m is the molar volume V/n, and where d is the hard-sphere diameter. Convert this equation into the virial form

$$\frac{PV_\mathrm{m}}{RT} = 1 + \frac{B_2}{V_\mathrm{m}} + \frac{B_3}{V_\mathrm{m}^2} + \dots$$

using the identity

$$\frac{1}{1} - x = 1 + x + x^2 + \dots$$

Compare your result for the second virial coefficient with that of Eq. (27.6-11).

27.23 Identify the following statements as either true or false. If a statement is true only under special circumstances, label it as false.

a. Molecular partition functions are not useful for the canonical ensemble approach to statistical mechanics.

b. The canonical ensemble approach is more easily used than the approach of Chapters 25 and 26 for dilute gases.

c. The canonical ensemble approach can be used only for dilute gases.

d. The statistical mechanical approach used in Chapters 25 and 26 is equivalent to using the microcanonical ensemble.

e. Classical statistical mechanics applies accurately to translations of molecules.

f. Classical statistical mechanics applies accurately to rotations of molecules.

g. Classical statistical mechanics applies accurately to vibrations of molecules.

h. Nonideal gases are more easily treated in classical statistical mechanics than in quantum statistical mechanics.

28

The Structure of Solids, Liquids, and Polymers

PRINCIPAL FACTS AND IDEAS

1. Crystalline solids possess a geometrically repeating lattice structure.
2. The Einstein and Debye crystal models describe vibrations in crystals.
3. The band theory describes the electronic structure of solids to a useful approximation.
4. Liquids can be modeled as though they were very dense gases or as though they were disordered solids.
5. Transport processes in liquids can be modeled as motions of molecules as though temporarily confined in cages made up of neighboring molecules.
6. Polymers are made up of monomer molecules covalently bonded into chains or networks.
7. Nanomaterials consist of particles roughly one nanometer in size.

28.1 The Structure of Solids

In liquids and solids the atoms, molecules, or other formula units are close to each other, and the balance between attractive and repulsive intermolecular forces holds a liquid or solid at nearly constant volume. A *crystalline solid* consists of a regular geometric array of repeating identical units of atoms or molecules. Although single crystals are occasionally found in nature, most common samples of crystalline substances are *polycrystalline*. That is, they are made up of many pieces of crystal lattice stuck together in various orientations. If you look at a broken piece of cast iron you can sometimes see grains that might be single crystals. Solids that are not crystalline are said to be *amorphous*. *Glasses* are amorphous materials that soften gradually as they are heated, becoming liquid without a definite melting temperature. They are sometimes considered to be supercooled liquids, although they can be very rigid. In an amorphous solid there are vestiges of a crystal lattice at short range, but the geometric regularity is not complete, and does not persist over large distances.

The *basis* of a crystal is the smallest set of atoms, ions, or molecules with fixed bond distances and angles (the same conformation) and with the same orientation that repeats again and again to make up the crystal. The basis of crystalline sodium chloride consists of one sodium ion and one chloride ion. The crystal could be reproduced by stacking replicas of the basis, all with the same orientation. The basis of crystalline carbon dioxide contains four molecules. Even though the four molecules have the same conformation, they have different orientations.

A *crystal lattice* is a set of points generated by placing a *lattice point* at the same location in each basis. A point at the center of an atom or ion can be chosen, but any point in the basis will do. A crystal lattice can be divided into identical *unit cells*. A unit cell is a *parallelepiped* (a solid bounded by planes such that opposite sides are parallel to each other). Lattice points are customarily located at the corners of the unit cell. The contents of the unit cell must have the same stoichiometry as the whole crystal and must consist of an integral number of basis units. The lattice could be reproduced by stacking replicas of the unit cell in straight rows, files, and columns, with no spaces between them.

Figure 28.1 shows the unit cell of the sodium chloride lattice with the sodium ions at the corners of the unit cell. An alternate unit cell could be taken by locating chloride ions at the corners of the unit cell. This unit cell is a cube with sides equal to 5.63×10^{-10} m. It contains four sodium ions: a one-eighth share of each of eight sodium ions at the corners of the unit cell and a one-half share of each of six sodium ions in the faces. There are four chloride ions: a one-fourth share of each of the twelve ions at the centers of the edges, plus the chloride ion at the center of the cell.

The edges of a unit cell and their lengths are denoted by the letters a, b, and c. The angle between a and b is called γ, the angle between a and c is called β, and the angle between b and c is called α. The directed line segments a, b, and c define the axes along which the unit cell is translated repeatedly to reproduce the lattice. These axes might or might not be not perpendicular to each other.

Crystal Systems and Bravais Lattices

There are seven different *crystal systems*, or unit cell shapes, which are listed in Table 28.1. The unit cells are depicted in Figure 28.2 with the lattice points indicated.

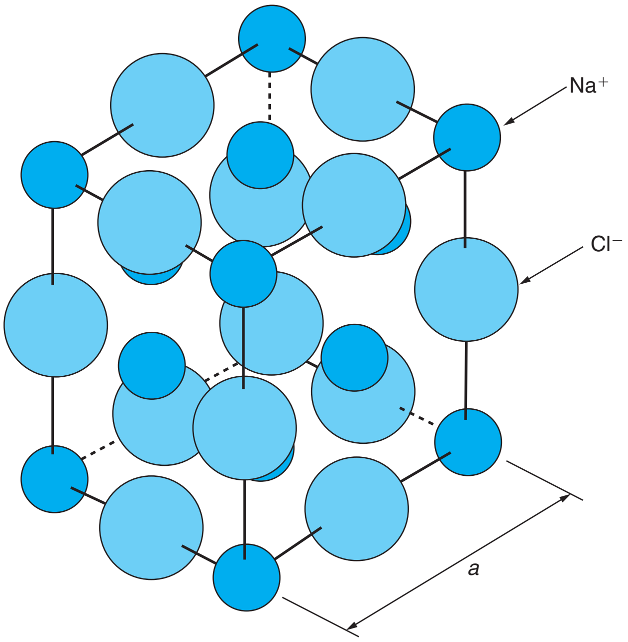


Figure 28.1 The Sodium Chloride Unit Cell.

Table 28.1 Crystal Systems and Lattices

System	Defining Conditions	Bravais Lattices
Cubic	$a = b = c$ $90^\circ = \alpha = \beta = \gamma$	P, I, F
Tetragonal	$a = b \neq c$ $90^\circ = \alpha = \beta = \gamma$	P, I
Orthorhombic	$a \neq b \neq c$ $90^\circ = \alpha = \beta = \gamma$	P, C, I, F
Monoclinic	$a \neq b \neq c$ $90^\circ = \alpha = \gamma \neq \beta$	P, C
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	P
Trigonal (rhombohedral)	$a = b = c$ $90^\circ \neq \alpha = \beta = \gamma < 120^\circ$	P
Hexagonal	$a = b \neq c$ $90^\circ = \alpha = \beta, \gamma = 120^\circ$	P

The hexagonal unit cell can be cut into three parallelepiped unit cells, which are identical except for their orientations. Either the full hexagonal unit cell or the smaller unit cell can be used, but the smaller unit cells must be rotated as well as translated to reproduce the crystal lattice.

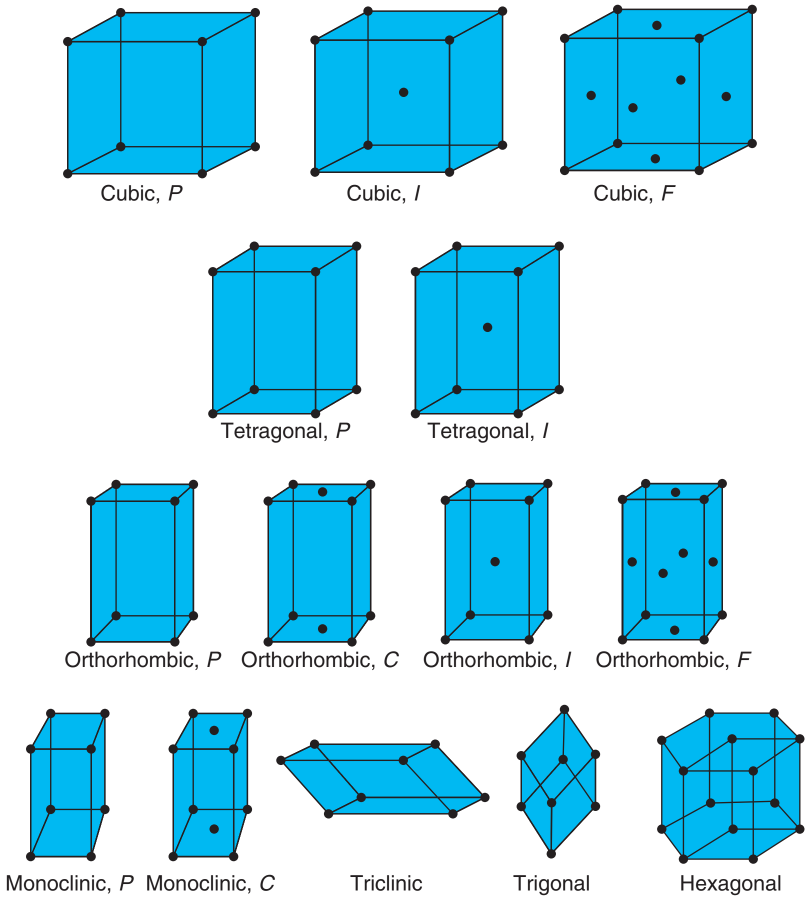


Figure 28.2 The Unit Cells of the Fourteen Bravais Lattices.

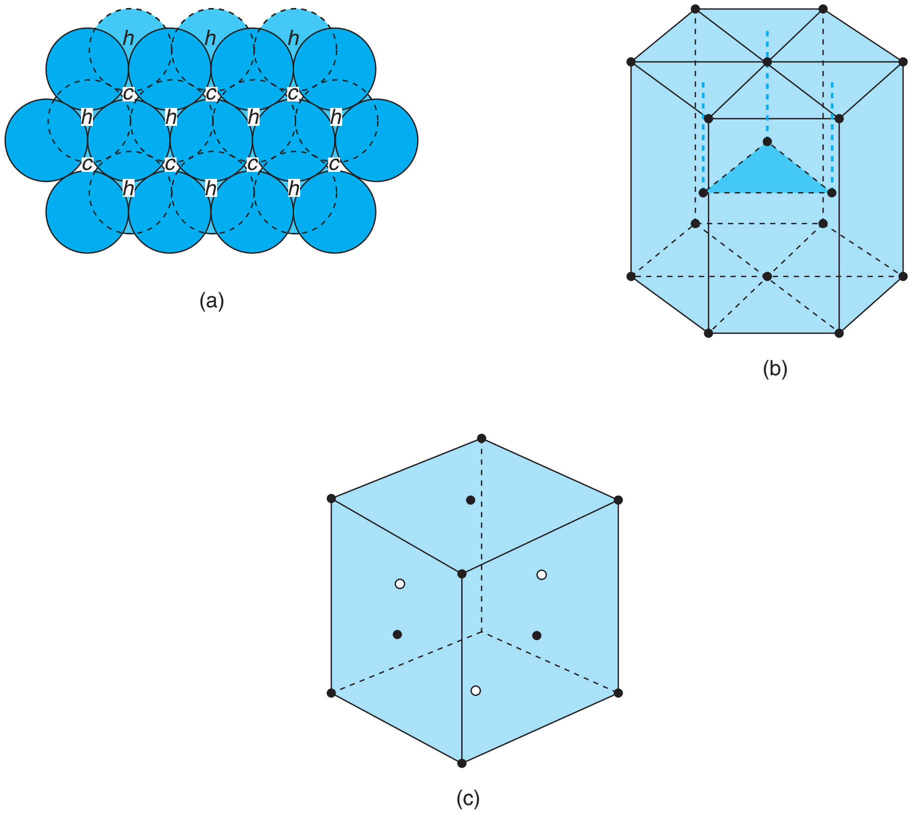
Some of the crystal systems have more than one kind of lattice. A *primitive lattice* or *simple lattice* (denoted by P) is one in which lattice points occur only at the corners of the unit cell. A unit cell of a primitive lattice contains one basis (one-eighth of the basis at each corner). A *body-centered* lattice (denoted by I, for German *innenzentriert*) is one in which there is a lattice point at the center of the unit cell as well as at the corners. A *face-centered* lattice (denoted by F) is one in which there is a lattice point at the center of each face of the unit cell as well as at the corners. The sodium chloride lattice is a face-centered cubic lattice. A *base-centered* lattice or *end-centered* lattice (denoted by C) is one in which there is a lattice point at the center of one pair of opposite faces as well as at the corners. Table 28.1 and Figure 28.2 show the 14 possible lattices, which are called *Bravais lattices*.

Exercise 28.1

For each of the 14 Bravais lattices, give the number of basis units in the unit cell.

A number of monatomic substances, including the inert gases and most metals, crystallize in *close-packed lattices*. If a collection of spheres of equal size is packed as closely as possible, each sphere is in contact with 12 other spheres. We say that the *coordination number* equals 12. There are two ways to accomplish this closest packing, as depicted in Figure 28.3. If one layer of spheres is laid down in a plane, another layer can be placed on it, as shown in Figure 28.3a (the lower layer is drawn in broken curves). There are now two choices for laying down a third layer: either in the locations marked *h* (directly over the spheres of the first layer), or in the locations marked *c*. If the third layer is laid down in the *h* locations, a lattice with a hexagonal unit cell results, as shown in Figure 28.3b. If the third layer is laid down in the *c* locations, a lattice with a face-centered cubic (fcc) unit cell results, as shown in Figure 28.3c. In the fcc lattice, the layers of lattice points are not parallel to the unit cell faces, but pass through alternate corners of the unit cell.

Both the hexagonal and the fcc close-packed lattices give the same *packing fraction*, the fraction of the unit cell volume occupied by the spheres, assuming that the spheres touch each other. (It is also called the "filling fraction" or the "packing efficiency.") The nearest-neighbor distance and the number of nearest neighbors are also identical. However, the spheres beyond the shell of nearest neighbors are not at the same distances in both lattices, and a given substance at equilibrium will crystallize in only one of these lattices. Nickel crystallizes in the face-centered cubic lattice, whereas



(a)

(b)

(c)

Figure 28.3 Closest Packing of Spheres. (a) Layers of spheres. (b) The hexagonal close-packed unit cell. This figure shows that the third layer has each sphere directly over a sphere of the first layer. (c) The face-centered cubic close-packed unit cell. This unit cell is oriented so that the layers of atoms in Figure 28.3a are parallel to a plane that passes through the lattice point at the top rear of the cell, the lower left of the cell, and the lower right of the cell.

cobalt crystallizes in the hexagonal lattice. All of the inert gases crystallize in the face-centered cubic lattice except for helium, which crystallizes in the hexagonal lattice.

EXAMPLE 28.1

Show that the packing fraction for the fcc close-packed lattice is equal to 0.74.

Solution

For spheres of radius r touching each other, the diagonal of the cube face is equal to $4r$, and is also equal to $\sqrt{2}\,a$, where a is the dimension of the unit cell.

$$r = \frac{1}{4}\sqrt{2}\,a = \frac{1}{2^{3/2}}a$$

There are 6 atoms in the faces of the unit cell, and half of each is in the cell:

$$(6)\left(\frac{1}{2}\right)\frac{4}{3}\pi r^3 = 4\pi r^3 = 4\pi 2^{-9/2}a^3 = 0.55536a^3$$

There are 8 atoms in the corners of the unit cell, and 1/8 of each is in the cell:

$$(8)\left(\frac{1}{8}\right)\frac{4}{3}\pi r^3 = \frac{4}{3}\pi r^3 = \frac{4}{3}\pi 2^{-9/2}a^3 = 0.18512a^3$$

The volume of the unit cell is a^3 and the total volume of the spheres in the unit cell is

$$V(\text{spheres}) = (0.5536 + 0.18512) = 0.74048a^3$$

$$\text{Packing fraction} = \frac{0.74048a^3}{a^3} = 0.74048$$

Exercise 28.2

Iron crystallizes in the body-centered cubic lattice. Give the coordination number for this lattice and calculate the packing fraction for this lattice, assuming spheres that touch.

X-Ray Diffraction and Miller Indices

Since X-rays are electromagnetic radiation with wavelengths roughly equal to crystal lattice spacings, crystals can act as diffraction gratings for X-rays. Study of the angles and intensities of diffracted X-ray beams can allow unit cell dimensions and positions of atoms within the unit cells to be calculated. To describe the diffraction of X-rays, it is necessary to specify the directions of planes that fit into a crystal lattice in such a way that the plane contains a repeating regular pattern of lattice points. These planes intersect with one or more of the axes within a unit cell. We define a plane that intersects with the a axis at a distance a/h from the origin, with the b axis at a distance b/k from the origin, and with the c axis at a distance c/l from the origin, where h, k, and l are integers. The three integers h, k, and l are called *Miller indices* and are denoted by their values inside parentheses, as in (hkl). The Miller indices are not required to be positive, and a zero value for an index means that the plane is parallel to that axis. Negative values are denoted by putting the negative sign above the digit, as in $(11\bar{1})$. Figure 28.4 shows a unit cell with several planes and their Miller indices. Some planes are parallel to other planes. For example, the $(00\bar{1})$ plane is parallel to the (002) plane, and the (222) plane is parallel to the (111) plane. However, two parallel planes do not necessarily contain the same pattern of lattice points.

Figure 28.5 shows schematically how a crystal acts like a diffraction grating. Two planes of lattice points are shown in which lattice points of the first plane are perpendicularly opposed to lattice points of the second plane. We assume that there

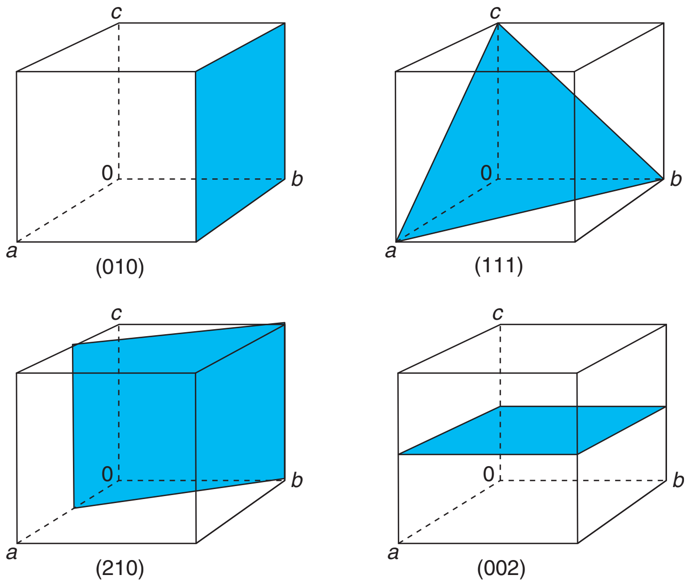


Figure 28.4 Some Planes and Their Miller Indices.

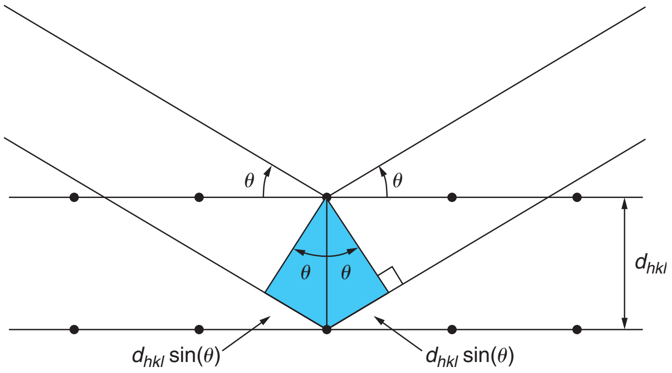


Figure 28.5 Diagram Showing the Bragg Condition for X-Ray Diffraction by a Crystal Lattice.

is a scattering center at each lattice point. Each scattering center diffracts incident electromagnetic radiation, sending a spherical electromagnetic wave out in all directions. The condition for constructive interference in a particular direction is that two waves from adjacent diffraction centers have crests and troughs at the same locations. If the distance between the planes is equal to d, and the wavelength of the radiation is λ, the condition for constructive interference is that the extra distance traveled by the wave diffracted from the second layer is an integral number (n) of wavelengths. The integer n is called the *order* of the reflection. Trigonometry gives the condition:

$$n\lambda = 2d\sin(\theta) \tag{28.1-1}$$

where θ is the angle between the plane and the direction of the radiation. Equation (28.1-1) is called the *Bragg equation*.

The Bragg equation is named after Sir William Henry Bragg, 1862–1942, and his son William Lawrence Bragg, 1890–1971, who jointly received the 1915 Nobel Prize in physics for their studies in X-ray diffraction.

At first glance, it might seem that the two angles labeled θ in the diagram would not have to be equal. However, one cannot consider just two atoms as scattering centers. In order for the scattering from other pairs of atoms in the same two planes to produce constructive interference, the two angles must be equal, so that the diffraction condition is similar to a reflection from the planes of atoms. Diffracted X-ray beams are therefore sometimes called “reflections.”

Exercise 28.3

By drawing a replica of Figure 28.5 and drawing incident and diffracted rays from other pairs of atoms, show that if the two angles labeled θ in Figure 28.5 are equal, all of the diffracted beams interfere constructively if the Bragg condition is satisfied.

Any planes specified by Miller indices can diffract X-rays, so we append the Miller indices to the distance between the planes in Eq. (28.1-1):

$$n\lambda = 2d_{hkl}\sin(\theta) \tag{28.1-2}$$

This equation is the same as

$$\lambda = 2d_{nh,nk,nl}\sin(\theta) \tag{28.1-3}$$

For example, the distance between the (200) planes is half as great as the distance between the (100) planes, so that the second-order ($n = 2$) diffraction from the (100) planes is at the same wavelength as the first-order ($n = 1$) diffraction from the (200) planes.

The diffraction of X-rays by a crystal lattice is more complicated than we have indicated. In some cases the diffracted beams interfere destructively and are not seen. This destructive interference is called *extinction*. Some extinction rules are:[1]

1. For a primitive lattice: no extinctions.
2. For a face-centered lattice: all three Miller indices must be even, or all three must be odd to avoid extinction.
3. For a body-centered lattice: the sum of the three Miller indices must be an even integer to avoid extinction.

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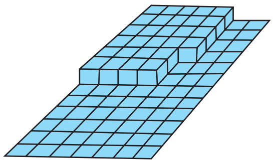
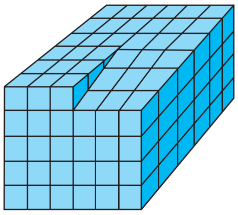
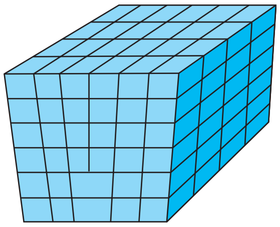
[1] M. J. Buerger, *Contemporary Crystallography*, McGraw-Hill Book Co., New York, 1970, chapter 5.



A step defect



A screw-type dislocation



An edge-type dislocation

Figure 28.6 Some Crystal Defects (Schematic). These types of defects are the most common simple types of crystal defects.

The simplest X-ray diffraction experiment is carried out with a finely powdered sample of the crystalline material placed in an X-ray beam. Since there are many small crystals with many different orientations, a collimated X-ray beam strikes some crystals at any given angle, and a number of diffracted beams come from the sample in cones of directions concentric with the incident beam. A photographic film or other detector is placed to intercept these beams and record their positions, allowing one to calculate the diffraction angles. Analysis of the pattern of the diffraction angles allows one to determine from the extinction conditions whether one has a primitive lattice, a face-centered lattice, or a body-centered lattice. From the wavelength of the radiation and the diffraction angles, one can determine the unit cell dimensions.

We have discussed the diffraction of X-rays as though each atom in the crystal lattice were a point from which the X-rays are scattered. In fact, the principal scattering is from electrons, which are distributed over the entire unit cell. The scattering from the different parts of the unit cell interferes constructively and destructively in ways that are determined by the electron density in the unit cell. Analysis of the relative intensities of the different diffracted beams allows in some cases for the reconstruction of the electron density as a function of position in the unit cell. This is a complicated process, which we do not describe. The first such structure determinations were done before the advent of programmable computers, with many hours of hand calculation. Present-day calculations are done automatically by computer programs, using intensity data taken with automated computer-driven diffractometers.

Modern studies in surface catalysis often use single crystals with an exposed face whose Miller indices are known,[2] and it is sometimes found that different planes have different catalytic activities. There can also be a variety of defects in a real crystal, some of which are schematically depicted in Figure 28.6, and these defects can be involved in catalysis.

PROBLEMS

Section 28.1: The Structure of Solids

28.1 Gold (Au) forms a face-centered cubic lattice. Its density is 19.3 g cm^{-3} at 300 K. Find the unit cell dimension and the interatomic distance at this temperature.

28.2 Chromium (Cr) forms a body-centered cubic lattice. Its density is 7.19 g cm^{-3}. Find the unit cell dimension and the interatomic distance.

28.3 Explain why a single crystal has a greater mechanical strength than a polycrystalline sample of the same material.

28.4 Tennis racquet frames and golf club shafts are commonly made of a composite material consisting of a polymer in which fibers of graphite are embedded. Explain why this makes a stronger material than the polymer alone or the graphite alone.

28.5 Gallium crystallizes in a primitive orthorhombic lattice. Its density is 5.92 g cm^{-3}. Find the unit cell volume.

28.6 What is the basis for a crystal of argon, which forms a face-centered cubic lattice? What is the number of atoms per unit cell? What is the number of bases per unit cell?

28.7 The CsCl crystal has a cubic unit cell with a cesium ion at each corner and a chloride ion at the center.

a. To which Bravais lattice does it belong?

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[2] D. W. Goodman, *Ann. Rev. Phys. Chem.*, **37**, 425 (1986).

b. How many bases are there in a unit cell?

c. The density of CsCl is 3988 kg m^{-3}. Find the unit cell dimension and the distance between nearest-neighbor Cs and Cl atoms.

28.8 Barium crystallizes in the body-centered cubic lattice.

a. Find the number of atoms per unit cell.

b. The density of barium is 3.5 g cm^{-3}. Find the unit cell dimension and the apparent radius of a barium atom.

c. Calculate the molar volume of solid barium and the volume of empty space in 1.00 mol of solid barium.

28.9 Argon forms a face-centered cubic lattice. Assume that in solid argon the nearest-neighbor distance is equal to the distance at the minimum in the Lennard–Jones potential function, 3.82×10^{-10} m.

a. Find the unit cell dimension.

b. Find the density of solid argon.

28.10 Iron forms a body-centered crystal with a unit cell dimension equal to 2.861×10^{-10} m. Calculate the density of iron. Compare it with the experimental value (look it up).

28.11 **a.** Find the perpendicular distance between the 110 planes in the iron crystal, which forms a body-centered cubic lattice with a unit cell dimension of 2.861×10^{-10} m.

b. Find the value of θ for the $n = 1$ reflection of X-rays with a wavelength of 1.5444 Å from these lattice planes.

28.12 **a.** Find the perpendicular distance between 111 planes in the molybdenum carbide lattice, which is face-centered cubic with $a = 4.28 \times 10^{-10}$ m.

b. If the $n = 1$ reflection from the 111 plane gives $\theta = 36.5°$, find the wavelength of the X-rays.

c. There are two molybdenum carbides, MoC and $\mathrm{Mo_2C}$. Determine which formula applies for this unit cell size and find the density of molybdenum carbide.

28.13 **a.** The stretching of a uniform bar due to a tensile (stretching) force is described by *Young's modulus*, E, defined by

$$E = \frac{\text{stress}}{\text{strain}} = \frac{F/\mathscr{A}}{\Delta L/L}$$

where F is the magnitude of the tensile force, A is the cross-section area, L is the length, and ΔL is the change in the length due to the force F. Derive an approximate expression for Young's modulus for a perfect crystalline substance with a simple cubic lattice and an intermolecular potential energy given by

$$u(r) = u(a) + \frac{k}{2}(r - a)^2$$

where k is a constant, r is the lattice spacing, and a is its equilibrium value. Include only nearest-neighbor interactions and assume that each unit cell stretches in the same ratio as the entire bar.

b. The value of Young's modulus for fused quartz is 7.17×10^{10} N m^{-2}. Estimate the force constant k for the Si–O bond, assuming (contrary to fact) that quartz has a simple cubic lattice. Assume that $a = 1.5 \times 10^{-10}$ m, the approximate Si–O bond distance. Comment on your value in view of the fact that force constants for most single bonds in molecules are roughly equal to 500 N m^{-1}.

28.14 The value of Young's modulus for iron is 2.8×10^{7} lb in^{2} (pounds per square inch). Make reasonable assumptions and estimate the force constant for an Fe–Fe bond. See the previous problem.

28.2 Crystal Vibrations

The atoms or ions making up a crystal can vibrate about their equilibrium positions. A crystal is like a very large molecule and if a crystal consists of N atoms it must have $3N - 6$ vibrational normal modes, all of which correspond to collective motions of many atoms. We will discuss two model systems that represent the vibrations of a crystal.

The Einstein Crystal Model

This model assumes that all of the vibrational normal modes act like harmonic oscillators with the same frequency. It is used to represent a crystal of a monatomic substance such as a solidified inert gas, a metal, or a network covalent crystal such as diamond. If a monatomic crystal has N atoms its vibrational energy is given by

$$E_{\mathrm{vib}} = U_0 + \sum_{i=1}^{3N-6} h\nu v_i \approx U_0 + \sum_{i=1}^{3N} h\nu v_i \tag{28.2-1}$$

where ν is the vibrational frequency and v_i is the quantum number for normal mode number i. The energy of the crystal in its ground vibrational state, including the zero-point energy, is denoted by U_0. In the second equality we ignore the difference between $3N-6$ and $3N$, since N is a large number.

The canonical partition function for the entire crystal is a sum over all values of the quantum numbers:

$$\mathcal{Z} = \sum_{v_1=0}^{\infty} \sum_{v_2=0}^{\infty} \cdots \sum_{v_{3N}=0}^{\infty} \exp\left(\frac{-U_0 - \sum_{i=1}^{3N} h\nu v_i}{k_{\mathrm{B}}T} \right) \tag{28.2-2}$$

The normal modes are distinguishable from each other, so the sums are independent, and this expression can be factored with one factor for each normal mode. The factors are all identical after summation, and we write

$$\begin{aligned} \mathcal{Z} &= e^{-U_0/k_{\mathrm{B}}T} \prod_{i=1}^{3N} \left(\sum_{v_i=0}^{\infty} e^{-h\nu v_i/k_{\mathrm{B}}T} \right) = e^{-U_0/k_{\mathrm{B}}T} \left(\sum_{v=0}^{\infty} e^{-h\nu v/k_{\mathrm{B}}T} \right)^{3N} \\ &= e^{-U_0/k_{\mathrm{B}}T} z^{3N} \end{aligned} \tag{28.2-3}$$

where each sum in the product is denoted by z, which is a partition function for a single vibration. The normal modes are assumed to be distinguishable from each other, so there is no need to divide by $N!$. The function z is the same as the vibrational partition function in Eq. (25.4-18):

$$z = \sum_{v=0}^{\infty} e^{-h\nu v/k_{\mathrm{B}}T} = \frac{1}{1 - e^{-h\nu/k_{\mathrm{B}}T}} \tag{28.2-4}$$

so that the canonical partition function is:

$$\mathcal{Z} = e^{-U_0/k_{\mathrm{B}}T} \left(\frac{1}{1 - e^{-h\nu/k_{\mathrm{B}}T}} \right)^{3N} \tag{28.2-5}$$

$$\begin{aligned} \ln(\mathcal{Z}) &= -\frac{U_0}{k_{\mathrm{B}}T} + 3N\ln(z) = -\frac{U_0}{k_{\mathrm{B}}T} + 3N\ln\left(\frac{1}{1 - e^{-h\nu/k_{\mathrm{B}}T}} \right) \\ &= -\frac{U_0}{k_{\mathrm{B}}T} - 3N\ln\left(1 - e^{-h\nu/k_{\mathrm{B}}T} \right) \end{aligned} \tag{28.2-6}$$

We can now write formulas for the thermodynamic functions of the Einstein model using equations from Chapter 27:

$$U = k_{\mathrm{B}}T^2\left(\frac{\partial \ln(\mathcal{Z})}{\partial T}\right)_V = U_0 + 3Nk_{\mathrm{B}}T^2\left(\frac{\partial \ln(z)}{\partial T}\right)_V$$

$$= U_0 + \frac{3Nh\nu}{e^{h\nu/k_{\mathrm{B}}T} - 1} \tag{28.2-7a}$$

$$C_{\mathrm{V}} = \left(\frac{\partial U}{\partial T}\right)_{V,N} = 3Nk_{\mathrm{B}}\left(\frac{h\nu}{k_{\mathrm{B}}T}\right)^2 \frac{e^{h\nu/k_{\mathrm{B}}T}}{(e^{h\nu/k_{\mathrm{B}}T} - 1)^2} \tag{28.2-7b}$$

$$S = \frac{U}{T} + k_{\mathrm{B}}\ln(\mathcal{Z}) = \frac{U_0}{T} + \frac{3Nh\nu}{T(e^{h\nu/k_{\mathrm{B}}T}) - 1} - \frac{U_0}{k_{\mathrm{B}}T} + 3Nk_{\mathrm{B}}\ln(z)$$

$$= \frac{3Nh\nu}{T(e^{h\nu/k_{\mathrm{B}}T} - 1)} - 3Nk_{\mathrm{B}}\ln\left(1 - e^{-h\nu/k_{\mathrm{B}}T}\right) \tag{28.2-7c}$$

$$A = -k_{\mathrm{B}}T\ln(\mathcal{Z}) = U_0 + 3Nk_{\mathrm{B}}T\ln\left(1 - e^{-h\nu/k_{\mathrm{B}}T}\right) \tag{28.2-7d}$$

$$P = k_{\mathrm{B}}T\left(\frac{\partial \ln(\mathcal{Z})}{\partial V}\right)_T = 3Nk_{\mathrm{B}}T\left(\frac{\ln(z)}{\partial V}\right)_T \tag{28.2-7e}$$

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} \approx \frac{A_N - A_{N-1}}{1} = \frac{U_0}{N} + 3k_{\mathrm{B}}T\ln\left(1 - e^{-h\nu/k_{\mathrm{B}}T}\right) \tag{28.2-7f}$$

We use the chemical potential per molecule as in Chapter 26, not the chemical potential per mole. We have replaced a derivative by a finite difference and have assumed that U_0 for a crystal of $N - 1$ atoms is equal to U_0 for a crystal of N atoms times $(N - 1)/N$.

There is a difficulty with the pressure of the Einstein crystal model. The model does not include any simple way to evaluate the derivative in Eq. (28.2-7e). We might try to evaluate the pressure by finding the difference between G and A, since $G = A + PV$. For a one-component system, G is given Eq. (26.1-29) as

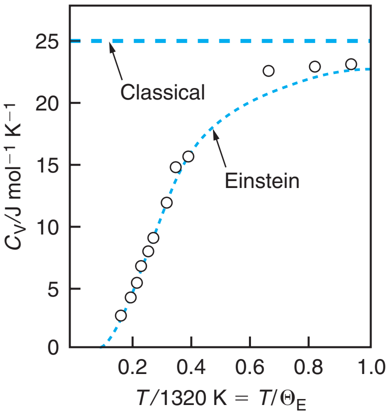

Figure 28.7 The Heat Capacity of Diamond Fit to the Einstein Crystal Model Result. The horizontal line corresponds to the law of Dulong and Petit. From J. S. Blakemore, *Solid State Physics*, 2nd ed., W. B. Saunders, Philadelphia, 1974, p. 121.

$$G = N\mu = U_0 - 3Nk_{\mathrm{B}}T\ln(z)$$

$$= U_0 + 3Nk_{\mathrm{B}}T\ln(1 - e^{-h\nu/k_{\mathrm{B}}T}) \tag{28.2-7g}$$

so that $G = A$, which leads to $PV = 0$. This result is a shortcoming of a crude model, but for a crystal the numerical value of PV is small compared with G and A, so that we can use the formulas for G and A to an adequate approximation.

The value of the frequency ν is determined by fitting the heat capacity formula to experimental data. The formulas for the thermodynamic functions can be restated in terms of the parameter

$$\Theta_{\mathrm{E}} = \frac{h\nu}{k_{\mathrm{B}}} \quad \text{(definition)} \tag{28.2-8}$$

The parameter Θ_{E} has the dimensions of temperature and is called the *Einstein temperature* or the *characteristic temperature*. Figure 28.7 shows the heat capacity of diamond as a function of temperature as well as the heat capacity of the Einstein crystal model with an Einstein temperature of 1320 K, which gives the best fit to the experimental data.

In the limit of high temperature

$$\lim_{T\to\infty} C_{\mathrm{V}} = 3Nk_{\mathrm{B}} = 3nR \tag{28.2-9}$$

This formula agrees with the empirical *law of Dulong and Petit*, which states that the molar heat capacity of atomic crystals is approximately equal to $3R$. Most metals have a sufficiently small Einstein temperature that the law of Dulong and Petit applies quite well near room temperature, but the Einstein frequency of diamond is sufficiently high that this law does not apply to it at room temperature.

EXAMPLE 28.2

Show that Eq. (28.2-9) is correct.

Solution

Equation (28.2-7b) is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = 3Nk_B\left(\frac{h\nu}{k_BT}\right)^2 \frac{e^{h\nu/k_BT}}{(e^{h\nu/k_BT}-1)^2}$$

$$\lim_{T\to\infty} C_V = \lim_{T\to\infty}\left(3Nk_B\left(\frac{h\nu}{k_BT}\right)^2 \frac{1-h\nu/k_BT}{(1-h\nu/k_BT-1)^2}\right) = 3Nk_B\left(\frac{h\nu}{k_BT}\right)^2 \frac{1}{(h\nu/k_BT)^2}$$

$$= 3Nk_B = 3nR$$

Exercise 28.4

Using the Einstein theory, calculate the molar heat capacity of a diamond crystal at 298.15 K, at 500.0 K, and at 1320 K. Compare each value with $3R$. The experimental value at 298.15 K is $6.113\ \mathrm{J\,K^{-1}\,mol^{-1}}$.

The Debye Crystal Model

This model is a physically motivated improvement over the Einstein crystal model. Debye sought a realistic way to assign different frequencies to the vibrational normal modes. He assumed that the normal modes could be represented by standing waves that vanish at the surfaces of the crystal. The quanta of energy of these waves are called **phonons** since the waves are essentially sound waves. Consider a cubic crystal with side L. The amplitude of a standing wave that vanishes at the boundaries of the cube is represented by

$$\text{Amplitude} = B\sin\left(\frac{s_x\pi x}{L}\right)\sin\left(\frac{s_y\pi y}{L}\right)\sin\left(\frac{s_z\pi y}{L}\right) \tag{28.2-10}$$

where B is a constant and where s_x, s_y, and s_z are positive integers. We let

$$s = \sqrt{s_x^2 + s_y^2 + s_z^2} \tag{28.2-11}$$

The wavelength is given by

$$\lambda = \frac{2L}{s} \tag{28.2-12}$$

and the frequency of the wave is given by

$$\nu = \frac{c}{\lambda} = \frac{cs}{2L} \tag{28.2-13}$$

where c is the speed of propagation of the waves (the speed of sound in the solid).

For fairly large values of the integers, the number of sets of integers such that s lies between s and $s + ds$ is approximately equal to

$$\text{Number of waves in the interval } (s, s + ds) = \frac{\pi s^2}{2} ds \tag{28.2-14}$$

In a solid there can be longitudinal waves in which the oscillation is parallel to the direction of the wave, and transverse waves in which the oscillation is perpendicular to the direction of the wave. The result in Eq. (28.2-14) must be multiplied by a factor of 3 for the two transverse waves (polarized at right angles to each other) and one longitudinal wave. If the speed of sound depends on the frequency and if the longitudinal and transverse waves do not move at the same speed we regard the constant value of c as an average speed that can be different for each solid substance.

EXAMPLE 28.3

Show that Eq. (28.2-14) is correct.

Solution

We construct a mathematical space in which s_x, s_y, and s_z are plotted on three Cartesian axes. The number of points inside a given region of this space corresponding to sets of integral values is nearly equal to the volume of that region, since there is one such point per unit volume. Consider a spherical shell of thickness ds. Only one octant of the coordinate system is included, since all of the integers are positive. The volume of a spherical shell of radius s and thickness ds is $4\pi s^2 ds$. The volume in the first octant is 1/8 of this, or $(\pi s^2/2)ds$.

Equations (28.2-13) and (28.2-14) can be combined:

$$\begin{aligned}(\text{Number of waves in } ds) &= \frac{3\pi}{2}\left(\frac{2L\nu}{c}\right)^2 ds \\ &= \frac{3\pi}{2}\left(\frac{2L\nu}{c}\right)^2 \frac{2L}{c} d\nu = 12\pi \frac{V}{c^3} \nu^2 d\nu = g(\nu) d\nu \end{aligned} \tag{28.2-15}$$

where V is the volume of the crystal. The function $g(\nu)$ is called the *frequency distribution*:

$$g(\nu) = 12\pi \frac{V}{c^3} \nu^2 \tag{28.2-16}$$

In a crystal of N atoms the total number of vibrational modes is equal to $3N - 6$, which we approximate by $3N$ since N is a large number. Debye chose a maximum frequency ν_D such that he had the correct number of vibrational normal modes:

$$3N = \int_0^{\nu_D} g(\nu) d\nu = \frac{12\pi V}{c^3} \int_0^{\nu_D} \nu^2 d\nu = \frac{4\pi V \nu_D^3}{c^3} \tag{28.2-17}$$

$$\nu_D^3 = \frac{3Nc^3}{4\pi V} \tag{28.2-18}$$

Debye's frequency distribution of vibrational frequencies for copper is shown in Figure 28.8 along with the experimental distribution.

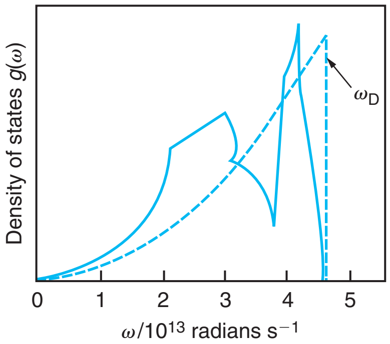

Figure 28.8 The Debye Distribution of Frequencies, with the Experimental Distribution of Frequencies for Copper. The distribution is shown as a function of $\omega = 2\pi\nu$. From J. S. Blakemore, *Solid State Physics*, 2nd ed., W. B. Saunders, Philadelphia, 1974, p. 126.

EXAMPLE 28.4

Calculate ν_{D} for copper, which has a density of 8.96 g cm^{-1}. The speed of sound in copper at room temperature is 4760 m s^{-1} for the longitudinal wave and 2325 m s^{-1} for the transverse waves.

Solution

The molar volume is

$$V_{\mathrm{m}} = \frac{63.456\ \mathrm{g\,mol^{-1}}}{8.96\ \mathrm{g\,cm^{-3}}} = 7.082\ \mathrm{cm^3\,mol^{-1}} = 7.082 \times 10^{-6}\ \mathrm{m^3\,mol^{-1}}$$

$$\frac{N}{V} = \frac{6.02214 \times 10^{23}\ \mathrm{mol^{-1}}}{7.082 \times 10^{-6}\ \mathrm{m^3\,mol^{-1}}} = 8.503 \times 10^{28}\ \mathrm{m^{-3}}$$

We take as an average value of c

$$\begin{aligned} c &= \frac{1}{3}\Big[c(\text{longitudinal}) + 2c(\text{transverse})\Big] \\ &= \frac{1}{3}\Big[(4760\ \mathrm{m\,s^{-1}}) + 2(2325\ \mathrm{m\,s^{-1}})\Big] = 3137\ \mathrm{m\,s^{-1}} \end{aligned}$$

$$\nu_{\mathrm{D}}^3 = \frac{3Nc^3}{4\pi V} = \frac{(3)(8.503 \times 10^{28}\ \mathrm{m^{-3}})(3137\ \mathrm{m\,s^{-1}})^3}{4\pi} = 6.2645 \times 10^{38}\ \mathrm{s^{-3}}$$

$$\nu_{\mathrm{D}} = (6.2645 \times 1038\ \mathrm{s^{-3}})^{1/3} = 8.557 \times 10^{12}\ \mathrm{s^{-1}}$$

If this value is multiplied by 2π, the result is 5.38×10^{13} radians s^{-1}, in rough agreement with the value in Figure 28.8.

Exercise 28.5

Find the value of the speed of sound in copper that corresponds to the cutoff frequency in Figure 28.8, 4.6×10^{13} radians s^{-1}.

The canonical partition function is given by Eq. (28.2-3) except that each normal mode has its own frequency, ν_i.

$$\mathcal{Z} = e^{-U_0/k_{\mathrm{B}}T}\prod_{i=1}^{3N}\left(\sum_{v_i=0}^{\infty} e^{-h\nu_i v_i/k_{\mathrm{B}}T}\right) = e^{-U_0/k_{\mathrm{B}}T}\prod_{i=1}^{3N} z_i \tag{28.2-19}$$

where z_i is the vibrational partition function for normal mode number i:

$$z_i = \sum_{v=0}^{\infty} e^{-h\nu_i v/k_{\mathrm{B}}T} = \frac{1}{1 - e^{-h\nu_i/k_{\mathrm{B}}T}} \tag{28.2-20}$$

The logarithm of the partition function of the crystal is given by

$$\ln(\mathcal{Z}) = -\frac{U_0}{k_{\mathrm{B}}T} + \sum_{i=1}^{3N}\ln(z_i) = -\frac{U_0}{k_{\mathrm{B}}T} - \sum_{i=1}^{3N}\ln\left(1 - e^{-h\nu_i/k_{\mathrm{B}}T}\right) \tag{28.2-21}$$

where U_0 is the vibrational ground-state energy. Since we have a continuous distribution of normal mode frequencies in the Debye model, we replace the sum by an integral

$$\ln(\mathcal{Z}) = -\frac{U_0}{k_B T} - \int_0^{\nu_D} \ln\left(1 - e^{-h\nu/k_B T}\right) g(\nu)\, d\nu \tag{28.2-22}$$

The vibrational energy of the Debye model is given by the analogue Eq. (28.2-7a)

$$\begin{aligned} U &= U_0 + \int_0^{\nu_D} \frac{h\nu}{e^{h\nu/k_B T} - 1} g(\nu)\, d\nu = U_0 + \frac{9N}{\nu_D^3} \int_0^{\nu_D} \frac{h\nu^3}{e^{h\nu/k_B T} - 1} d\nu \\ &= U_0 + \frac{9Nk_B T}{u_D^3} \int_0^{u_D} \frac{u^3}{e^u - 1} du \end{aligned} \tag{28.2-23}$$

where $u = h\nu/k_B T$ and $u_D = h\nu_D/k_B T$. The integral in Eq. (28.2-23) cannot be evaluated in closed form, and must be evaluated numerically.

Differentiation of the formula for U gives a formula for C_V:

$$C_V = \frac{9Nk_B}{\nu_D^3} \int_0^{\nu_D} \left(\frac{h\nu}{k_B T}\right)^2 \frac{e^{h\nu/k_B T} \nu^2}{\left(e^{h\nu/k_B T} - 1\right)^2} d\nu = 3Nk_B D(\Theta_D/T) \tag{28.2-24}$$

which defines the *Debye function*, $D = D(\Theta_D/T)$. The *Debye temperature*, Θ_D, is defined by

$$\Theta_D = \frac{h\nu_D}{k_B} \quad \text{(definition)} \tag{28.2-25}$$

Tables of the value of the Debye function D are available.[3] A software package such as Mathematica can easily carry out the evaluation. The appropriate value of Θ_D for a given crystal is chosen by fitting heat capacity data to Eq. (28.2-24).

The Helmholtz energy is given by

$$\begin{aligned} A &= U_0 - k_B T \int_0^{\nu_D} \ln\left(\frac{1}{1 - e^{-h\nu/k_B T}}\right) g(\nu)\, d\nu \\ &= U_0 + k_B T \int_0^{\nu_D} \ln\left(1 - e^{-h\nu/k_B T}\right) g(\nu)\, d\nu \end{aligned} \tag{28.2-26}$$

The entropy is given by combining the expressions for U and A:

$$\begin{aligned} S &= \frac{U - A}{T} \\ &= \frac{9N}{\nu_D^3 T} \int_0^{\nu_D} \frac{h\nu^3}{e^{h\nu/k_B T} - 1} d\nu + k_B \int_0^{\nu_D} \ln\left(\frac{1}{1 - e^{-h\nu/k_B T}}\right) g(\nu)\, d\nu \end{aligned} \tag{28.2-27}$$

Figure 28.9 shows the heat capacities of several elements, along with curves representing the Debye function for the Debye temperatures given. At high temperatures, the Debye expression conforms to the law of Dulong and Petit.

Exercise 28.6

Show that the energy expression in Eq. (28.2-23) reduces to $U = U_0 + 3Nk_B T$ for high temperatures, so that $C_V = 3Nk_B$, conforming to the law of Dulong and Petit. Use the fact that for small values of u, e^u can be approximated by $1 + u$.

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[3] N. Davidson, *Statistical Mechanics*, McGraw-Hill, New York, 1962, p. 359.

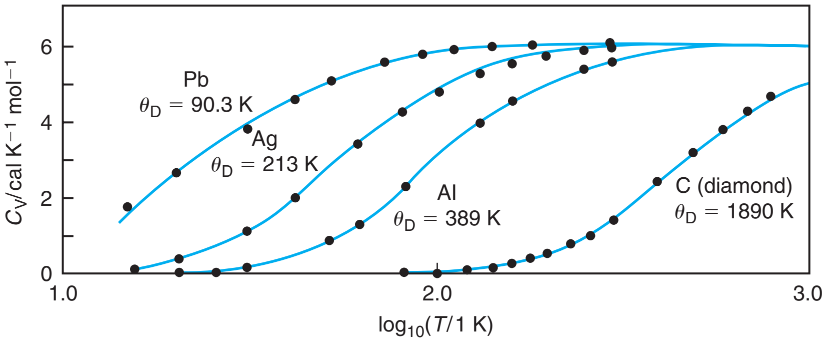

Figure 28.9 The Heat Capacity of Several Elements as a Function of Temperature, with Debye Curves. From G. N. Lewis and M. Randall, *Chemical Thermodynamics*, 2nd ed., rev. by K. S. Pitzer and L. Brewer, McGraw-Hill, New York, 1961, p. 56.

The Debye temperature of diamond is equal to 1890 K, whereas its Einstein temperature is 1320 K. Since the Einstein frequency should correspond to an average frequency in the Debye model, the relationship between these values is reasonable.

EXAMPLE 28.5

Obtain a formula for an average Debye frequency

$$\langle \nu \rangle = \frac{\int_0^{\nu_D} \nu g(\nu)d\nu}{\int_0^{\nu_D} g(\nu)d\nu}$$

Solution

Since $g(\nu) \propto \nu^2$,

$$\nu_{av} = \frac{\int_0^{\nu_D} \nu^3 d\nu}{\int_0^{\nu_D} \nu^2 d\nu} = \frac{\frac{1}{4}\nu_D^4}{\frac{1}{3}\nu_D^3} = \frac{3}{4}\nu_D$$

$$\nu_E = \frac{k_B \theta_E}{h} = \frac{(1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}})(1320\,\mathrm{K})}{6.6261 \times 10^{-34}\,\mathrm{J\,s}} = 2.75 \times 10^{13}\,\mathrm{s^{-1}}$$

$$\nu_{av} = \frac{3}{4}\frac{k_B \theta_D}{h} = \frac{3(1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}})(1890\,\mathrm{K})}{4(6.6261 \times 10^{-34}\,\mathrm{J\,s})} = 2.95 \times 10^{13}\,\mathrm{s^{-1}}$$

The average frequency is larger than the Einstein frequency by only 7%.

For small temperatures (T smaller than $\Theta_D/10$), u_D is large compared with values of $u = h\nu/k_B T$ that make significant contributions to the integral in Eq. (28.2-23), and the upper limit of the integral can be extended to infinity without serious error. The integral is then equal to $\pi^4/15$, and for small values of the temperature

$$\boxed{U = U_0 + \frac{3\pi^4 Nk_B T^4}{5\Theta_D^3}} \tag{28.2-28}$$

For small values of the temperature, the heat capacity is

$$\boxed{C_V = \frac{12\pi^4}{5}\frac{Nk_B T^3}{\Theta_D}} \tag{28.2-29}$$

In electrical conductors, there is also a contribution to the heat capacity from the electronic motion (see Section 28.3). Heat capacities are hard to measure at low temperatures, and data for temperatures below 15 K are hard to find. Equation (28.2-29) is commonly used as a substitute for experimental data between 0 K and 15 K. Modifications to the Debye theory have been devised that use a temperature-dependent Debye temperature and give improved agreement with experiment.[4]

Exercise 28.7

Verify Eq. (28.2-28).

PROBLEMS

Section 28.2: Crystal Vibrations

28.15 The formulas for the thermodynamic functions of an Einstein crystal can also be derived by slightly modifying the approach of Chapter 25, recognizing that the normal modes of vibration are distinguishable from each other. Carry out this analysis.

28.16 The value of Θ_E that fits the Einstein crystal model heat-capacity formula to data for aluminum is 240 K.

a. What is the vibrational frequency corresponding to this value of the parameter?

b. Draw a graph of the heat capacity of aluminum from 0 K to 300 K, according to the Einstein model.

c. At what temperature does the prediction of the Einstein model for the heat capacity of aluminum come within 5.00% of the law of Dulong and Petit? At what temperature does it come within 1.00% of the law of Dulong and Petit?

28.17 The value of Θ_E that fits the Einstein crystal model heat-capacity formula to data for diamond is 1320 K.

a. What is the vibrational frequency corresponding to this value of the parameter?

b. Construct an accurate graph of the heat capacity of diamond from 0 K to 300 K, according to the Einstein model.

c. At what temperature does the prediction of the Einstein model for the heat capacity of diamond come within 5.00% of the law of Dulong and Petit? At what temperature does it come within 1.00% of the law of Dulong and Petit?

28.18 **a.** Express the thermodynamic functions of an Einstein crystal in terms of the Einstein temperature.

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[4] See J. S. Blakemore, *Solid State Physics*, 2nd ed., W. B. Saunders, Philadelphia, 1974, p. 128ff.

b. Find the value of the frequency ν corresponding to the Einstein temperature of 1320 K assigned to diamond.

c. Calculate the molar energy of a diamond crystal at 298.15 K and at 500.0 K relative to the ground-state energy U_0.

d. Calculate the molar Gibbs energy of a diamond crystal at 298.15 K and at 500.0 K relative to the ground-state energy U_0.

e. Calculate the molar entropy of a diamond crystal at 298.15 K and at 500.0 K.

28.19 **a.** Write a computer program to evaluate the Debye function, using Simpson's rule.[5]

b. Use this program to evaluate the heat capacity of aluminum at several temperatures, using the Debye temperature of 428 K. Construct a graph of the heat capacity of solid aluminum as a function of temperature from 0 K to its melting temperature of 933 K.

28.20 Consider a modified Einstein crystal model with two frequencies. There are N atoms in the crystal. One-third of them oscillate in three dimensions with frequency ν, and two-thirds of them oscillate in three dimensions with frequency 2ν.

a. Write a formula for C_V.

b. Draw a graph of C_V versus T for $\nu = 3.94 \times 10^{12}\ \mathrm{s}^{-1}$ (one-half of the Debye frequency for germanium).

c. If a table of the Debye function is available[6] find the ratio of your result to the Debye result for several values of T.

28.3 The Electronic Structure of Crystalline Solids

If we ignore the intermolecular forces, the electronic wave function of a molecular or ionic crystal can be approximately represented as a product of wave functions for individual molecules or ions. For example, the wave function of a sample of solid argon would be approximated by a product of atomic wave functions of the argon atoms. An approximate description of the electronic structure of network covalent crystals can include localized covalent bonding similar to that described in Chapter 21.

EXAMPLE 28.6

Describe the bonding in diamond.

Solution

In diamond each carbon atom is tetrahedrally bonded to four adjacent carbon atoms. To describe the bonding in diamond, we form the $2sp^3$ hybrid orbitals on each carbon atom. The lobes of these orbitals point in the tetrahedral directions, and each forms a localized bonding orbital with a $2sp^3$ hybrid on the adjacent atom. Each pair of $2sp^3$ hybrid orbitals also forms an antibonding orbital, which is vacant.

Exercise 28.8

Describe the bonding in quartz, in which each silicon atom is bonded to four oxygen atoms. Each oxygen atom is bonded to two silicon atoms.

The atoms in metallic crystals are bonded to each other by delocalized covalent bonds similar to those described in Chapter 21 for substances such as benzene. Consider gold

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[5] S. I. Grossman, *Calculus*, 3rd ed., Academic Press, Orlando, FL, 1984, p. 518ff, or any standard calculus text.

[6] N. Davidson, *op. cit.*, p. 359 (note 3).

as an example. A gold atom in its ground state has filled subshells except for one electron in the 6*s* subshell. We use the orbitals in filled shells as nonbonding orbitals and construct N delocalized LCAOMOs using the 6*s* orbitals from the N atoms of the crystal as basis functions. The system is modeled as a collection of ions (“cores”) and a “sea” of mobile electrons occupying the delocalized LCAOMOs. These N LCAOMOs will have slightly different energies, constituting a *band* of closely spaced energy levels, analogous to the four delocalized pi energy levels of a benzene molecule, but with many more members and larger degeneracies. As with these benzene LCAOMOs, the lower-energy LCAOMOs have more bonding character and the higher-energy LCAOMOs have more antibonding character.

At low temperature $N/2$ orbitals will be occupied by pairs of electrons with opposite spins. The occupied orbitals have more bonding character than antibonding character, like the occupied pi orbitals in benzene. The crystal is therefore held together very strongly, as illustrated by the fact that gold melts at a high temperature (1063°C).

Exercise 28.9

Explain in simple terms why mercury, which has two 6*s* electrons, melts at a low temperature (−38.4°C). A more complete discussion of the low melting temperature of mercury involves relativistic quantum mechanics.[7]

The Band Theory of the Electronic Structure of Solid

In our crude description of the gold crystal, we used the atomic orbitals in filled shells as nonbonding orbitals and constructed a band of delocalized LCAOMOs from the 6*s* orbitals. We can also make delocalized LCAOMOs from all of the orbitals. There is a band made from the 1*s* orbitals, another band from the 2*s* orbitals, a third band from the 2*p* orbitals, and so on. Figure 28.10 shows the X-ray photoelectron spectrum of a gold foil, in which the energies of several bands can be seen, as well as the 1*s* band from a carbon impurity. The subscript on each band label is the value of j, the quantum number for the total angular momentum of one electron.

Electrical Conductors and Insulators

If a band is created from orbitals that are partly filled in the separated atoms, as in the 6*s* band of gold, the resulting band is only partly filled. There will be a number of vacant orbitals in the band for electrons to move into. The electrons can easily move from one orbital to another, and the crystal will be an electrical *conductor*. If the highest occupied band in a crystal is completely filled, an electron can move from one orbital to another in the band only if another electron vacates the second orbital. If there is no way to create a vacancy the crystal will not conduct electricity, and is an *insulator*.

Semiconductors

In a semiconductor there is generally a band that is completely filled in the ground state and a *band gap* between the highest energy of this band and the lowest energy

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[7] P. Pyykkö, *Chem. Rev.*, **88**, 563 (1988).

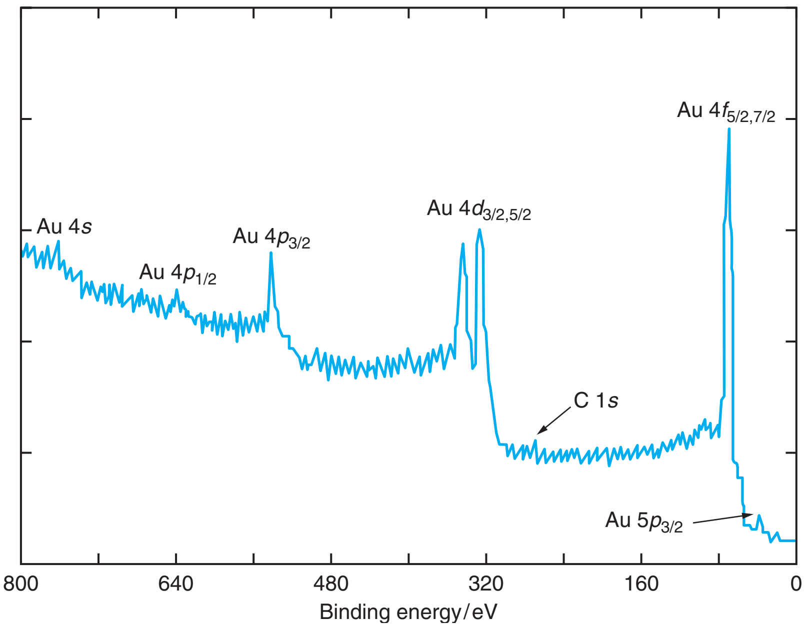

Figure 28.10 X-Ray Photoelectron Spectrum of Gold. Each peak is labeled with the subshell and the value of J, the quantum number for the total angular momentum. Courtesy of Dr. Kevin Ogle.

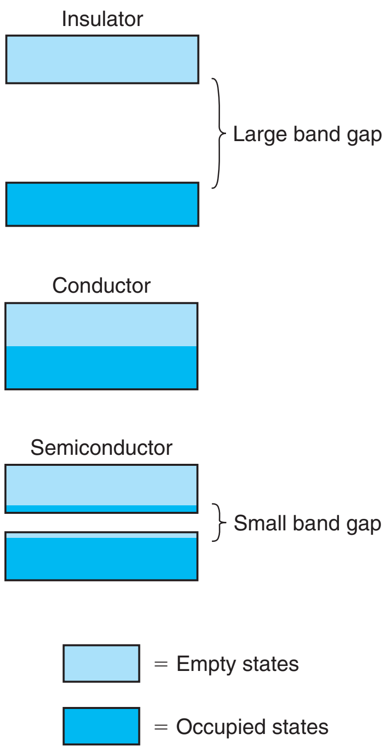

Figure 28.11 Bands of Orbital Energies in a Hypothetical Insulator, Conductor, and Semiconductor. The top figure, for an insulator, shows the band gap, which is large compared with k_BT. The middle figure, for a conductor, shows a partly filled band, so that there is no band gap. The bottom figure, for a semiconductor, shows a band gap that is not large compared with k_BT.

of an upper band that is empty in the ground state. If the band gap between the lower band and the upper band is not large compared with $k_\mathrm{B}T$, some electrons from the lower-energy band will occupy states of the upper band and the crystal will conduct some electricity. Figure 28.11 schematically depicts the band occupations in insulators, conductors, and semiconductors.

Electrons are fermions. If we neglect the interaction between the electrons the probability distribution of states is given by Eq. (26.5-4):

$$f(\varepsilon_i) = \frac{e^{(\mu-\varepsilon_i)/k_\mathrm{B}T}}{1 + e^{(\mu-\varepsilon_i)/k_\mathrm{B}T}} = \frac{1}{e^{(\varepsilon_i-\mu)/k_\mathrm{B}T} + 1} \tag{28.3-1}$$

The value of μ, the chemical potential of the electrons, is called the *Fermi level*, and is denoted by ε_F. At 0 K all of the states with energies at or below the Fermi level will be fully occupied and those above the Fermi level will be vacant. If the temperature is increased from 0 K, some of the states with energies just below the Fermi level become unpopulated, and some of the states just above the Fermi level become populated. The range of energy over which the probability distribution ranges from roughly unity to nearly zero is approximately equal to $k_\mathrm{B}T$. Figure 28.12 schematically shows the fermion probability distribution for 0 K and for two nonzero temperatures.

If the Fermi level lies at the top of a band or between two bands the crystal will be an insulator at 0 K. If the band gap is not large compared with $k_\mathrm{B}T$ for some nonzero temperature, some of the highest-energy states in the filled band will be vacant, some of the low-lying states in the first vacant band will be occupied, and the crystal will

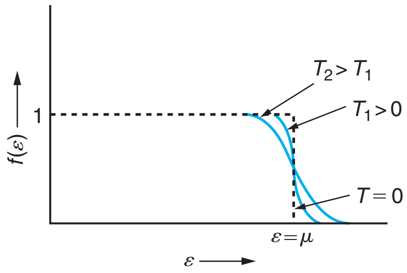

Figure 28.12 The Fermion Probability Distribution for 0 K and for Two Nonzero Temperatures.

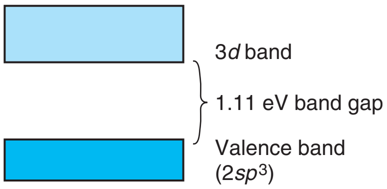

Figure 28.13 The Electron Bands of Silicon (Schematic). The band gap, 1.11 eV, is roughly 43 times as large as k_BT at room temperature.

be a semiconductor. If the band gap is large compared with k_BT, there will be little chance that electrons can move to the vacant band, and the crystal will be an insulator at nonzero temperature.

Silicon is the most widely used semiconductor. The structure of the silicon crystal is similar to that of diamond, with each silicon atom covalently bonded to four other silicon atoms that are arranged tetrahedrally around it. To a first approximation the bonding orbitals can be approximated as localized bonding LCAOMOs made from two $3sp^3$ hybrid orbitals on adjacent atoms. This can be considered to be a filled band of orbitals. There is a band of delocalized orbitals that can be represented as linear combinations of the 3*d* orbitals, which are vacant in the separated atoms. Figure 28.13 shows an approximate energy level diagram of silicon. The band gap between the bonding orbitals and the 3*d* band is approximately equal to 1.1 eV. At 0 K, no electrons in the silicon crystal would occupy orbitals in the 3*d* band, and silicon would be an insulator like diamond. Near room temperature, this band gap is still much larger than k_BT, and very few electrons in silicon occupy orbitals in this band. Pure silicon conducts only a very small amount of electricity at room temperature.

Silicon is frequently "doped" with other substances. If aluminum atoms replace some silicon atoms, there are "holes" in the bonding orbitals, because aluminum has 13 electrons whereas silicon has 14. This makes the doped silicon into a *p-type semiconductor* that would conduct some electricity even at 0 K. (The "p" designation refers to the "positive holes" that can be thought of as moving around.) If arsenic atoms replace silicon atoms, the doped silicon becomes an *n-type semiconductor*, because arsenic atoms have five valence electrons instead of silicon's four valence electrons, and the fifth electron would be found in the 3*d* band. (The "n" designation refers to the conduction by negative electrons.)

Ferromagnetism

Nickel is ferromagnetic (can be permanently magnetized), but copper is not. We present a few facts about ferromagnetism, and additional information can be found in solid-state chemistry and physics textbooks.[8] Figure 28.14 shows the 4*s* and 3*d* bands for both nickel and copper. In both elements, the two bands overlap in energy with no band gap. In copper, which has one 4*s* electron and ten 3*d* electrons in the isolated atom ground state, the Fermi level is at the middle of the 4*s* band (the higher-energy band). At 0 K the 3*d* band is fully occupied and the 4*s* band is 50% occupied. Nickel has two 4*s* electrons and eight 3*d* electrons. The Fermi level is lower and lies below the top of the 3*d* band. The spin-up states of the 3*d* band have a slightly lower energy than the spin-down states, due to "exchange interaction," and at 0 K there is an average of 0.54 hole per atom in the spin-down states of the 3*d* band and an average of 2.54 electrons per atom in the 4*s* band. The spins of the excess spin-up electrons interact strongly with each other, and tend to form domains in the crystal in which all of the excess spins are aligned parallel to each other. These domains can be aligned to produce a permanent macroscopic magnetic moment, a characteristic of *ferromagnetism*. Above 631 K, the *Curie temperature* for nickel, thermal energy overrides the exchange interaction, and the ferromagnetism disappears, with an average of 0.27 hole per atom in each of the 3*d* spin-up and 3*d* spin-down states, as shown in the last part of the figure.

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[8] N. B. Hannay, *Solid-State Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1967, p. 38.

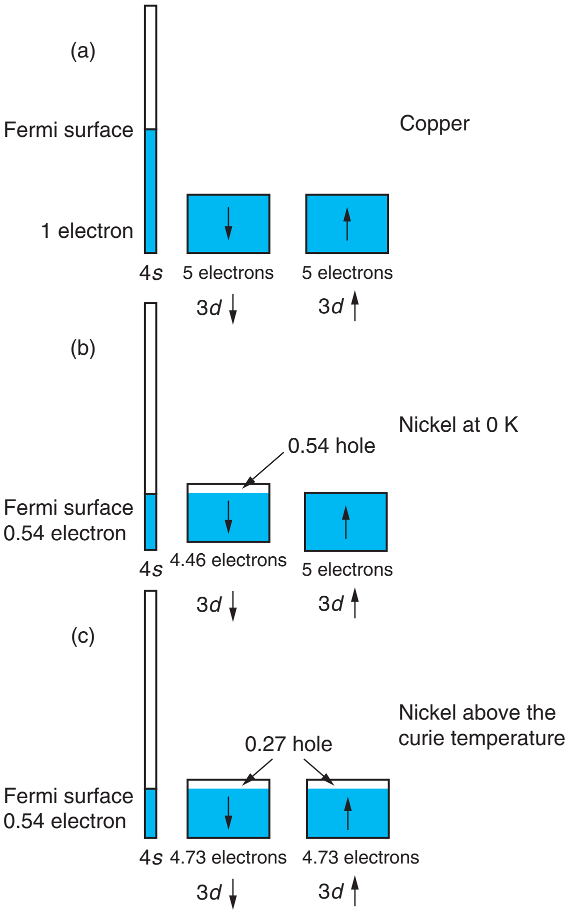

Figure 28.14 The 4*s* and 3*d* Bands of Nickel and Copper. The vertical axis in each diagram represents the electronic energy. From N. B. Hannay, *Solid-State Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1967, p. 38.

The Free-Electron Theory

This simple theory is based on the assumption that the mobile electrons in a solid can be represented as a gas of noninteracting fermions. The orbitals for the electrons are free-particle wave functions like those of Eq. (15.3-41):

$$\psi = e^{i\mathbf{k}\cdot\mathbf{r}} = e^{i(k_x x + k_y y + k_z z)} \tag{28.3-2}$$

The vector **k** is called the *wave vector* and the vector **r** is the position vector of the electron. The scalar product (dot product) $\mathbf{k} \cdot \mathbf{r}$ is equal to $k_x x + k_y y + k_z z$, as described in Appendix B.

Consider a cubic region with dimensions L by L by L that is part of a very large crystal. We impose *periodic boundary conditions*, which means that

$$\psi(x + L, y, z) = \psi(x, y, z) \tag{28.3-3}$$

with similar equations for y and z. To satisfy this condition,

$$k_x = 2\pi n_x/L, \quad k_y = 2\pi n_y/L, \quad k_z = 2\pi n_z/L \tag{28.3-4}$$

where n_x, n_y, and n_z are integers. The situation is similar to that of a particle in a three-dimensional box, except that these integers are not required to be positive.

The kinetic energy of the electron is given by

$$\varepsilon_k = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) = \frac{\hbar^2}{2m} k^2 \tag{28.3-5}$$

where m is the electron mass and $k^2 = k_x^2 + k_y^2 + k_z^2$. We let n equal to $\sqrt{n_x^2 + n_y^2 + n_z^2}$ and consider a small increment in n, denoted by dn. The number of sets of integers in the range dn is similar to that in Eq. (28.2-14):

$$\text{Number of sets in the range } (n, n + dn) = 4\pi n^2 dn \tag{28.3-6}$$

This number is 8 times as large as that given by Eq. (28.2-14) to account for the occurrence of negative integers. There are two possible spin states for each electron so we double this expression to get the number of states. From Eq. (28.3-4) for a cubical crystal of dimension L:

$$\text{Number of states in the range } dk = g(k)dk = \frac{L^3 k^2}{\pi^2} dk \tag{28.3-7}$$

Using Eq. (28.3-5) and the chain rule (see Appendix B),

$$\text{Number of states in } d\varepsilon = \frac{L^3 \sqrt{2}\, m^{3/2}}{\pi^2 \hbar^3} \varepsilon^{1/2} d\varepsilon \tag{28.3-8a}$$

$$\begin{pmatrix}\text{Number of states in} \\ d\varepsilon \text{ per unit volume}\end{pmatrix} = g(\varepsilon)d\varepsilon = \frac{\sqrt{2}\, m^{3/2}}{\pi^2 \hbar^3} \varepsilon^{1/2} d\varepsilon \tag{28.3-8b}$$

This degeneracy is depicted in Figure 28.15. At 0 K, electrons will occupy all of the states from zero energy up to the Fermi level. This occupation is shown by the shaded area in Figure 28.15. At nonzero temperatures the occupation of states is given by Eq. (28.3-1), and the occupation of the levels is given by $g(\varepsilon)\, f(\varepsilon)$, represented by the curve in the figure.

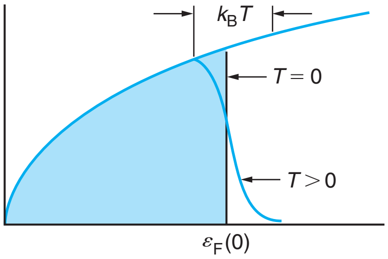

Figure 28.15 The Degeneracy of Energy Levels in the Free-Electron Theory. From N. B. Hannay, *Solid-State Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1967, p. 26.

We denote the number of mobile electrons per unit volume by $\mathscr{N}$:

$$\mathscr{N} = \int_0^\infty g(\varepsilon)\, f(\varepsilon) d\varepsilon \tag{28.3-9}$$

At 0 K, each of the states with energy less than the Fermi level is occupied by one electron, and all of the states above the Fermi level are vacant. At 0 K the upper limit of the integral can be changed from infinity to the Fermi level and $f(\varepsilon)$ can be replaced by unity:

$$\mathscr{N} = \frac{\sqrt{2} m^{3/2}}{\pi^2 \hbar^3} \int_0^{\mu_0} \varepsilon^{1/2}\, d\varepsilon = \frac{1}{3\pi^2}\left(\frac{2m\mu_0}{\hbar^2}\right)^{3/2} \tag{28.3-10}$$

The Fermi level at 0 K is

$$\mu_0 = \varepsilon_{F0} = (3\pi^2 \mathscr{N})^{2/3} \frac{\hbar^2}{2m} = (5.842 \times 10^{-38}\,\mathrm{J\,m^2})\mathscr{N}^{2/3} \tag{28.3-11}$$

A typical metal has a density of mobile electrons approximately equal to $10^{28}\ \mathrm{m}^{-3}$, corresponding to a value of the Fermi level equal to several electron volts.

EXAMPLE 28.7

The density of copper is $8960\,\mathrm{kg\,m^{-3}}$. Find the density of mobile electrons, assuming one mobile electron from each atom and find the zero-temperature value of the Fermi level in joules and in electron volts.

Solution

$$\mathcal{N} = \frac{(8960\,\mathrm{kg\,m^{-3}})(6.022\times 10^{23}\,\mathrm{mol^{-1}})}{0.063546\,\mathrm{kg\,mol^{-1}}} = 8.49\times 10^{28}\,\mathrm{m^{-3}}$$

$$\varepsilon_{\mathrm{F0}} = (5.842\times 10^{-38}\,\mathrm{J\,m^2})(8.49\times 10^{28}\,\mathrm{m^{-3}})^{2/3} = 1.129\times 10^{-18}\,\mathrm{J} = 7.04\,\mathrm{eV}$$

In the free-electron theory the Fermi level for nonzero temperature is approximately[9]

$$\mu = \varepsilon_{\mathrm{F}} \approx \varepsilon_{\mathrm{F0}}\left(1 - \frac{(\pi k_{\mathrm{B}}T)^2}{12\varepsilon_{\mathrm{F0}}^2}\right) \tag{28.3-12}$$

where $\varepsilon_{\mathrm{F0}}$ is the Fermi level at 0 K.

The energy per unit volume of the free-electron gas at 0 K is

$$U_0 = \int_0^{\varepsilon_{\mathrm{F0}}} \varepsilon g(\varepsilon)d\varepsilon = \frac{1}{5\pi^2}\left(\frac{2m}{\hbar^2}\right)^{3/2}\varepsilon_{\mathrm{F0}}^{5/2} = \frac{3\mathcal{N}\varepsilon_{\mathrm{F0}}}{5} \tag{28.3-13}$$

where m is the electron mass. If $T << \varepsilon_{\mathrm{F}}/k_{\mathrm{B}}$, the energy at a nonzero temperature is approximately[10]

$$U_{\mathrm{el}} \approx U_0 + \frac{\mathcal{N}\pi^2 k_{\mathrm{B}}^2 T^2}{4\varepsilon_{\mathrm{F}}} \tag{28.3-14}$$

The heat capacity per unit volume is

$$C_{\mathrm{el}} \approx \left(\frac{\partial U}{\partial T}\right)_V = \frac{\mathcal{N}\pi^2 k_{\mathrm{B}}^2 T}{2\varepsilon_{\mathrm{F}}} \tag{28.3-15}$$

If the electron gas obeyed classical mechanics the heat capacity would be $3k_{\mathrm{B}}/2$ per electron so that

$$C_{\mathrm{el}} = \frac{\pi^2 k_{\mathrm{B}}T}{3\varepsilon_{\mathrm{F}}} C_{\mathrm{class}} \tag{28.3-16}$$

The quantum mechanical electron gas is sometimes called the *degenerate electron gas* because its heat capacity is “degenerated” from the classical value by the factor given in Eq. (28.3-16). This meaning of the word “degenerate” is different from the usage in previous chapters, where it applied to the number of states in an energy level.

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[9] J. S. Blakemore, *op. cit.*, p. 176 (note 4).

[10] J. S. Blakemore, *op. cit.*, p. 176 (note 4).

EXAMPLE 28.8

a. Find the electronic contribution to the heat capacity of copper at 15 K, using the same assumptions and data as in Example 28.7.

b. Find the ratio of the electronic contribution to the classical prediction of the electronic contribution.

c. Find the ratio of the electronic contribution to the lattice vibration contribution for copper at 15 K, using the Debye theory result with the Debye temperature 315 K.

Solution

a. From Example 28.7, $\varepsilon_{F0} = 1.129 \times 10^{-18}$ J.

$$\begin{aligned}\varepsilon_F &= \varepsilon_{F0}\left(1 - \frac{(\pi k_B T)^2}{12\varepsilon_{F0}^2}\right)\\ &= 1.129 \times 10^{-18}\,\mathrm{J}\left(1 - \frac{[\pi(1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}})(15\,\mathrm{K})]^2}{12(1.129 \times 10^{-18}\,\mathrm{J})^2}\right)\\ &= 1.129 \times 10^{-18}\,\mathrm{J}\end{aligned}$$

This value is not significantly different from ε_{F0}. From Equation (28.3-15) the electronic contribution to the heat capacity per unit volume is

$$\begin{aligned}C_{\mathrm{elec}} &= \frac{\pi^2 \mathcal{N} k_B^2 T}{2\varepsilon_F} = \frac{\pi^2(8.49 \times 10^{28}\,\mathrm{m^{-3}})(1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}})^2(15\,\mathrm{K})}{2(1.129 \times 10^{-18}\,\mathrm{J})}\\ &= 1.06 \times 10^3\,\mathrm{J\,K^{-1}\,m^{-3}}\end{aligned}$$

$$C_{\mathrm{m,elec}} = \frac{(1.06 \times 10^3\,\mathrm{J\,K^{-1}\,m^{-3}})(0.063546\,\mathrm{kg\,mol^{-1}})}{8960\,\mathrm{kg\,m^{-3}}} = 0.00753\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

b. Ratio $= \dfrac{\pi^2 k_B T}{3\varepsilon_F} = \dfrac{\pi^2(1.38 \times 10^{-23}\,\mathrm{J\,K^{-1}})(15\,\mathrm{K})}{3(1.129 \times 10^{-18}\,\mathrm{J})} = 0.0060$

c. At 15 K,

$$\begin{aligned}C_{\mathrm{Debye}} &= \frac{9Nk_B}{n_D^3}\int_0^{\nu_D}\left(\frac{h\nu}{k_B T}\right)^2 \frac{e^{h\nu/k_B T}\,\nu^2}{\left(e^{h\nu/k_B T} - 1\right)^2}\,d\nu = 3Nk_B D\left(\frac{\theta_D}{T}\right)\\ u_D &= \frac{\theta_D}{T} = \frac{315\,\mathrm{K}}{15\,\mathrm{K}} = 21.0\end{aligned}$$

The integral must be evaluated numerically or by use of tabulated values.[a] The value of the Debye function for 15 K is

$$D(21.0) = \frac{3}{u_D^3}\int_0^{21.0} u^4 \frac{e^u}{(e^u - 1)^2}\,du = \frac{3}{(21.0)^3}(26.0) = 0.0084$$

$$C_{V,\mathrm{m,Debye}} = 3RD = 3(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}})(0.0084) = 0.21\,\mathrm{J\,K^{-1}\,mol^{-1}}$$

The ratio of the electronic contribution to the vibrational contribution is

$$\text{Ratio} = \frac{0.00753\ \mathrm{J\,K^{-1}\,mol^{-1}}}{0.21\ \mathrm{J\,K^{-1}\,mol^{-1}}} = 0.036$$

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[a] K. S. Pitzer and L. Brewer, *Thermodynamics*, McGraw-Hill, New York, 1961, p. 660.

PROBLEMS

Section 28.3: The Electronic Structure of Crystalline Solids

28.21 Construct an accurate graph of the fermion distribution, Eq. (28.3-1), using $\varepsilon/k_\mathrm{B}T$ as the independent variable and assuming (a) that $T = \mu/10\,k_\mathrm{B}$, (b) that $T = \mu/k_\mathrm{B}$, and (c) that $T = 10\,\mu/k_\mathrm{B}$.

28.22 Evaluate the Fermi level for copper at 298 K using Eq. (28.3-12). Find the percent error of using Eq. (28.3-11).

28.23 **a.** Evaluate the Fermi level of silver at 298.15 K using Eq. (28.3-12).

b. Find the electronic contribution to the molar heat capacity of silver at 15.00 K and at 298.15 K.

28.24 The Fermi level for sodium is equal to 3.1 eV.

a. Find the number of mobile electrons per cubic meter and per mole. The density of sodium is 0.971 g cm^{-3}. State any assumptions.

b. Find the speed of electrons that have kinetic energy equal to the Fermi level for sodium.

28.25 In silicon, the band gap between the highest filled band (the valence band) and the lowest vacant band (the conduction band) is equal to 1.11 eV.

a. Assuming the Boltzmann distribution, find the ratio of the population of the lowest conduction band states and the highest valence band states at 300 K.

b. Assuming the fermion distribution with the Fermi level at the top of the valence band, repeat part a.

28.26 Calculate the electronic contribution to the heat capacity of copper at 298.15 K. Find the percent contribution to the total heat capacity, using the law of Dulong and Petit for the vibrational contribution.

28.4 Electrical Resistance in Solids

An electric current in a metallic conductor consists of moving electrons. The Drude model[12] pictures a metal as consisting of mobile electrons and positively charged "**cores**," which are the ions produced when the conduction electrons are removed from the atoms. Dilute occupation of the electron states is assumed. The electrons are pictured as colliding with the cores, impeding their motion. We define a period of time τ by

$$(\text{Collision probability per unit time}) = \frac{1}{\tau} \tag{28.4-1}$$

Let $\mathcal{N}(t)$ be the number of electrons per unit volume that have not yet collided with a core at time t. The rate of change of $\mathcal{N}$ is given by

$$\frac{d\mathcal{N}}{dt} = -\frac{1}{\tau}\mathcal{N}$$

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[12] J. S. Blakemore, *op. cit.*, p. 158ff (note 4); D. Tabor, *Gases, Liquids and Solids*, 2nd ed., Cambridge University Press, Cambridge, England, 1979, p. 188ff.

We divide this equation by $\mathcal{N}$, multiply by dt, and perform an integration from $t = 0$ to $t = t'$:

$$\frac{1}{\mathcal{N}}\frac{d\mathcal{N}}{dt}dt = \frac{1}{\mathcal{N}}d\mathcal{N} = -\frac{1}{\tau}dt$$

$$\int_{\mathcal{N}(0)}^{\mathcal{N}(t')}\frac{1}{\mathcal{N}}d\mathcal{N} = -\frac{1}{\tau}\int_0^{t'} dt$$

$$\ln\left(\frac{\mathcal{N}(\tau)}{\mathcal{N}(0)}\right) = -\frac{t}{\tau}$$

$$\mathcal{N}(t) = \mathcal{N}(0)\, e^{-t/\tau} \tag{28.4-2}$$

where we replace t' by t in the equation for $\mathcal{N}(t)$.

In an external electric field $\mathscr{E}$ the force on an electron is $\mathscr{e}\mathscr{E}$. The Drude model assumes that we can apply classical mechanics to the electrons. Classical mechanics cannot successfully be applied to individual electrons, but it can sometimes be an adequate approximation for some average properties. From Newton's second law the electric field produces a constant acceleration equal to $-\mathscr{e}\mathscr{E}/m$. If the electron does not undergo a collision, the change in velocity of an electron in time t is

$$\Delta\mathbf{v}(t) = -\frac{\mathscr{e}\mathscr{E}t}{m} \tag{28.4-3}$$

This change in velocity is imposed on whatever velocity the electron originally had. Before the field was imposed no current was flowing, so that the average velocity of the conduction electrons vanished. After the change in velocity is imposed on every electron, Eq. (28.4-3) represents the average final velocity. The average distance traveled during the time from 0 to time t' is obtained by integrating Eq. (28.4-3) from time 0 to time t':

$$\mathbf{r}(t') = -\frac{\mathscr{e}\mathscr{E}t'^2}{2m} \tag{28.4-4}$$

We assume that the average velocity returns to zero value after the collision.

The rate at which electrons are undergoing collisions at time t is

$$\frac{d\mathcal{N}}{dt} = -\frac{\mathcal{N}(t)}{\tau} = -\frac{\mathcal{N}(0)}{\tau}\, e^{-t/\tau} \tag{28.4-5}$$

The contribution of all electrons to the "electron transport" (equivalent to electrons per unit area per second times the time of transport) is

$$\int_0^{\infty}\mathbf{r}(t)\frac{d\mathcal{N}}{dt}dt = \frac{-\mathscr{e}\mathscr{E}n(0)}{2m}\int_0^{\infty} t^2 e^{-t/\tau}dt = -\frac{\mathscr{e}\mathscr{E}\mathcal{N}(0)^2}{m} \tag{28.4-6}$$

This formula for the electron transport is the same as if $\mathcal{N}(0)$ electrons per unit volume all had the "drift velocity" given by Eq. (28.4-3) for an acceleration time equal to τ,

$$\mathbf{v}_{\text{drift}} = -\frac{\mathscr{e}\mathscr{E}\tau}{m} \tag{28.4-7}$$

and traveled for a time equal to τ. The electric current per unit area, $\mathbf{j}$, is equal to the charge on one electron, $-\mathscr{e}$, times the electron flux

$$\mathbf{j} = (-\mathscr{e})\left(-\frac{\mathscr{e}\mathscr{E}\mathcal{N}(0)\tau}{m}\right) = \frac{\mathcal{N}\mathscr{e}^2\tau}{m}\mathscr{E} \tag{28.4-8}$$

This equation conforms to Ohm's law with the conductivity given by

$$\boxed{\sigma = \frac{\mathcal{N} e^2 \tau}{m}} \tag{28.4-9}$$

EXAMPLE 28.9

From the density of gold and assuming that one conduction electron comes from each atom, the density of conduction electrons in gold is equal to $5.90 \times 10^{28}\ \mathrm{m}^{-3}$. The resistivity (reciprocal of the conductivity) is equal to 2.24 microohm cm at 20°C. Find the value of τ that corresponds to these values.

Solution

$$\sigma = \frac{1}{2.24\,\text{microohm cm}}\left(\frac{10^6\,\text{microohm}}{1\,\text{ohm}}\right)\left(\frac{100\,\text{cm}}{1\,\text{m}}\right)$$

$$= 4.46 \times 10^7\,\text{ohm}^{-1}\,\text{m}^{-1}$$

$$\tau = \frac{m\sigma}{\mathcal{N} e^2} = \frac{(9.1 \times 10^{-31}\,\text{kg})(4.46 \times 10^7\,\text{ohm}^{-1}\,\text{m}^{-1})}{(5.90 \times 10^{28}\,\text{m}^{-3})(1.60 \times 10^{-19}\,\text{C})^2} = 2.7 \times 10^{-14}\,\text{s}$$

EXAMPLE 28.10

a. In classical gas kinetic theory, the root-mean-square speed of particles of mass m is given by

$$v_{\mathrm{rms}} = \sqrt{\frac{3k_{\mathrm{B}}T}{m}}$$

Find the mean speed of electrons at 293 K using this formula.

b. If a current per unit area of $1.00 \times 10^6\ \mathrm{A\ m^{-2}}$ is flowing in a sample of gold at 293 K, find the mean drift speed. Find the ratio of the mean drift speed to the root-mean-square speed of electrons at this temperature.

Solution

a. $v_{\mathrm{rms}} = \left(\dfrac{3(1.3807 \times 10^{-23}\,\mathrm{J\,K^{-1}})(293\,\mathrm{K})}{9.1094 \times 10^{-31}\,\mathrm{kg}}\right)^{1/2} = 1.154 \times 10^5\,\mathrm{m\,s^{-1}}$

b. From Example 28.9 we take the density of mobile electrons in gold to be $5.90 \times 10^{28}\ \mathrm{m}^{-3}$. The current in electrons $\mathrm{m}^{-2}\ \mathrm{s}^{-1}$ is

$$(1.00 \times 10^6\,\mathrm{C\,s^{-1}\,m^{-2}})\left(\frac{1\ \text{electron}}{1.6022 \times 10^{-19}\,\mathrm{C}}\right) = 6.24 \times 10^{24}\,\text{electrons}\,\mathrm{m^{-2}\,s^{-1}}$$

The drift speed times the density of mobile electrons equals the number of electrons passing per second.

$$v_{\mathrm{drift}} = \frac{6.24 \times 10^{24}\,\text{electrons}\,\mathrm{m^{-2}\,s^{-1}}}{5.90 \times 10^{28}\,\mathrm{m^{-3}}} = 1.06 \times 10^{-4}\,\mathrm{m\,s^{-1}}$$

The ratio of the drift speed to the average speed is

$$\text{Ratio} = \frac{1.06 \times 10^{-4}\ \text{m s}^{-1}}{1.154 \times 10^{5}\ \text{m s}^{-1}} = 9.2 \times 10^{-10}$$

The expression for the conductivity can also be expressed in terms of the mean free path between collisions. The mean free path is approximately given by

$$\lambda = \langle v \rangle \tau \tag{28.4-10}$$

where $\langle v \rangle$ is an average speed of the electrons. This is not the average drift speed, which is a small speed superimposed on a large speed. It is an average of the actual speeds, which is nearly the same as the equilibrium value, because of the smallness of the drift velocity. If we use the root-mean-square speed of Example 28.10, the conductivity is

$$\sigma = \frac{\mathcal{N} e^2 \lambda}{(3mk_{\text{B}}T)^{1/2}} \tag{28.4-11}$$

EXAMPLE 28.11

Find the mean free path for electrons in gold at 20°C.

Solution

$$\lambda = \frac{(3mk_{\text{B}}T)^{1/2}\sigma}{\mathcal{N} e^2}$$

$$= \frac{[3(9.11 \times 10^{-31}\ \text{kg})(1.38 \times 10^{-23}\ \text{J K}^{-1})(293\ \text{K})]^{1/2}(4.46 \times 10^{7}\ \text{ohm}^{-1}\ \text{m}^{-1})}{(5.90 \times 10^{28}\ \text{m}^{-3})(1.60 \times 10^{-19}\ \text{C})}$$

$$= 3.1 \times 10^{-9}\ \text{m}$$

This value seems reasonable, as it is roughly 10 lattice distances, and an electron might pass a number of cores before it collides with one.

The Drude model is a crude model, but it contains the accepted mechanism for electrical resistance in solids, which is the effect of collisions with the cores of the crystal. There are a number of more sophisticated theories than the Drude theory. However, the results of these theories are similar in their general form to Eq. (28.4-9). The major differences are in the interpretation of the quantities $\mathcal{N}$, τ, and m.[13] One problem with the Drude theory is that the conductivities of most common metals are found experimentally to be approximately inversely proportional to the temperature, instead of being inversely proportional to the square root of the temperature, as in Eq. (28.4-11). One can rationalize this by arguing that the mean free path should decrease as the temperature rises, because of the increased vibrational amplitude of the cores, making them into targets with larger effective sizes at higher temperature.

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[13] J. S. Blakemore, *op. cit.*, p. 162ff (note 4).

Superconductivity

Heike Kamerlingh Onnes, 1853–1926, was a Dutch physicist working at the University of Leiden when he discovered superconductivity. He essentially invented low-temperature physics, and received the 1913 Nobel Prize in physics for this work.

The Meissner effect is named for Walter Meissner, 1882–1974, who with Robert Ochsenfeld discovered the effect in 1933.

Superconductivity was discovered in 1911 by Kamerlingh Onnes,[14] who found that the conductivity of solid mercury suddenly rose to a value at least as large as $10^{15}\,\mathrm{ohm}^{-1}\,\mathrm{m}^{-1}$ (and possibly infinite) when the mercury was cooled below 4.2 K. Onnes coined the name "superconductivity" for the phenomenon. Since that time, other substances have been found to exhibit superconductivity, generally with a transition temperature below 23 K. Silicon has recently been found to exhibit super conductivity when doped with boron.[15] It has a transition temperature of 0.35 K.

A superconducting material rejects a magnetic field. That is, within the surface of the sample of material that is exposed to a magnetic field, a compensating magnetic field is generated that exactly cancels the magnetic field within the material, except for a surface layer of thickness 10 to 100 nm. This effect is called the *Meissner effect*, and can cause the levitation of a magnet above a superconductor. However, if the magnetic field is increased above a certain critical value, which depends on temperature and on the substance, the superconductivity disappears.

There is a generally accepted theory of superconductivity in metals.[16] This theory is based on the notion that under certain conditions the electrons interact with the lattice of the solid in such a way that two electrons form a pair with opposite spins having a lower energy than two single uncorrelated electrons. The pair of electrons is called a *Cooper pair*. Unless the pair is broken up, it is not possible for one of the electrons to be scattered by a nucleus. Below a temperature called the *transition temperature*, there is not enough thermal energy to break up the pair, so that scattering does not occur and an electrical current can flow without observable resistance.

Beginning in 1986, a number of ceramic compounds were discovered that exhibit superconductivity with transition temperatures as high at 138 K (−135°C).[17] These "high-temperature" semiconductors are oxides, containing copper along with two or three other metals, such as barium and yttrium, or thallium, barium, and calcium. The first substance to exhibit a transition temperature above that of boiling liquid nitrogen (77 K) was $\mathrm{YBa_2Cu_3O}_x$, where x ranges from 6.5 to 7.2. If x were equal to 9, the substance could have the crystal structure of a perovskite, with six oxygens surrounding each copper and the copper atoms in layers.[18] The crystal has four oxygen atoms around each copper atom, all in the plane of the copper atoms.[19]

In 1988, $\mathrm{Tl_2Ca_2Ba_2Cu_3O}_{10+y}$, where $y < 1$, was found to have a transition temperature of 125 K. The crystal structure of this compound was determined, and found to have planes containing copper and oxygen atoms, as well as planes containing thallium and oxygen atoms.[20] The theory of Cooper pairs does not seem adequate to explain the superconductivity of the high-temperature superconductors, and the relationship of their structures to their superconductivity is apparently not yet clear. Blackstead and Dow have proposed a theory according to which the oxygen atom layer is the superconducting layer, with the oxygens in an undercharged state and compressed into a quasi-metallic state.[21] A convenient website about superconductivity is

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[14] H. Kamerlingh Onnes, *Akad. van Wetenschappen (Amsterdam)*, **14**, 113 (1911).

[15] E. Bustarret, *et al.*, *Nature*, **444**, 465 (2006).

[16] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.*, **108**, 1175 (1957). This theory is known as the BCS theory.

[17] A. M. Thayer, *Chem. Eng. News*, **67**(48), 9 (Nov. 27, 1989).

[18] See the website http://www.superconductors.org/.

[19] R. Dagani, *Chem. Eng. News*, **65**(19), 7 (May 11, 1987).

[20] S. S. P. Parkin, *Phys. Rev. Letters*, **61**, 750 (1988).

[21] H.A. Blackstead and J.D. Dow, *Phys. Rev. B*, **51**, 11830 (1995).

http://www.superconductors.org. It was reported on this site in 2007 that the highest transition temperature observed at that time was 138 K.

PROBLEMS

Section 28.4: Electrical Resistance in Solids

28.27 Without looking up the value, estimate the resistivity of copper. Look up the correct value and compare your estimate to it.

28.28 The resistivity of silver at 20°C is 1.59 microohm cm and its density is 10.5 g cm^{-3}. Assume that there is one conduction electron per atom.

a. Find the value of τ.

b. Find the mean free path for electrons in silver.

c. Give a simple explanation for the comparison of the mean free path of electrons in silver and gold (see Example 28.11).

28.29 The resistivity of solid mercury at −39.2°C is equal to 25.5 microohm cm, and that of liquid mercury at −36.1°C is equal to 80.6 microohm cm. Give a qualitative explanation for this behavior.

28.30 **a.** Assume that an electric field can be instantaneously turned off. Estimate the length of time for a current to drop to $1/e$ of its initial value when an electric field is instantaneously turned off in gold at 20°C.

b. A current has been flowing in a superconducting ring since about 1940, without an applied electric field. Estimate a minimum value of the conductivity.

28.5 The Structure of Liquids

When a solid melts to form a liquid, its lattice structure suddenly collapses, although vestiges of this structure remain. The molar volume of most substances increases by 5% to 15%, although that of water decreases by about 8%. In monatomic solids such as argon each atom has 12 nearest neighbors. When the solid melts, the average number of nearest neighbors drops from 12 to a value between 10 and 11. In liquids there are generally numerous small vacant spaces that move around and change their sizes as the nearest neighbor molecules move. When this disorder is passed on to additional "shells" of nearest neighbors, next-nearest neighbors, and so on, the long-range order of the solid is absent.

The Classical Statistical Mechanics Approach to Liquid Structure

Many of the equilibrium properties of such systems can be obtained through the two-body reduced coordinate distribution function and the radial distribution function, defined in Eqs. (27.6-5) and (27.6-7). There are a number of theories that are used to calculate approximate radial distribution functions for liquids, using classical statistical mechanics.[22] Some of the theories involve approximate integral equations. Others are "perturbation" theories similar to quantum mechanical perturbation theory (see Section 19.3). These theories take a hard-sphere fluid or other fluid with purely repulsive forces as a zero-order system and consider the attractive part of the forces to be a perturbation.[23]

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[22] H. L. Friedman, *A Course in Statistical Mechanics*, Prentice-Hall, Englewood Cliffs, NJ, 1985, Chs. 7, 8, and 9; D. A. McQuarrie, *Statistical Mechanics*, Harper & Row, New York, 1976, Chs. 13 and 14.

[23] See for example P. J. Camp, *Phys. Rev. E*, **67**, 11503 (2003).

The radial distribution function can be determined experimentally by neutron diffraction, because neutrons can exhibit de Broglie wavelengths roughly equal to intermolecular spacings in liquids. Figure 28.16 shows the experimental radial distribution functions of liquid and solid mercury.

EXAMPLE 28.12

a. Find the speed of a neutron such that its de Broglie wavelength is 1.50×10^{-10} m.

b. In gas kinetic theory the root-mean-square speed of gas molecules of mass m is given by

$$v_{\mathrm{rms}} = \sqrt{\frac{3k_{\mathrm{B}}T}{m}} = \sqrt{\frac{3RT}{M}}$$

where R is the ideal gas constant, k_{B} is Boltzmann's constant, T is the absolute temperature, and M is the molar mass. Find the temperature such that the root-mean-square speed of thermally equilibrated neutrons is equal to the speed of part a.

Solution

a.

$$v = \frac{h}{m\lambda} = \frac{6.6261 \times 10^{-34}\ \mathrm{J\,s}}{(1.6749 \times 10^{-27}\ \mathrm{kg})(1.50 \times 10^{-10}\ \mathrm{m})} = 2.637 \times 10^{3}\ \mathrm{m\,s^{-1}}$$

b.

$$v_{\mathrm{rms}} = 2.637 \times 10^{3}\ \mathrm{m\,s^{-1}} = \sqrt{\frac{3k_{\mathrm{B}}T}{m}}$$

$$T = \frac{mv_{\mathrm{rms}}^2}{3k_{\mathrm{B}}} = \frac{(1.6749 \times 10^{-27}\ \mathrm{kg})(2.637 \times 10^{3}\ \mathrm{m\,s^{-1}})^2}{3(1.3807 \times 10^{-23}\ \mathrm{J\,K^{-1}})} = 281\ \mathrm{K}$$

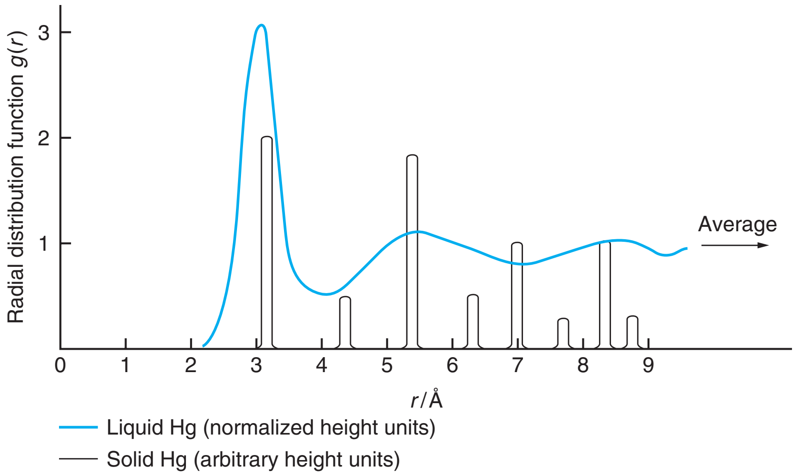

Figure 28.16 The Radial Distribution Function of Solid and Liquid Mercury. Since the solid has a lattice structure, the positions of neighboring atoms give narrow "blips" in the radial distribution function. In the liquid, the disorder that is present makes the function into a smooth curve, which shows vestiges of the crystal lattice. From D. Tabor, *Gases, Liquids and Solids*, 2nd ed., Cambridge University Press, Cambridge, England, 1979, p. 197.

Solid-Like Liquid Models

There are several model theories that treat a liquid like a disordered solid. In the *cell model*[24] each atom of a monatomic fluid such as liquid argon is assumed to be confined in a cell whose walls are made up of its nearest neighbors. In the simplest version, this cell is approximated as a spherical cavity inside which the potential energy of the moving atom is constant and outside of which the potential energy is infinite. Because each atom moves independently, the classical canonical partition function can be written as a product of molecular partition functions. The classical canonical partition function is

$$\mathcal{Z}_{\text{cl}} = (2\pi m k_{\text{B}} T)^{3N/2}\left(V_{\text{f}} e^{-u_0/k_{\text{B}}T}\right)^{N} \tag{28.5-1}$$

where V_{f} is the "free volume" in which the center of the atom can move, and where u_0 is the constant potential energy of an atom in the cell. Since the atoms are confined in distinguishable cells, there is no correction for indistinguishability.

At 0 K the substance is a solid, and we assume that the atoms are hard spheres of diameter d in contact with each other, so that the centers of nearest neighbor atoms are at a distance d from each other (d equals twice the radius). In the liquid at nonzero temperature, the thermal expansion of the lattice moves the centers of nearest neighbors to an average distance that is larger than d, which we denote by b. The center of the atom can now move in a small region at the center of the cell, approximated as a sphere with radius equal to $b - d$.

The free volume is

$$V_{\text{f}} = \frac{4}{3}\pi(b-d)^3 \tag{28.5-2}$$

We can relate d and b to the molar volumes. We assume a face-centered close-packed lattice and assume that the spheres are in contact in the solid. For spheres in contact in a face-centered cubic lattice, the diagonal of a unit cell face is equal to 4 times the radius of the spheres, equal to $2d$, where d is their diameter. The edge of the unit cell is equal to $\sqrt{2}d$. Each unit cell contains 4 spheres, so the molar volume of the solid is

$$V_{\text{m,s}} = \frac{N_{\text{Av}}}{4}\left(\sqrt{2}\,d\right)^3 = N_{\text{Av}}\frac{d^3}{\sqrt{2}}$$

$$d^3 = \frac{\sqrt{2}V_{\text{m,s}}}{N_{\text{Av}}}$$

where $V_{\text{m,s}}$ is the molar volume of the solid and N_{Av} is Avogadro's constant. Similarly, for the liquid

$$b^3 = \frac{\sqrt{2}V_{\text{m}}}{N_{\text{Av}}} \tag{28.5-3a}$$

where V_{m} is the molar volume of the liquid.

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[24] T. L. Hill, *Statistical Thermodynamics*, Addison-Wesley, Reading, MA., 1960, Ch. 16. H. Eyring and M. S. Jhon, *Significant Liquid Structures*, Wiley, New York 1969, Ch. 2.

Using Eq. (28.5-3), the classical canonical partition function of a monatomic liquid of N atoms is

$$\mathcal{Z}_{\mathrm{cl}} = (2\pi m k_{\mathrm{B}} T)^{3N/2} \left\{ \frac{4}{3}\pi \left[\left(\frac{\sqrt{2}V_{\mathrm{m}}}{N_{\mathrm{Av}}} \right)^{1/3} - \left(\frac{\sqrt{2}V_{\mathrm{m,s}}}{N_{\mathrm{Av}}} \right)^{1/3} \right]^3 e^{-u_0/k_{\mathrm{B}}T} \right\}^N \tag{28.5-4}$$

The pressure can be calculated from Eq. (27.5-7) using this partition function:

$$P = k_{\mathrm{B}} T \left(\frac{\partial \ln(\mathcal{Z})}{\partial V} \right)_T = \frac{N k_{\mathrm{B}} T}{V} \frac{1}{1 - \left(V_{\mathrm{m,s}}/V_{\mathrm{m}} \right)^{1/3}} \tag{28.5-5}$$

Exercise 28.10

Carry out the differentiation to obtain Eq. (28.5-5).

The formula for the pressure given in Eq. (28.5-5) approaches the ideal gas value for large molar volume, and diverges as the molar volume approaches the molar volume of the solid at 0 K. This behavior is qualitatively correct, but the cell model does not predict accurate values of the pressure. Lennard–Jones and Devonshire[25] developed an improved version of the cell model, in which they explicitly summed up the potential energy contributions for the nearest neighbors, obtaining better results.

Computer Simulations of Liquid Structure

With the advent of fast computers, numerical simulations of liquid structure have become practical. There are two principal simulation methods, the *Monte Carlo* method and *molecular dynamics*. The Monte Carlo method is so named because it uses a random number generator, reminiscent of the six-sided random number generators (dice) used in gambling casinos, such as those in Monte Carlo. This method was pioneered by Metropolis.[26]

In the Monte Carlo method a system of several hundred or a few thousand molecules is considered. An initial set of coordinates for all of the molecules is generated in some way, and further states are generated as follows: A random number generator is used to pick a number, b, between -1 and 1. A particle is moved a distance $\Delta x = ab$ in the x direction, where a is a predetermined maximum displacement. The change in potential energy of the system, $\Delta\mathcal{V}$, is then calculated. If $\Delta\mathcal{V} < 0$, the particle is left at the new location. If $\Delta\mathcal{V} > 0$, the particle is assigned a probability of staying at the new location. This is done by choosing a new random number, c, between 0 and 1. If $c > \exp(-\Delta\mathcal{V}/k_{\mathrm{B}}T)$, the particle is left at the new location. Otherwise, it is returned to its old location. Similar displacements are taken in the y and z directions for the first particle, and then in all three directions for all other particles.

Each time a new set of locations is obtained (including a set obtained by returning a particle to its old position), the value of the quantity to be averaged is calculated and

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[25] J. E. Lennard–Jones and A. F. Devonshire, *Proc. Roy Soc. (London)*, **A163**, 53 (1937) and **A165**, 1 (1938).

[26] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, *J. Chem. Phys.*, **21**, 1087 (1953).

added to the sum that is producing an average value. It was shown by Metropolis and his coworkers that if sufficient terms are taken, this procedure produces averages that are correctly weighted by the canonical probability distribution. In order to make the system act somewhat like a piece of a larger system, periodic boundary conditions are applied: If a move carries a particle out of the system, which is usually contained in a cube, the particle is reintroduced into the system through the same location on the opposite face of the cube.

The second simulation technique is *molecular dynamics.* In this technique, which was pioneered by Alder,[27] initial positions of the particles of a system of several hundred particles are assigned in some way. Displacements of the particles are determined by numerically simulating the classical equations of motion. Periodic boundary conditions are applied as in the Monte Carlo method. The first molecular dynamics calculations were done on systems of hard spheres, but the method has been applied to monatomic systems having intermolecular forces represented by the square-well and Lennard–Jones potential energy functions, as well as on model systems representing molecular substances. Commercial software is now available to carry out molecular dynamics simulations on desktop computers.[28]

Both equilibrium and nonequilibrium information can be obtained by the molecular dynamics technique. If the initial state of the system simulates a specific nonequilibrium state, the relaxation of the system toward equilibrium can be studied, giving information on transport properties.[29] After a sufficient time, the molecules will settle into motions that simulate the motions of molecules in equilibrium liquids, and equilibrium properties can be calculated.

PROBLEMS

Section 28.5: The Structure of Liquids

28.31 The density of ice at 0°C is equal to 0.917 g $\mathrm{mL^{-1}}$, and that of liquid water is equal to 1.000 g $\mathrm{mL^{-1}}$. The water molecules in the ice crystal have four nearest neighbors. Estimate the number of nearest neighbors in liquid water at 0°C. Comment on your answer.

28.32 At the normal melting temperature, 83.78 K, the molar volume of solid argon is 0.0246 L $\mathrm{mol^{-1}}$ and that of liquid argon is 0.0282 L $\mathrm{mol^{-1}}$.[30] Find the pressure according to Eq. (28.5-5), and compare it with the correct value, 1.00 atm.

28.33 The density of solid xenon is 3540 kg $\mathrm{m^{-3}}$ and that of liquid xenon is 3057 kg $\mathrm{m^{-3}}$. Find the pressure according to Eq. (28.5-5), and compare it with 1.00 atm, which is the correct value at the normal melting temperature, 161.36 K.

28.6

Approximate Theories of Transport Processes in Liquids

Transport processes include diffusion, viscous flow, and heat conduction. There are a number of approximate theories of transport processes in liquids, most of which are based on classical statistical mechanics.

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[27] B. J. Alder and T. E. Wainwright, *J. Chem. Phys.*, **31**, 459 (1959).

[28] Chem3D can carry out molecular dynamics calculations on laptop or desktop computers. It also carries out molecular mechanics calculations. Information is available at http://www.cambridgesoft.com.

[29] See W. G. Hoover, *Ann. Rev. Phys. Chem.*, **34**, 103 (1983) for a review of work in this field.

[30] K.-C. Kan, *Chin. J. Phys.*, **17**, 32 (1979).

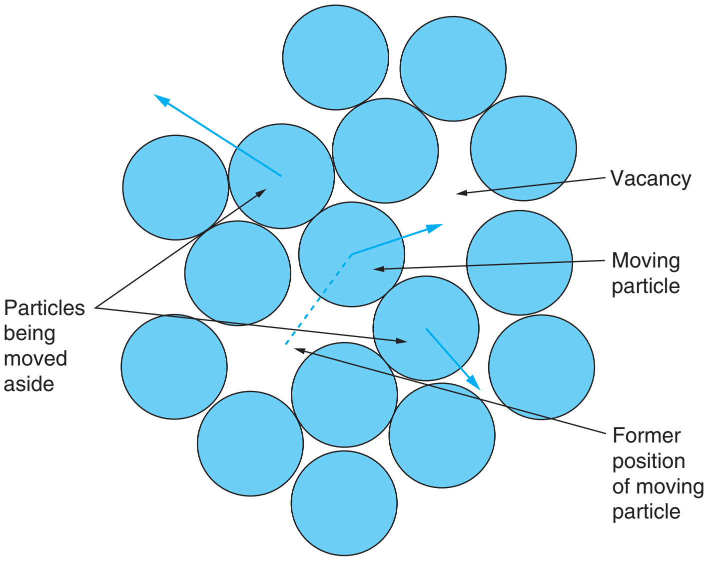

Figure 28.17 Motion of a Molecule into a Vacancy in a Liquid. This figure attempts to illustrate the position of maximum potential energy of a molecule moving from one shell of neighbors to another.

Diffusion

Diffusion is a process by which molecules of a substance in a mixture move from a region of higher concentration to a region of lower concentration. It is described quite accurately by Fick's law of diffusion, which for diffusion in the z direction is

$$J_{iz} = -D_i \frac{\partial c_i}{\partial z} \tag{28.6-1}$$

where J_i denotes the diffusion flux, defined as the net amount of substance in moles passing through unit area of a plane per unit time, and where the concentration of substance i is denoted by c_i. The coefficient D_i is called the *diffusion coefficient*. If Fick's law is obeyed, D_i is independent of concentration.

We now apply the activated complex theory of Eyring and Polanyi to diffusion in liquids. In the thermodynamic formulation of the activated complex theory, the rate constant of a first-order reaction is given by the analogue of Eq. (26.4-16):

$$k = \frac{k_B T}{h} e^{-\Delta G^{\ddagger\circ}/RT} \tag{28.6-2}$$

where $\Delta G^{\ddagger\circ}$ is the standard-state Gibbs energy change per mole to form the activated complex, excluding motion along the reaction coordinate. We represent our liquid by a model system that resembles a disordered crystal with fluctuating vacancies, and assume that a molecule can occasionally move into a vacancy. As it does so, it must push some neighboring molecules aside, moving through a state of high potential energy, as depicted schematically in Figure 28.17. This potential energy maximum is analogous to the maximum along the reaction coordinate for a chemical reaction described in Section 26.4, and we treat the state of high potential energy as an activated complex.

Consider a two-component liquid system, with a concentration of component 2 that is smaller for larger values of the z coordinate. Assume that a vacancy occurs at $z = z'$.

On the average, there will be a slightly smaller concentration of component 2 above the vacancy than below. The rate at which molecules move into the vacancy from below is equal to

$$\text{Rate}_b = kc_2(z' - a) \tag{28.6-3}$$

where a is an average z component of the displacement into the vacancy, and where $c_2(z' - a)$ is the concentration of component 2 evaluated at $z' - a$. The proportionality constant k is analogous to a rate constant and we assume that it is given by Eq. (28.6-2). The rate at which molecules move into the vacancy from above is equal to

$$\text{Rate}_a = kc_2(z' + a) \tag{28.6-4}$$

We assume that the molecules coming from above on the average have the same rate constant as those coming from below.

The net contribution to the diffusion flux is

$$J_{2z} = k[c_2(z' - a) - c_2(z' + a)]a \tag{28.6-5}$$

Let us represent $c_2(z' + a)$ as a Taylor series around the point $z' - a$:

$$c_2(z' + a) = c_2(z' - a) + \left.\frac{\partial c_2}{\partial z}\right|_{z'-a}(2a) + \cdots \tag{28.6-6}$$

where the subscript indicates that the derivative is evaluated at $z = z' - a$. If we neglect the terms not shown in Eq. (28.6-6), Eq. (28.6-5) becomes

$$J_{2z} = -\frac{k_B T}{h}\left(2a^2\right)e^{-\Delta G^{\ddagger\circ}/RT}\left(\frac{\partial c_2}{\partial z}\right) \tag{28.6-7}$$

Comparison with Fick's law, Eq. (28.6-2), gives an expression for the diffusion coefficient:

$$D_2 = 2a^2\frac{k_B T}{h}e^{-\Delta G^{\ddagger\circ}/RT} \tag{28.6-8}$$

EXAMPLE 28.13

Many liquids with molecules of ordinary size have diffusion coefficients approximately equal to 10^{-9} m^2 s^{-1}. Assume that a is equal to 1×10^{-10} m and estimate the value of $\Delta G^{\ddagger\circ}$ for $T = 300$ K.

Solution

$$\begin{aligned}\Delta G^{\ddagger\circ} &= -RT\ln\left(\frac{D_2 h}{2a^2 k_B T}\right)\\ &= -(8.3\,\text{J K}^{-1}\,\text{mol}^{-1})(300\,\text{K})\ln\left(\frac{(10^{-9}\,\text{m}^2\,\text{s}^{-1})(6.6\times10^{-34}\,\text{J s})}{2(10^{-10}\,\text{m})^2(1.4\times10^{-23}\,\text{J K}^{-1})(300\,\text{K})}\right)\\ &= 1\times10^{4}\,\text{J mol}^{-1} = 10\,\text{kJ mol}^{-1}\end{aligned}$$

This value is reasonable, being about one-fourth of a typical energy change of vaporization.

The temperature dependence of a diffusion coefficient is sometimes represented by a formula due to Arrhenius that is used for chemical reaction rate constants:

$$D = A_{\mathrm{d}} e^{-\Delta E_{\mathrm{ad}}/RT} \tag{28.6-9}$$

where E_{ad} is the activation energy and A_{d} is the preexponential factor for the diffusion process. To compare Eq. (28.6-8) with this equation, we assume that the enthalpy change of activation and the energy change of activation are nearly equal, since there is little change in PV in a liquid-state process. Therefore,

$$D_2 = 2\frac{k_{\mathrm{B}}T}{h} a^2 e^{-\Delta S^{\ddagger\circ}/R} e^{-\Delta U^{\ddagger\circ}/RT} \tag{28.6-10}$$

and if we identify $\Delta U^{\ddagger\circ}$ with E_{a}, the preexponential factor is

$$A_{\mathrm{d}} = 2\frac{k_{\mathrm{B}}T}{h} a^2 e^{-\Delta S^{\ddagger\circ}/R} \tag{28.6-11}$$

This preexponential factor is temperature-dependent, but its temperature dependence is much weaker than that of the exponential factor.

EXAMPLE 28.14

The diffusion coefficient for 1,1,1-trichloroethane in a mixed solvent of 2,2-dichloropropane and carbon tetrachloride was measured to be 1.41×10^{-9} m^2 s^{-1} at 25°C and 2.02×10^{-9} m^2 s^{-1} at 45°C. Find the value of the apparent energy of activation and the value of the preexponential factor.

Solution

$$E_{\mathrm{a}} = \frac{R\ln\left(\dfrac{k_2}{k_1}\right)}{\dfrac{1}{T_1} - \dfrac{1}{T_2}} = \frac{\left(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}\right)\ln\left(\dfrac{2.02 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}}{1.41 \times 10^{-9}\,\mathrm{m^2\,s^{-1}}}\right)}{\dfrac{1}{298.15\,\mathrm{K}} - \dfrac{1}{318.15\,\mathrm{K}}}$$

$$= 14200\,\mathrm{J\,mol^{-1}}$$

$$A_{\mathrm{d}} = ke^{E_{\mathrm{a}}/RT}$$

$$= (1.4110^{-9}\,\mathrm{m^2\,s^{-1}})\exp\left(\frac{\left(14200\,\mathrm{J\,mol^{-1}}\right)}{\left(8.3145\,\mathrm{J\,K^{-1}\,mol^{-1}}\right)(298.15\,\mathrm{K})}\right)$$

$$= 4.29 \times 10^{-7}\,\mathrm{m^2\,s^{-1}}$$

Exercise 28.11

Estimate the value of $\Delta S^{\ddagger\circ}$ for the data of the preceding example, assuming that $a = 4 \times 10^{-10}$ m. Comment on the magnitude and sign of your answer.

The motion of a single molecule into a molecule-size hole is not the only simple molecular diffusion process that can be treated in a simple model theory. A variety of processes, including the exchange in position of two adjacent molecules, have been considered.[31] If there is a vacancy adjacent to the pair of molecules, this process might make a significant contribution. The exchange in position of two molecules of different solute species moves a molecule of one species in one direction and a molecule of another species in the opposite direction. Such process can lead to "cross-effects," so that Fick's law must be written in an extended form, in which the concentration gradient of one species makes a contribution to the diffusion flux of another species:

$$J_{iz} = -\sum_{j=1}^{c} D_{ij}\frac{\partial c_j}{\partial z} \tag{28.6-12}$$

In the theory of nonequilibrium thermodynamics, such cross-effects are systematically studied, and thermodynamic theorems relating the cross-coefficients are proved.[32]

Viscosity

In viscous (shearing) flow in a liquid, one layer of molecules flows past an adjacent layer. Newton's law of viscous flow is

$$P_{zy} = \eta\left(\frac{\partial u_y}{\partial z}\right) \quad \text{(Newton's law)} \tag{28.6-13}$$

Where u_y is the velocity component of the fluid in the y direction and $\partial u_y/\partial z$ is called the *rate of shear*. The force per unit area required to maintain the shearing flow is denoted by P_{zy}, and η is the viscosity coefficient.

If we use a moving coordinate system, one layer of molecules is stationary and the adjacent layer moves relative to it. In our simple model, this motion is accomplished by the motion of individual molecules into holes in the liquid, rather than by concerted motion of a whole sheet of molecules at once. Therefore the rate of shear is proportional to the rate constant in Eq. (28.6-2). By Eq. (28.6-13), the viscosity is inversely proportional to the rate of shear, so that the viscosity should obey a formula of the Arrhenius type,

$$\eta = A_\eta\, e^{+E_{a\eta}/RT} \tag{28.6-14}$$

where $E_{a\eta}$ is an activation energy and A_η is a preexponential factor. This activation energy should roughly equal that for diffusion in the same liquid.

Exercise 28.12

The viscosity of carbon tetrachloride at 20°C is equal to 9.69×10^{-4} kg m^{-1} s^{-1}, and is equal to 6.51×10^{-4} kg m^{-1} s^{-1} at 50°C. Calculate the Arrhenius activation energy for viscosity.

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[31] R. G. Mortimer and N. H. Clark, *Ind. Eng. Chem. Fundam.*, **10**, 604 (1971).

[32] S. R. DeGroot and P. Mazur, *Nonequilibrium Thermodynamics*, North Holland Publishing Co., Amsterdam, 1962.

More Advanced Theories of Transport in Liquids

There are numerous more advanced theories of transport coefficients in liquids, mostly based on nonequilibrium classical statistical mechanics. Some are based on approximate representations of the time-dependent reduced distribution function and others are based on the analysis of *time correlation functions*, which are ensemble averages of the product of a quantity evaluated at time 0 and the same quantity or a different quantity evaluated at time t.[33] For example, the self-diffusion coefficient of a monatomic liquid is given by[34]

$$D = \frac{1}{3}\int_0^\infty \langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle dt \tag{28.6-15}$$

where $\mathbf{v}$ is the velocity of a molecule, and where the ensemble average $\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle$ is the time-correlation function of the velocity. At $t = 0$, the time-correlation function in Eq. (28.6-15) is equal to the average of the square of the velocity, which in a classical system is equal to $3k_\mathrm{B}T/m$. Evaluation of the time correlation function involves the study of the time dependence of the probability distribution, which we have not discussed, so we make only a few elementary comments. As time passes, the time-correlation function eventually approaches zero, representing the fact that the velocity of a molecule after a long time loses its "memory" of its initial velocity.

EXAMPLE 28.15

Assume that the velocity time correlation function of a molecule in a liquid is given by the formula

$$\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle = \frac{3k_\mathrm{B}T}{m}e^{-t/\tau} \tag{28.6-16}$$

where τ is a *correlation time*. The self-diffusion coefficient of liquid $\mathrm{CCl_4}$ is equal to $1.30 \times 10^{-9}\ \mathrm{m^2\,s^{-1}}$ at 298.15 K. Find the value of τ.

Solution

$$D = \frac{k_\mathrm{B}T}{m}\int_0^\infty e^{-t/\tau}dt = \frac{k_\mathrm{B}T\tau}{m}$$

$$\tau = \frac{mD}{k_\mathrm{B}T} = \frac{\left(2.56\times10^{-25}\ \mathrm{kg}\right)\left(1.3\times10^{-9}\ \mathrm{m^2\,s^{-1}}\right)}{\left(1.38\times10^{-23}\ \mathrm{J\,K^{-1}}\right)(298\ \mathrm{K})} = 8.1\times10^{-14}\ \mathrm{s}$$

Other transport coefficients are expressed in terms of different time-correlation functions. A variety of techniques have been developed to obtain approximate time-correlation functions.[35]

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[33] D. A. McQuarrie, *Statistical Mechanics*, Harper & Row, New York, 1976, p. 467ff.

[34] *Ibid.*

[35] *Ibid.*

PROBLEMS

Section 28.6: Approximate Theories of Transport Processes in Liquids

28.34 The self-diffusion coefficient of liquid CCl_4 is given by Rathbun and Babb:[36]

$t_C/°C$	25.0	40.0	50.0	60.0
$D/10^{-9}\,m^2\,s^{-1}$	1.30	1.78	2.00	2.44

Find the value of A_d and the value of E_{ad} in Eq. (28.6-9). Assuming that $a = 4 \times 10^{-10}$ m, find $\Delta S^{\ddagger\circ}$ and $\Delta G^{\ddagger\circ}$.

28.35 The viscosity of water at 20°C is equal to $0.001005\,\mathrm{kg\,m^{-1}\,s^{-1}}$, and at 50°C it is equal to $0.0005494\,\mathrm{kg\,m^{-1}\,s^{-1}}$. Calculate the Arrhenius activation energy for water's viscosity.

28.36 Using the data in Problem 28.34, calculate the value of the correlation time τ in Eq. (28.6-16) for carbon tetrachloride at 50°C. Explain the temperature dependence of this parameter.

28.7 Polymer Conformation

The simplest polymers have linear chain-like molecules, which can take on a large number of possible conformations. The principal piece of information about the conformation of a polymer molecule is the end-to-end distance. Even if we had a monodisperse sample of a polymer (one in which all molecules had the same molecular mass) there would be a distribution of end-to-end distances, because each molecule would coil up differently from the others.

We approximate a chain-like polymer molecule by a *freely jointed chain*, which is a model system consisting of a set of links of fixed length a fastened together end-to-end such that each joint can rotate into any orientation, even folding one link back onto the previous link. Since singly bonded carbon atoms can form a ring of six atoms, each link might represent a set of about three carbon atoms in a chain of singly bonded carbon atoms. To simplify the problem even further we suppose that each link of the chain can be directed in one of only six directions, parallel to the x, y, and z axes of a Cartesian coordinate system. We place one end of the chain at the origin, so that the ends of the links can fall only on the lattice points of a simple cubic lattice with lattice spacing a, very much like a crystal lattice.

The probability that the end of link number $n+1$ is at a lattice point with Cartesian coordinates (x, y, z) is denoted by $p(n+1, x, y, z)$. If the end of link number $n+1$ is at (x, y, z), then the end of link number n can be at one of only six possible locations: $(x+a, y, z), (x-a, y, z), (x, y+a, z), (x, y-a, z), (x, y, z+a)$, or $(x, y, z-a)$. We assume that the probabilities of the six possible directions of a link are equal so that

$$\begin{aligned} p(n+1, x, y, z) = \frac{1}{6}[&p(n, x+a, y, z) + p(n, x-a, y, z) + p(n, x, y+a, z) \\ &+ p(n, x, y-a, z) + p(n, x, y, z+a) + p(n, x, y, z-a)] \end{aligned} \tag{28.7-1}$$

Equation (28.7-1) is a *difference equation* that can be solved.[37] We assume that the beginning of the chain is at the origin:

$$p(0, x, y, z) = \begin{cases} 1 & \text{if } x = 0, y = 0, \text{ and } z = 0 \\ 0 & \text{otherwise} \end{cases} \tag{28.7-2}$$

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[36] R. E. Rathbun and A. L. Babb, *J. Phys. Chem.*, **65**, 1072 (1961).

[37] F. T. Wall, *Chemical Thermodynamics*, 2nd ed., W. H. Freeman, San Francisco, 1974, p. 341ff.

The difference equation will maintain the normalization

$$\sum_{x=-\infty}^{\infty}\sum_{y=-\infty}^{\infty}\sum_{z=-\infty}^{\infty} p(n,x,y,z) = 1 \tag{28.7-3}$$

where the summations are over all values of x, y, and z corresponding to lattice points and where we recognize that the lattice is not limited in size (although the probabilities for locations very far from the origin will be zero).

We define a one-dimensional probability by summing $p(n+1,x,y,z)$ over all values of y and z. We omit the limits on the sum and write

$$p(n+1,x) = \sum_{y}\sum_{z} p(n+1,x,y,z) \tag{28.7-4}$$

which is the probability that the end of link number $n+1$ is at x, irrespective of the y and z values. Equation (28.7-1) is now summed over all values of y and z to give

$$p(n+1,x) = \frac{1}{6}[p(n,x+a) + 4p(n,x) + p(n,x-a)] \tag{28.7-5}$$

where we have recognized that the y and z directions are mathematically equivalent so that four terms are equal to each other after the summation.

A variable that characterizes the width of a distribution is the mean of the square of the distance, called the *second moment* or the *variance*, which is equal to the square of the standard deviation of the distribution. The variance of the x coordinate for link number $n+1$ is given by

$$\begin{aligned}\langle x^2\rangle_{n+1} &= \sum_{x} x^2 p(n+1,x)\\ &= \frac{1}{6}\sum_{x} x^2 p(n,x+a) + \frac{2}{3}\sum_{x} x^2 p(n,x) + \frac{1}{6}\sum_{x} x^2 p(n,x-a)\end{aligned} \tag{28.7-6}$$

In the first term let $x+a=x'$, and in the third sum let $x-a=x''$. The second sum is equal to $\langle x^2\rangle_n$, so that

$$\begin{aligned}\langle x^2\rangle_{n+1} = {}&\frac{1}{6}\sum_{x'}\left(x'^2 - 2ax' + a^2\right)p\left(n,x'\right) + \frac{2}{3}\langle x^2\rangle_n\\ &+ \frac{1}{6}\sum_{x''}\left(x''^2 + 2ax'' + a^2\right)p\left(n,x''\right)\end{aligned} \tag{28.7-7}$$

Since the limits of the sum are $-\infty$ to ∞, there is no distinction between a sum over x, x', or x'' after the summation is done. Therefore, we can replace x' or x'' by x in the sums. The two sums containing $2ax$ cancel. The two sums containing x^2 give $\langle x^2\rangle_n$, and the two sums containing a^2 can be combined:

$$\langle x^2\rangle_{n+1} = \left(\frac{2}{3}+\frac{2}{6}\right)\langle x^2\rangle_n + \frac{2}{3}a^2\sum_{x} p(n,x) = \langle x^2\rangle_n + \frac{a^2}{3} \tag{28.7-8}$$

where we have used the fact that the distribution is normalized as in Eq. (28.7-3). Equation (28.7-8) is a *recursion relation*, analogous to the recursion relation used in the solution of the Schrödinger equation for the harmonic oscillator in Chapter 15. If the value for $n=0$ is known the value for $n=1$ can be calculated, and from this the value for $n = 2$ can be calculated, and so on. From the initial condition in Eq. (28.7-2)

$$\langle x^2 \rangle_0 = 0 \tag{28.7-9}$$

so that

$$\langle x^2 \rangle_1 = \frac{a^2}{3} \tag{28.7-10}$$

Each iteration of Eq. (28.7-8) adds a term equal to $a^2/3$, so that

$$\langle x^2 \rangle_n = \frac{na^2}{3} \tag{28.7-11}$$

The three directions are all equivalent so that $\langle x^2 \rangle_n = \langle y^2 \rangle_n = \langle z^2 \rangle_n$. By the theorem of Pythagoras, the mean-square end-to-end distance in three dimensions is

$$\langle r^2 \rangle_n = \langle x^2 \rangle_n + \langle y^2 \rangle_n + \langle z^2 \rangle_n = na^2 \tag{28.7-12}$$

and the root-mean-square end-to-end distance is

$$r_{\text{rms}} = \langle r^2 \rangle^{1/2} = n^{1/2} a \tag{28.7-13}$$

As expected, the root-mean-square distance is proportional to the length of a link. It is proportional to the square root of the number of links in the polymer chain, not to the number of links. This comes from the fact that a longer chain has more ways to coil up than does a short chain, so that adding more links increases the root-mean-square distance less rapidly than the number of links.

In order to solve for the distribution of end-to-end lengths, we approximate Eq. (28.7-1) by a differential equation.[38] We expand the function p in four different Taylor series in n, x, y, and z, treating n as though it could take on nonintegral values:

$$p(n+1, x, y, z) = p(n, x, y, z) + \frac{\partial p}{\partial n} a + \cdots \tag{28.7-14}$$

$$p(n, x \pm a, y, z) = p(n, x, y, z) \pm \frac{\partial p}{\partial x} a + \frac{1}{2} \frac{\partial^2 p}{\partial x^2} a^2 \pm \cdots \tag{28.7-15}$$

with equations like Eq. (28.7-15) for y and z. These series are substituted into Eq. (28.7-1). The lowest-order terms that do not cancel are kept, and the higher-order terms are neglected:

$$\frac{\partial p}{\partial n} = \frac{a^2}{6} \left[\frac{\partial^2 p}{\partial x^2} + \frac{\partial^2 p}{\partial y^2} + \frac{\partial^2 p}{\partial z^2} \right] = \frac{a^2}{6} \nabla^2 p \tag{28.7-16}$$

where ∇^2 is called the *Laplacian operator*. Equation (28.7-16) is valid in the case that n is large compared with unity and that a is small compared with the values of x, y, and z that are important.

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[38] F. T. Wall, *op. cit.*, p. 341ff (note 37).

We transform the equation to spherical polar coordinates, in which p is a function of r, θ, and ϕ. However, all directions in space are equivalent, so that p cannot depend on θ and ϕ, and we write $p = p(n, r)$. From the expression for the ∇^2 operator in spherical polar coordinates in Eq. (B-45) in Appendix B,

$$\frac{\partial p}{\partial n} = \frac{a^2}{6r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial p}{\partial r} \right) \tag{28.7-17}$$

The solution to Eq. (28.7-17) is[39]

$$p(n, r) = \left(\frac{3}{2\pi n a^2} \right)^{3/2} e^{-3r^2/2na^2} \tag{28.7-18}$$

where the constant $(3/2\pi \eta a^2)^{3/2}$ provides for normalization:

$$\int_0^\infty p(n, r) 4\pi r^2 dr = 1 \tag{28.7-19}$$

Exercise 28.13

a. Carry out the substitution of the Taylor series into Eq. (28.7-1) to obtain Eq. (28.7-16).
b. Verify that the function of Eq. (28.7-18) satisfies Eq. (28.7-17).
c. Verify that the function of Eq. (28.7-18) is normalized.

The freely jointed chain that we have discussed is only a crude first approximation for real polymers. Every real polymer has some rigidity built into its bonds so that the chain is not freely jointed. We have also ignored the problem of *excluded volume*, which means that two parts of a polymer chain cannot occupy the same location at the same time. We have also ignored the effects of intermolecular attractions on the conformation. Any of the books on polymer chemistry contain more elaborate theories. The Polymer Science Department of the University of Southern Mississippi maintains the *Macrogalleria* website (http://www.pslc.usm.edu/macrog), which is a good source of information about polymers.

There are many naturally occurring polymers. Proteins, which are polymers of amino acids, can form intramolecular hydrogen bonds that hold the chains in a helical conformation or a pleated sheet conformation. The proper conformation is essential to the biological function of the molecule. If the molecule is transformed into a more random conformation, it loses its biological function and is said to be *denatured*.

Nucleic acids are polymers of five-carbon sugars (either ribose or deoxyribose), phosphoric acid residues, and certain ring-containing molecules called nitrogen bases. Deoxyribonucleic acid (DNA) is held in a double helix of two chains by hydrogen bonds between specific pairs of bases: cytosine (C) hydrogen-bonds to guanine (G), and adenine (A) hydrogen-bonds to thymine (T), so that in an intact DNA molecule a C must be opposite every G on the other chain and a T must be opposite every A on the other chain.

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[39] F. T. Wall, *op. cit.*, p. 341ff (note 37).

PROBLEMS

Section 28.7: Polymer Conformation

28.37 Show that Eq. (28.7-10) is compatible with the fact that a "chain" of one link is rigid.

28.38 For a freely jointed chain with links 3×10^{-10} m long, find the root-mean-square end-to-end distance and the ratio of this length to the sum of the link lengths for

a. 100 links

b. 10000 links

28.39 For a freely jointed chain with links 3.5×10^{-10} m long, find the root-mean-square end-to-end distance and the ratio of this length to the sum of the link lengths for

a. 1000 links

b. 100,000 links

28.40 Assume that a polymer chain is constrained to lie in a plane. Find the formula for the root-mean-square end-to-end distance using the same approximations as were used to derive Eq. (28.7-13).

28.8 Polymers in Solution

The conformation of polymer molecules in solution is affected by intermolecular forces between polymer molecules and solvent molecules and between solvent molecules and other solvent molecules. Polar polymer molecules will tend to form tight balls in nonpolar solvents, but can attract solvent molecules and can swell in polar solvents. A nonpolar polymer molecule will attract polar solvent molecules less strongly than the polar solvent molecules attract each other and will tend to form a tight ball in a polar solvent such as water. Similarly, nonpolar polymers can swell in nonpolar solvents (try placing a rubber object in benzene or toluene).

The *expansion coefficient* α is defined by the relation

$$\langle r^2 \rangle = \alpha^2 \langle r^2 \rangle_0 \tag{28.8-1}$$

where $\langle r^2 \rangle_0$ is the mean-square end-to-end distance in the pure polymer and $\langle r^2 \rangle$ is the mean-square end-to-end distance of the polymer in the solution. A solvent in which α is equal to 1 is called a *theta solvent*. In a poor solvent for the particular polymer, α will be smaller than unity, and in a solvent that causes the polymer to swell, α will exceed unity.

In a typical polymer solution, a polymer molecule and its associated solvent molecules will occupy a roughly spherical region in space with a diameter approximately equal to the end-to-end distance of the molecule, and will move through a solution in much the same way as would a sphere of that size. If the total volume of the spheres in a solution is denoted by v and the volume of the entire suspension is denoted by V, the volume fraction of the spheres in the solution is denoted by ϕ:

$$\phi = v/V \tag{28.8-2}$$

Einstein solved the hydrodynamic equations for flow around hard spheres in a dilute suspension in a viscous fluid. His result was that the viscosity of a suspension of hard spheres is given by[40]

$$\eta = \eta_0\left(1 + \frac{5}{2}\phi\right) \tag{28.8-3}$$

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[40] A. Einstein, *Ann. Physik*, **19**, 289 (1906). Einstein's productivity around the year 1905, when he was pursuing theoretical physics in his spare time, is truly astounding.

where η_0 is the viscosity of the pure solvent. Equation (28.8-3) can be written in the form

$$\eta_{\mathrm{sp}} = \frac{\eta}{\eta_0} - 1 = \eta_r - 1 = \frac{5}{2}\phi \tag{28.8-4}$$

where η_{sp} is called the *specific viscosity* and η_r is called the *relative viscosity*. Since the volume of the spherical particles is proportional to their number, the specific viscosity of a dilute suspension of spheres is proportional to the concentration of the spheres. We denote the mass concentration of the polymer by c, usually expressed in grams per deciliter. The specific viscosity divided by c is independent of the concentration:

$$\frac{1}{c}\eta_{\mathrm{sp}} = \frac{5}{2}\frac{1}{c}\frac{v}{V} = \frac{5}{2}\frac{1}{M}\frac{4}{3}\pi r^3 \tag{28.8-5}$$

where M and r are the mass and the radius of one of the spheres.

Exercise 28.14

Verify Eq. (28.8-5).

The behavior of a dilute solution of polymer molecules becomes more and more like that of a suspension of spheres as the concentration is made smaller, because the polymer molecules become more distant from each other and interfere less with each other. We define the *intrinsic viscosity*, $[\eta]$, also called the *limiting viscosity number*, by

$$[\eta] = \lim_{c\to 0}\left(\frac{1}{c}\eta_{\mathrm{sp}}\right) = \lim_{c\to 0}\left[\frac{1}{c}\left(\frac{\eta}{\eta_0} - 1\right)\right] \tag{28.8-6}$$

We assume that the radius of the sphere occupied by a polymer molecule and associated solvent molecules is proportional to the root-mean-square end-to-end distance and is thus proportional to the square root of the molecular mass, denoted by M. The volume of the sphere is proportional to $M^{3/2}$ and the intrinsic viscosity is proportional to $M^{1/2}$:

$$[\eta] = K'M^{1/2} \tag{28.8-7}$$

where K' depends on temperature and on the identities of the solvent and polymer, but not on M. Equation (28.8-7) is called the *Mark–Houwink equation*. It is considered to be valid for a polymer in a theta solvent. For other solvents we can write a modified equation:

$$[\eta] = KM^a \tag{28.8-8}$$

where the constant K and the exponent a are determined by experiment. Flory and Leutner prepared monodisperse samples (samples with molecules of nearly the same molecular mass) of polyvinyl alcohol (PVA) and found that for aqueous solutions of PVA at 25°C[41]

$$[\eta] = (2.0 \times 10^{-4}\ \mathrm{dL\ g^{-1}})(\mathrm{M}/1\ \mathrm{amu})^{0.76} \tag{28.8-9}$$

so that $a = 0.76$ for PVA.

For a polydisperse sample of a single polymer, one can apply Eq. (28.8-8) to each molecular mass that is present, multiply each equation by W_i, the mass fraction for

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[41] P. J. Flory and F. S. Leutner, *J. Polymer. Sci.*, **5**, 267 (1950).

molecular mass M_i, and sum the equations over all possible molecular masses. Since K has the same value for all molecules of a given polymer, we can write

$$[\eta] = K \sum_i W_i M_i^a \tag{28.8-10}$$

where the sum is over different molecular masses. We define the *viscosity-average molecular mass*:

$$\langle M \rangle_v = \left(\sum_i W_i M_i^a \right)^{1/a} \tag{28.8-11}$$

Combining Eq. (28.8-10) and Eq. (28.8-11) gives

$$[\eta] = K(\langle M \rangle_v)^a \tag{28.8-12}$$

The viscosity-average molecular mass is not equal to the mean molecular mass, which is called the *number-average molecular mass*. There is also an average molecular mass called the *mass-average molecular mass*, in which each molecule is given an importance in the average proportional to its mass. The viscosity-average molecular mass is numerically more nearly equal to the mass-average value than to the number-average value.

PROBLEMS

Section 28.8: Polymers in Solution

28.41 Find the number-average and mass-average molecular masses for a sample of a polyvinyl alcohol that has molecules with the following percentages and molecular masses:

10.00%	5000 amu
25.00%	15,000 amu
60.00%	25,000 amu
5.00%	35,000 amu

28.42 Assume that the diameter of a molecule of polyvinyl alcohol is equal to the root-mean-square end-to-end distance. Assume that (since 6 carbon atoms can make a ring) each set of three carbons constitutes a link in a freely jointed chain, of length 2.57×10^{-10} m. (Each link constitutes one and one-half monomer units.)

a. Find the volume of a sphere containing one molecule of polyvinyl alcohol of mass 60,000 amu.

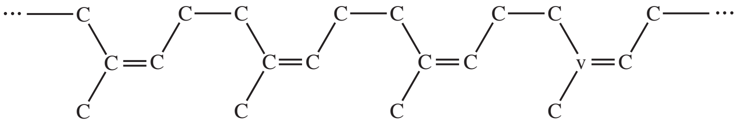
b. Find the viscosity at 20°C of a solution of such molecules (all assumed identical) of $1.00\ \mathrm{g\ L^{-1}}$, using the Einstein equation, Eq. (28.8-3).

c. Find the viscosity at 20°C of the solution of part a using Eq. (28.8-9) and assuming that the limiting value of the specific viscosity can be used at this concentration.

28.43 Find the viscosity-average molecular mass of the polyvinyl alcohol sample of Problem 28.41.

28.9 Rubber Elasticity

Rubber is a naturally occurring polymer, first used as pencil erasers, which was the origin of the English name. It is an addition polymer of isoprene (2-methyl-1,3-butadiene). In forming an addition polymer, a double bond "opens up" to link each monomer to the chain without forming a second product. Since each molecule of the monomer has two double bonds, there remains one double bond per monomer after polymerization. Natural rubber has the *cis* configuration at each of these bonds. A portion of the structural formula for a rubber molecule is (hydrogens have been omitted):



Charles Goodyear, 1800–1860, was an American inventor whose patent was widely infringed upon, and who died in debt.

Natural rubber is a sticky, semifluid substance. In 1839, after 10 years of trial-and-error experimentation in his kitchen, Charles Goodyear invented *vulcanization*, a process in which sulfur is reacted with natural rubber. In this process, sulfur reacts with double bonds in two adjacent chains, forming short chains of sulfur atoms between the polymer chains, producing a more nearly solid and elastic product than natural rubber. The extent of this cross-linking and the presence of various additives such as "carbon black" (finely powdered carbon) determine the physical properties of the rubber. Vulcanized rubber can be made in varying degrees of hardness, from flexible rubber like that in inner tubes, through the less flexible rubber used in tires, to the hard rubber used in combs.

Before 1955, various synthetic rubbers were invented, but were found to be inferior to natural rubber. It was possible to make polyisoprene, but the double bonds were in a random mixture of the *cis* and *trans* configurations. In 1955, catalysts were developed that can produce a synthetic rubber that is identical to natural rubber, and automobile tires made of synthetic rubber are now common.[42]

The Thermodynamics of Rubber

A piece of vulcanized rubber is not a simple system in the thermodynamic sense, because work other than compression work can be done on it. When it is stretched reversibly, the total work in an infinitesimal displacement is given by

$$dw = -PdV + fdL \tag{28.9-1}$$

where L is the length of the piece of rubber and f is the *tension force*.

It is found experimentally that the stretching of a rubber object approximately obeys three properties: (1) the volume remains constant; (2) the tension force is proportional to the absolute temperature; and (3) the energy is independent of the length at constant temperature. An *ideal rubber* exactly conforms to these three properties. Since the volume is constant, the first term on the right-hand side of Eq. (28.9-1) vanishes for an ideal rubber. For reversible processes in a closed system made of ideal rubber, the first and second laws of thermodynamics give the relation:

$$dU = dq + dw = TdS + fdL \quad \text{(ideal rubber)} \tag{28.9-2}$$

We define an enthalpy-like variable, K

$$K = U - fL \quad \text{(definition)} \tag{28.9-3}$$

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[42] J. Natta *et al.*, *J. Am. Chem. Soc.*, 77, 1708 (1955); K. Ziegler *et al.*, *Angew. Chem.*, **67**, 426 (1955a). See the Macrogalleria website (http://www.pslc.usm.edu/macrog) to view an animation of this catalytic action.

The Helmholtz energy is defined in the standard way:

$$A = U - TS \quad \text{(definition)} \tag{28.9-4}$$

We denote the analogue to the Gibbs energy by J:

$$J = K - TS = U - fL - TS \quad \text{(definition)} \tag{28.9-5}$$

Just as in Section 26.1 we can write differential expressions:

$$dK = TdS - Ldf \tag{28.9-6a}$$

$$dA = -SdT + fdL \tag{28.9-6b}$$

$$dJ = -SdT - Ldf \tag{28.9-6c}$$

We can write Maxwell relations similar to the relation in Eq. (4.2-18) from these equations. For example, from Eq. (28.9-6b),

$$\left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial f}{\partial T}\right)_L \tag{28.9-7}$$

Exercise 28.15

Write the other three Maxwell relations from Eqs. (28.9-2), (28.9-6a), and (28.9-6c).

Using Eqs. (28.9-2) and (28.9-7), we can derive a useful equation:

$$\left(\frac{\partial U}{\partial L}\right)_T = T\left(\frac{\partial S}{\partial L}\right)_T + f = T\left(\frac{\partial f}{\partial T}\right)_L + f \tag{28.9-8}$$

This is an **equation of state** for an ideal rubber. We can now show that property (3) of an ideal rubber follows from property (2). Since f is proportional to T for an ideal rubber,

$$f = T\varphi(L) \tag{28.9-9}$$

where φ is some function of L that is independent of T. We now have

$$T\left(\frac{\partial f}{\partial T}\right)_L = T\varphi = f \tag{28.9-10}$$

so that

$$\left(\frac{\partial U}{\partial L}\right)_T = -f + f = 0 \tag{28.9-11}$$

Equation (28.9-11) shows the difference between a rubber band and a spring. When a spring is stretched at constant temperature, the energy increases as work is done on the spring. When a rubber band is stretched at constant temperature, doing work on the rubber band, the energy remains constant, so that heat must flow out. Stretching a rubber band at constant temperature must decrease its entropy. This fact seems reasonable from a molecular point of view, because the polymer molecules will be more nearly parallel and more nearly ordered in the stretched state than in the relaxed state. From Eqs. (28.9-8) and (28.9-11) we can derive a relation for this decrease in entropy:

$$f = -T\left(\frac{\partial S}{\partial L}\right)_T \tag{28.9-12}$$

A Molecular Theory of Rubber Elasticity

We represent an ideal rubber by a model system that has the following properties:[43] (1) The equilibrium system consists of a set of polymer molecules with an equilibrium distribution of end-to-end lengths given by the freely jointed chain formula of Eq. (28.9-37). (2) A certain number, N, of randomly selected polymer chains are cross-linked. For simplicity, we assume that they are cross-linked only at their ends and that all of the cross-linked molecules have the same number of links, n. (3) When the rubber is stretched in the x direction, the y and z dimensions change so that the volume remains constant, and the x, y, and z components of all end-to-end vectors change in the same ratio as the x, y, and z dimensions of the rubber.

At equilibrium, there will be N_i molecules with an end-to-end vector $\mathbf{r}_i = (x_i, y_i, z_i)$. If an elongation in the x direction preserves the original volume, the end-to-end vector of these molecules will be (x_i', y_i', z_i'):

$$x_i' = \alpha x_i; \quad y_i' = \frac{y_i}{\alpha^{1/2}}; \quad z_i' = \frac{z_i}{\alpha^{1/2}} \tag{28.9-13}$$

where α is the degree of elongation, equal to L/L_0, the elongated x dimension divided by the original x dimension. The number of molecules with this new end-to-end vector is still equal to N_i.

To calculate the entropy change on elongation, we use the definition of the statistical entropy of Eq. (26.1-1):

$$S_{\text{st}} = k_{\text{B}} \ln(\Omega) + \text{const} \tag{28.9-14}$$

where Ω is the number of system mechanical states that are compatible with the thermodynamic state of the system, assuming all of these states to have equal energy. To use this formula, we calculate the probability, P, that the elongation would occur spontaneously, equal to the probability that N_1 chains will have end-to-end vector $\mathbf{r}_1'$, that N_2 chains will have end-to-end vector $\mathbf{r}_2'$, etc. We assume that the chains act independently so that this probability is the product of the probabilities of the individual chains. This probability is then multiplied by the number of ways to divide the set of polymer molecules into the specified subsets:

$$P' = N! \prod_i \frac{1}{N_i!} p(n, x_i', y_i', z_i')^{N_i} = N! \prod_i \frac{1}{N_i!} (p_i')^{N_i} \tag{28.9-15}$$

where the factor $N!/\prod_i N_i!$ is the number of ways to divide the N chains into the required subsets and where we have abbreviated $p(n, x_i', y_i', z_i')$ by p_i'. Using Stirling's approximation for $\ln(N!)$ and $\ln(N_i!)$ from Eq. (25.2-21)

$$\begin{aligned} \ln(P') &= N\ln(N) - N + \sum_i [N_i \ln(p_i') - N_i \ln(N_i) + N_i] \\ &= \sum_i N_i \ln(p_i' N/N_i) \end{aligned} \tag{28.9-16}$$

We now write this equation for the equilibrium distribution:

$$\ln(P) = \sum_i N_i \ln(p_i N/N_i) \tag{28.9-17}$$

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[43] F. T. Wall, *op. cit.*, Ch. 16 (note 37).

Since all microstates are assumed equally probable, P is proportional to Ω and we can write a formula for the entropy change:

$$\begin{aligned}\Delta S &= S(\text{stretched}) - S(\text{equilibrium}) = k[\ln(P') - \ln(P)] \\ &= k_\text{B}\sum_i N_i \ln\left(\frac{p'_i}{p_i}\right) = Nk_\text{B}\sum_i p_i \ln\left(\frac{p'_i}{p_i}\right) \end{aligned} \tag{28.9-18}$$

where we have used the fact that $p_i = N_i/N$.

We pretend that x, y, and z range continuously and replace the sum by an integral:

$$\Delta S = Nk_\text{B}\int p\ln\left(\frac{p'}{p}\right)dxdydz \tag{28.9-19}$$

where the integral is over all values of x, y, and z. From Eq. (28.7-18) and Eq. (28.9-13),

$$\ln\left(\frac{p'}{p}\right) = \frac{3}{2na^2}\left[-x^2(\alpha^2-1) - (y^2+z^2)\left(\frac{1}{\alpha}-1\right)\right] \tag{28.9-20}$$

When Eq. (28.9-20) is substituted into Eq. (28.9-19), we obtain

$$\begin{aligned}\Delta S &= \frac{3Nk_\text{B}}{2na^2}\left[-\langle x^2\rangle_n(\alpha^2-1) - \left(\langle y^2\rangle_n + \langle z^2\rangle_n\right)\left(\frac{1}{\alpha}-1\right)\right] \\ &= -\frac{Nk_\text{B}}{2}\left(\alpha^2 + \frac{2}{\alpha} - 3\right)\end{aligned} \tag{28.9-21}$$

where we have used Eq. (28.7-11) for the equilibrium value of $\langle x^2\rangle_n$, which is also equal to $\langle y^2\rangle_n$ and $\langle z^2\rangle_n$. Using Eqs. (28.9-21) and (28.9-12), we can write an equation of state for ideal rubber:

$$f = -T\left(\frac{\partial S}{\partial L}\right)_T = -\frac{T}{L_0}\left(\frac{\partial S}{\partial \alpha}\right)_T = \frac{Nk_\text{B}T}{L_0}\left(\alpha - \frac{1}{\alpha^2}\right) \tag{28.9-22}$$

This equation of state agrees fairly well with experiment for values of α no larger than 3.[44]

EXAMPLE 28.16

Derive an expression for the reversible work done in stretching a piece of ideal rubber at constant temperature.

Solution

Let α' be the final value of the extent of elongation.

$$dw = fdL = \frac{Nk_\text{B}T}{L}\left(\alpha - \frac{1}{\alpha^2}\right)dL = Nk_\text{B}T\left(\alpha - \frac{1}{\alpha^2}\right)d\alpha$$

$$w = Nk_\text{B}T\int_1^{\alpha'}\left(\alpha - \frac{1}{\alpha^2}\right)d\alpha = \frac{Nk_\text{B}T}{2}\left(\alpha'^2 + \frac{2}{\alpha'} - 3\right)$$

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[44] F. T. Wall, *op. cit.*, Ch. 16 (note 37).

Exercise 28.16

a. Write the formula for the heat transferred in the isothermal elongation of an ideal rubber.
b. For an ideal rubber that contains 1.00×10^{-6} mole of cross-linked polymer chains, find the value of q and w for stretching it to 3.00 times its original length at 298.15 K.

PROBLEMS

Section 28.9: Rubber Elasticity

28.44 **a.** Write a general expression for $C_f - C_L$, the difference between the heat capacity at constant f and that at constant L, for rubber.

b. Write the expression for part a for ideal rubber.

28.10 Nanomaterials

Richard P. Feynman (1918–1988) was a professor of theoretical physics at the California Institute of Technology. He worked on the Manhattan Project during World War II, and was the co-recipient of the 1965 Nobel Prize in physics for his work on quantum electrodynamics. He became one of the best-known scientists of his time.

Gerd Binnig, 1947– , and Heinrich Rohrer, 1933– , were employed at the IBM Research Laboratory in Zurich when they invented the STM. They shared half of the 1986 Nobel Prize in physics for their invention.

Richard E. Smalley, 1943–2005, was professor of chemistry, physics, and astronomy at Rice University. He received the 1996 Nobel Prize in chemistry for his work on nanomaterials.

In 1959 Richard Feynman gave a talk entitled “There’s Plenty of Room at the Bottom,” in which he discussed the possibility of writing the entire *Encyclopedia Britannica* on the head of a pin.[45] He offered to give a prize of $1000 of his own money to anyone who could reduce the size of a printed page by a linear factor of 1/25000, and anticipated the scanning electron microscope to read such an image. He also offered to give a prize of $1000 to anyone who could build a functioning electric motor that would fit into a cube 1/64 of an inch on a side. This prize was claimed within a few years, but the first prize was apparently not claimed before Feynman’s death in 1988.

The modern era of nanotechnology probably began with two developments: (1) the invention of the scanning tunneling microscope (STM) by Binnig and Rohrer in 1981,[46] and (2) the creation of “buckyballs” in 1985.[47] The STM provides the ability to read the miniaturized page envisioned by Feynman in 1959. Various websites give the history of the STM.[48] This device involves ceramic piezo-electric substances that can move a molecularly sharp stylus over a solid surface by molecular distances while measuring the height of features on the surface by the amount of current that flows through the stylus. It was the first device that produced images of individual atoms.

Smalley and his coworkers irradiated graphite with intense laser beams. This created C_{60} molecules that are balls of 60 carbon atoms arranged in 20 hexagons and 12 pentagons, with bonds in a pattern like the seams on a soccer ball. The equilibrium conformation of a buckyball corresponds to a point group called the icosahedral group, containing numerous rotations and reflections. There are now also buckyballs of different sizes, and “nanotubes” that are cylindrical analogues of buckyballs. Multiwalled carbon nanotubes have been found in a 400-year old dagger made of Damascus steel.[49]

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[45] R. P. Feynman, *Science and Engineering*, California Institute of Technology, 1960.

[46] See for example http://www.ifs.tu-darmstadt.de/fileadmin/phil/nano/baird-shew.pdf, which shows the famous IBM logo created with 35 xenon atoms.

[47] Buckminsterfullerene is named after Buckminster Fuller, a famous architect who incorporated geodesic domes into many of his building designs.

[48] A. S. Duwez, *Nature Nanotechnology*, **1**, 22 (2006); S. Katano *et al.*, *Science*, **316**, 1883 (2007).

[49] P. Paufler, *Nature*, **440**, 286 (2006).

The diameter of a C_{60} buckyball is approximately 1 nanometer (1×10^{-9} m or 10 Å), so it is called a *nanomaterial*. Its interior cavity is able to contain a single atom such as an argon atom. A variant of the C_{60} buckyball is also the right size to fit into the active site of the protease enzyme of the AIDS virus and thereby inhibit its action. There are now numerous applications of nanomaterials, including automobile paints with nanometer-size particles suspended in them. Nanocontainers and nanocorrals have been created that have interior cavities capable of containing various sizes of atoms or molecules.[50] Nanomotors and nanocars have been invented,[51] as well as a light-triggered nanovalve.[52] Nanoparticles are used for polishing silicon surfaces, and a means to produce spherical nanoparticles for this purpose has been developed.[53] Platinum nanoparticles with 24 facets have been created that have 200% to 400% greater catalytic activity than spherical platinum nanoparticles.[54] Many other applications of nanomaterials are being developed, and the field promises to become economically and industrially important, as well as academically interesting. The field of nanomaterials is so active that almost every issue of *Chemical and Engineering News* contains an article about new advances in the field.

Summary of the Chapter

In this chapter, we have discussed the structure of solids and liquids. Many solids are crystalline, with molecular units arranged in a regular three-dimensional lattice. There are two principal theories for the vibrations of lattices of atoms, the Einstein and the Debye theories. In the Einstein theory the normal vibrational modes of the lattice are assumed to vibrate with the same frequency. In the Debye model, the normal modes of the lattice are assumed to vibrate with the same distribution of frequencies as would a structureless solid. In each theory, the formula for the heat capacity of the solid lattice conforms to the law of Dulong and Petit at high enough temperature.

The band theory of the electronic structure of solids was discussed. In this theory the electrons are assumed to occupy delocalized orbitals that comprise bands of energy levels. The differences between conductors, semiconductors, and insulators were discussed.

The structure of liquids is more difficult to discuss than is the structure of solids, because the liquids are more disordered than solids, but not completely disordered as are gases. Some elementary comments on the structure of liquids were presented, including the definition of the radial distribution function, which gives the probability of finding a second molecule at a given distance from another molecule.

The conformation of a simple polymer model, a freely jointed chain, was also presented. The conformation of polymers in solution was introduced. A model system to represent rubber elasticity was discussed, and a brief introduction to nanomaterials was presented.

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[50] X. Liu *et al.*, *Angew. Chem. Int. Ed.*, **45**, 901 (2006).

[51] B. L. Feringa, *Nature*, **437**, 1337 (2005), *Proc. Natl. Acad. Sci., USA*, **103**, 1178 (2006); R. Eelkema *et al.*, *Nature*, **440**, 143 (2006).

[52] A. Coser *et al.*, *Science*, **309**, 755 (2005).

[53] X. Feng and Z. L. Wang, *Science*, **312**, 1504 (2006).

[54] N. Tian *et al.*, *Science*, **316**, 732 (2007).

ADDITIONAL PROBLEMS

28.45 Label each of the following statements as either true or false. If a statement is true only under special circumstances, label it as false.

a. All solids are crystalline.

b. The melting temperature is an indicator of the strength of the forces holding a solid together.

c. Liquid crystals are intermediate in their properties between liquids and solids.

d. The properties of gases arise primarily from the molecular kinetic energy, whereas the properties of liquids and solids arise primarily from the molecular potential energy.

e. The stretching of a rubber band can be treated thermodynamically just like the stretching of a coil spring.

f. The Einstein temperature of a crystal is generally smaller than the Debye temperature of the same crystal.

g. The effective volume of a polymer molecule in a theta solvent is approximately proportional to $N^{3/2}$, where N is the number of monomer units.

h. All solids obey the law of Dulong and Petit at sufficiently high temperature.

i. The molar mass of a polymer determined by a viscosity experiment will always be different from the molar mass determined by an osmotic pressure measurement.

j. The heat capacity of a nonconductor is approximately proportional to T^3 at sufficiently low temperature.

k. The electrical conductivity of a typical metal increases with increasing temperature.

l. Zinc should be a better electrical conductor than copper because it has two $4s$ electrons, whereas copper has only one.

A

Appendices

Tables of Numerical Data

Table A.1 Isothermal Compressibilities of Liquids

Substance	Pressure/atm	$\kappa_T \times 10^{10}/\text{Pa}^{-1}$			
		Temperature			
		25°C	45°C	65°C	85°C
Aniline	1	4.67	5.22	5.84	6.56
	1000	3.23	3.48	3.76	4.04
Benzene	1	9.67	11.32	13.39	
	1000	5.07	5.50	5.98	
Bromobenzene	1	6.68	7.52	8.50	9.65
	1000	4.09	4.39	4.72	5.06
Carbon tetrachloride	1	10.67	12.54	14.87	
	1000	5.30	5.75	6.22	
Chlorobenzene	1	7.51	8.55	9.76	11.23
	1000	4.39	4.73	5.10	5.49
Nitrobenzene	1	5.03	5.59	6.24	6.99
	1000	3.39	3.64	3.91	4.20
Water	1	4.57	4.41	4.48	4.65
	1000	3.48	3.40	3.42	3.53

From R. C. Weast, ed., *Handbook of Chemistry and Physics*, 66th ed., CRC Press, Boca Raton, 1985, p. F12ff.

Table A.2 Coefficients of Thermal Expansion at 20°C

Substance	$\alpha \times 10^3/\text{K}^{-1}$
Benzene	1.237
Carbon disulfide	1.218
Carbon tetrachloride	1.236
Chloroform	1.273
Phenol	1.090
Sulfuric acid	0.558
Water	0.207

From C. D. Hodgman, ed., *Handbook of Chemistry and Physics*, 33rd ed., Chemical Rubber Publishing Co., Cleveland, 1951, p. 1855.

Table A.3 Parameters for Some Equations of State

Parameters for the van der Waals Equation of State

$$\left(P + \frac{a}{V_\mathrm{m}^2}\right)(V_\mathrm{m} - b) = RT; \qquad P = \frac{RT}{V_\mathrm{m} - b} - \frac{a}{V_\mathrm{m}^2}$$

Substance	$a/\mathrm{Pa\,m^6\,mol^{-2}}$	$b \times 10^5/\mathrm{m^3\,mol^{-1}}$
Ammonia	0.4225	3.707
Argon	0.1363	3.219
Carbon dioxide	0.3640	4.267
Helium	0.003457	2.370
Hydrogen	0.02476	2.661
Methane	0.2283	4.278
Neon	0.8636	1.709
Nitrogen	0.1408	3.913
Oxygen	0.1378	3.183
Xenon	0.4250	5.105
Water	0.5536	3.049

Parameters for the Berthelot Equation of State

$$\left(P + \frac{a}{TV_\mathrm{m}^2}\right)(V_\mathrm{m} - b) = RT; \qquad P = \frac{RT}{V_\mathrm{m} - b} - \frac{a}{TV_\mathrm{m}^2}$$

Substance	$a/\mathrm{Pa\,m^6\,mol^{-2}\,K}$	$b \times 10^5/\mathrm{m^3\,mol^{-1}}$
Ammonia	171	3.70
Argon	20.5	3.20
Carbon dioxide	111	4.28
Helium	0.019	2.41
Methane	43.6	4.27
Neon	0.98	1.77
Nitrogen	17.3	3.87
Oxygen	21.3	3.18
Xenon	121	5.13
Water	357	3.04

Parameters for the Dieterici Equation of State

$$Pe^{a/V_\mathrm{m}RT}(V_\mathrm{m} - b) = RT; \qquad P = \frac{RT}{V_\mathrm{m} - b}e^{-a/V_\mathrm{m}RT}$$

Substance	$a/\mathrm{Pa\,m^6\,mol^{-2}}$	$b \times 10^5/\mathrm{m^3\,mol^{-1}}$
Ammonia	0.540	4.00
Argon	0.174	3.47
Carbon dioxide	0.468	4.63
Helium	0.0046	2.60
Hydrogen	0.031	2.83
Methane	0.293	4.62
Neon	0.028	1.91
Nitrogen	0.176	4.19
Oxygen	0.177	3.45
Xenon	0.536	5.56
Water	0.709	3.29

(*continued*)

Table A.3 (*continued*)

Parameters for the Redlich-Kwong Equation of State

$$P = \frac{RT}{V_m - b} - \frac{a}{T^{1/2} V_m (V_m + b)}$$

Substance	$a/\mathrm{Pa\,m^6\,mol^{-2}\,K^{1/2}}$	$b \times 10^5/\mathrm{m^3\,mol^{-1}}$
Ammonia	8.59	2.56
Argon	1.69	2.22
Carbon dioxide	6.44	2.96
Helium	0.00835	1.67
Hydrogen	0.14195	1.813
Methane	3.20	2.96
Neon	0.149	1.22
Nitrogen	1.56	2.68
Oxygen	1.74	2.21
Xenon	7.20	3.56
Water	14.24	2.11

From R. C. Weast, ed., *Handbook of Chemistry and Physics*, 64th ed., CRC Press, Boca Raton, FL, 1983, p. D191.

Table A.4 Second Virial Coefficients

	$B_2 \times 10^5/\mathrm{m^3\,mol^{-1}}$					
	Temperature/°C					
Substance	−100	−50	0	50	100	150
Argon	−6.43	−3.74	−2.15	−1.12	−0.42	0.11
Carbon dioxide			−15.4	−10.3	−7.3	−5.1
Helium	1.17	1.19	1.18	1.16	1.14	1.10
Nitrogen	−5.19	−2.64	−1.04	−0.04	0.63	1.19
Water			−45.0	−28.4		
Xenon			−8.12			

Data from D. P. Shoemaker, C. W. Garland, and J. I. Steinfeld, *Experiments in Physical Chemistry*, 4th ed., McGraw-Hill, New York, 1981, p. 64, and J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1954, pp. 167, 227.

Table A.5 Critical Constants

Substance	T_c/K	P_c/bar	$V_{mc} \times 10^6/\mathrm{m^3\,mol^{-1}}$	$P_c V_{mc}/RT_c$
Ammonia	405.6	114.0	70.4	0.238
Argon	151	49	75.2	0.291
Carbon dioxide	304.1	73.8	93.8	0.274
Helium	5.3	2.29	57.8	0.300
Methane	190.7	46.4	99.0	0.290
Neon	44.5	26.2	41.7	0.296
Nitrogen	126.1	33.9	90.1	0.292
Oxygen	154.4	50.4	74.4	0.292
Xenon	289.81	58.66	120.2	0.293
Water	647.2	221.2	54.5	0.224

From J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1954, p. 245, and R. C. Weast, ed., *Handbook of Chemistry and Physics*, 64th ed., Boca Raton, 1983, pp. F66–F67.

Table A.6 Molar Heat Capacities

Gases

$C_{P,m} = a + bT + cT^{-2}$

(Applicable between 298 K and 2000 K)

Substance	a/J K^{-1} mol^{-1}	$b \times 10^3$/J K^{-2} mol^{-1}	$c \times 10^{-5}$/J K mol^{-1}
H_2	27.3	3.3	0.50
O_2	30.0	4.18	−1.67
N_2	28.6	3.8	−0.50
CO	28.4	4.1	−0.46
CO_2	44.2	8.79	−8.62
H_2O	30.5	10.3	0
CH_4	23.6	47.86	−1.8

Liquids

Substance	T/K	$C_{P,m}$/J K^{-1} mol^{-1}
H_2O	273−373	75.48
CO	80	60.7
C_2H_6	100	68.6
Hg	234	28.286

Solids

Substance	T/K	$C_{P,m}$/J K^{-1} mol^{-1}
H_2O	273	37.15
Hg	234	28.274
Cu	1357	31.0
Zn	693	29.7
Sn	505	30.5

From K. S. Pitzer and L. Brewer, *Thermodynamics*, McGraw-Hill, New York, 1961, pp. 63, 66.

Table A.7 Specific Enthalpy Changes of Fusion and Vaporization

Substance	M.P./°C	$\Delta_{\text{fus}} H_m$/J g^{-1}	B.P./°C	$\Delta_{\text{vap}} H_m$/J g^{-1}
Ammonia	66.7		−33.35	1372
Benzene	5.5	127	80.1	394
Carbon dioxide	−56.6[a]	180.7	−78.5[b]	526.6
Carbon monoxide	−199	29.8	−191.5	240.98
Carbon tetrachloride	−22.99	17.5	76.54	207.5
Ethane	−183.3	95.10	−88.6	520.32
Ethanol	−117.3	109.0	78.5	878.58
Methane	−182	58.41	−164	555.19
Water	0.0	333.5	100.0	2257.5

From R. C. Weast, *Handbook of Chemistry and Physics*, 64th ed., CRC Press, Boca Raton, FL, 1983, pp. B227ff, C691ff.

[a] At 5.2 atm pressure.

[b] Sublimation temperature at 1.000 atm pressure.

Table A.8 Values of Thermodynamic Functions

Quantities						
T	$C^\circ_{V,m}$	S°_m	$-\dfrac{G^\circ_m - H^\circ_{m,298}}{T}$	$H^\circ_m - H^\circ_{m,298}$	$\Delta_f H^\circ$	$\Delta_f G^\circ$
Units						
K	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
			Ag(cr)			
0				−5.745		
298	25.351	42.55	–	0	0	0
			Ag^+(ao)			
298	21.8	72.78			105.579	77.107
			AgBr(cr)			
298	52.38	107.1			−100.37	−96.90
			AgCl(cr)			
298	50.79	96.2			−127.068	−109.78
			AgI(cr)			
298	56.82	115.5			−61.84	−66.19
			Ag_2S(cr, α, orthorhombic)			
0					−33.999	
298	76.53	144.01			−32.59	−40.67
			Ag_2S(cr, β)			
298		150.6			−29.41	−39.46
			Ar(g)			
0	0	0		−6.197	0	0
298	20.786	154.845	154.845	0	0	0
500	20.786	165.591	157.200	4.196	0	0
1000	20.786	179.999	165.410	14.589	0	0
2000	20.786	194.407	176.719	35.375		
			Br(g)			
0						117.942
298	20.786	175.022		6.197	111.884	82.396
500	20.798	185.765	177.372	4.196	96.900	70.100
1000	21.365	200.301	185.603	14.698	98.028	42.873
			Br^-(ao)			
298	−141.8	82.4			−121.55	−103.96
			Br_2(g)			
0	0	0		−9.722	45.702	45.697
298	36.048	245.394	245.394	0	30.910	3.126
500	37.077	264.329	249.526	7.402	0	0
1000	37.787	290.293	264.143	26.150	0	0
2000	38.945	316.785	283.569	64.432	0	0
			Br_2(l)			
298	75.674	152.206	152.206	0	0	0
500	75.302	191.150			−23.208	13.481

(continued)

Table A.8 (*continued*)

Quantities						
T	$C^\circ_{V,m}$	S°_m	$-\dfrac{G^\circ_m - H^\circ_{m,298}}{T}$	$H^\circ_m - H^\circ_{m,298}$	$\Delta_f H^\circ$	$\Delta_f G^\circ$
Units						
K	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
C(cr, graphite)						
0	0	0		−1.051	0	0
298	.517	5.740	5.740	0	0	0
500	14.623	11.662	6.932	2.365	0	0
1000	21.610	24.457	12.662	11.795	0	0
2000	25.094	40.771	23.008	35.525	0	0
C(cr, diamond)						
0				−0.523	2.423	
298	6.113	2.377		0	1.895	2.900
C(g)						
0	0	0		−6.536	711.185	711.185
298	20.838	158.100	158.100	0	716.170	671.244
500	20.804	168.863	160.459	4.202	718.507	639.906
1000	20.791	183.278	168.678	14.600	719.475	560.654
2000	20.952	197.713	179.996	35.433	716.577	402.694
CH_4(g)						
0	0	0		−10.024	−66.911	−66.911
298	35.639	186.251	186.251	0	−74.873	−50.768
500	46.342	207.014	190.614	8.200	−80.802	−32.741
1000	71.795	247.549	209.370	38.179	−89.849	19.492
2000	94.399	305.853	244.057	123.592	−92.709	130.802
CO(g)						
0	0	0		−8.671	−113.805	−113.805
298	29.142	197.653	197.653	0	−110.527	−137.163
500	29.794	212.831	200.968	5.931	−110.003	−155.414
1000	33.183	234.538	212.848	21.690	−111.983	−200.275
2000	36.250	258.714	230.342	56.744	−118.896	−286.034
CO(ao)						
298		104.6			−120.96	−119.90
CO_2(g)						
0	0	0		−9.364	−393.151	−393.151
298	37.129	213.795	213.795	0	−393.522	−394.389
500	44.627	234.901	281.290	8.054	−393.676	−394.939
1000	54.308	269.299	235.901	33.397	−394.623	−395.886
2000	60.350	309.293	263.574	91.439	−396.784	−396.333
CO_2(ao)						
298		117.6			−413.80	−385.98
CH_3OH(g)						
298	43.89	289.81		0	−201.17	−162.46

(*continued*)

Table A.8 (*continued*)

Quantities						
T	$C^\circ_{\mathrm{V,m}}$	S°_{m}	$-\dfrac{G^\circ_{\mathrm{m}} - H^\circ_{\mathrm{m,298}}}{T}$	$H^\circ_{\mathrm{m}} - H^\circ_{\mathrm{m,298}}$	$\Delta_{\mathrm{f}} H^\circ$	$\Delta_{\mathrm{f}} G^\circ$
Units						
K	J $\mathrm{K^{-1}\,mol^{-1}}$	J $\mathrm{K^{-1}\,mol^{-1}}$	J $\mathrm{K^{-1}\,mol^{-1}}$	kJ $\mathrm{mol^{-1}}$	kJ $\mathrm{mol^{-1}}$	kJ $\mathrm{mol^{-1}}$
C_2H_2(g)						
0	0	0		−10.012	235.755	235.755
298	44.095	200.958	200.958	0	226.731	248.163
500	54.869	226.610	206.393	10.108	220.345	264.439
1000	68.275	269.192	227.984	41.208	202.989	315.144
2000	81.605	321.335	262.733	117.203	166.980	441.068
C_2H_4(g)						
0	0	0		−10.518	60.986	60.986
298	42.886	219.330	219.330	0	52.467	68.421
500	62.477	246.215	224.879	10.668	46.641	80.933
1000	93.899	300.408	249.742	50.665	38.183	119.122
2000	118.386	374.791	295.101	159.381	34.894	202.070
C_2H_6(g)						
0				−11.950	−69.132	
298	52.63	229.60		0	−84.68	−32.82
Ethanol, C_2H_5OH(l)						
298	111.46	160.7			−277.69	−174.78
Ethanol, C_2H_5OH(ao)						
298		148.5			−288.3	−181.64
Acetic acid, CH_3CO_2H(l)						
298	124.3	282.5			−484.5	−389.9
Acetic acid, CH_3CO_2H(ai)						
298	−6.3	86.6			−486.01	−369.31
Acetic acid, CH_3CO_2H(ao)						
298		178.7			−485.76	−396.46
Acetate ion, $CH_3CO_2^-$(ao)						
298	−6.3	86.6			−486.01	−369.31
Propane, C_3H_8(g)						
298	73.51	270.02			−103.85	−23.27
***n*-Butane, C_4H_{10}(g)**						
298	97.45	310.23		0	−201.17	−162.46
Benzene, C_6H_6(g)						
298	81.67	269.31		0	82.93	129.73
Benzene, C_6H_6(l)						
298	135.31	172.8			49.028	124.50
Benzoic acid, C_6H_5COOH(cr)						
298	146.8	167.6		0	−385.1	−245.3
Cyclohexane, C_6H_{12}(g)						
298	106.3	298.2			−123.1	31.8

(*continued*)

Table A.8 (*continued*)

Quantities						
T	$C^{\circ}_{V,m}$	S°_{m}	$-\dfrac{G^{\circ}_{m}-H^{\circ}_{m,298}}{T}$	$H^{\circ}_{m}-H^{\circ}_{m,298}$	$\Delta_f H^{\circ}$	$\Delta_f G^{\circ}$
Units						
K	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
Cyclohexane, C_6H_{12}(l)						
298	156	204.4			−156.2	26.7
Octane, C_8H_{18}(l)						
298		361.1			−249.9	6.4
Iso-octane (2,2,4-trimethyl pentane), C_8H_{18}(g)						
298		423.2			−224.1	13.7
Iso-octane (2,2,4-trimethyl pentane), C_8H_{18}(l)						
298		328.0			−255.1	6.90
Ca(cr)						
298	25.951	43.070	43.070	0	1.056	0.61
Ca^{2+}(ao)						
298		−53.1			−542.83	−553.58
$CaCl_2$(cr)						
298		72.59	104.6		−795.8	−748.1
Calcite, $CaCO_3$(cr)						
298	81.88	92.9			−1206.92	−1128.79
Aragonite, $CaCO_3$(cr)						
298	81.25	88.7			−1207.13	−1127.75
CaO(cr)						
298	42.120	38.212	38.212	0	−635.089	−603.501
500	48.982	61.980	43.305	9.338	−634.242	−582.316
1000	53.735	97.700	62.463	35.237	−634.273	−530.677
Cl(g)						
0	0	0		−6.272	119.621	119.621
298	21.838	165.189	165.189	0	121.302	105.306
500	22.744	176.752	167.708	4.522	122.272	94.203
1000	22.233	192.430	176.615	15.815	124.334	65.288
2000	21.341	207.505	188.749	37.512	127.058	5.081
Cl^-(g)						
298	22.958	167.5567	167.556	0	1378.801	1355.845
500	23.706	179.700	170.205	4.748	1384.192	1338
Cl_2(g)						
0	0	0		−9.181	0	0
298	33.949	223.079	223.079	0	0	0
500	36.064	241.228	227.020	7.104	0	0
1000	37.438	266.767	241.203	25.565	0	0
2000	38.428	293.033	261.277	63.512	0	0
Cl^-(ao)						
298	−136.4	56.5			−167.159	−131.228

(*continued*)

Table A.8 (*continued*)

			Quantities			
T	$C^\circ_{\mathrm{V,m}}$	S°_{m}	$-\dfrac{G^\circ_{\mathrm{m}} - H^\circ_{\mathrm{m},298}}{T}$	$H^\circ_{\mathrm{m}} - H^\circ_{\mathrm{m},298}$	$\Delta_{\mathrm{f}} H^\circ$	$\Delta_{\mathrm{f}} G^\circ$
			Units			
K	$\mathrm{J\ K^{-1}\ mol^{-1}}$	$\mathrm{J\ K^{-1}\ mol^{-1}}$	$\mathrm{J\ K^{-1}\ mol^{-1}}$	$\mathrm{kJ\ mol^{-1}}$	$\mathrm{kJ\ mol^{-1}}$	$\mathrm{kJ\ mol^{-1}}$
			Cu(cr)			
298	24.435	33.150			0	0
			Cu^{2+}(ao)			
298		−99.6			64.77	65.49
			CuO(cr)			
298	42.246	42.594	42.594	0	−156.063	−128.292
			Cu_2O(cr)			
298	35.693	234.617	234.617	0	306.269	276.788
			F(g)			
0	0	0		−6.518	77.284	77.284
298	22.746	158.750	158.750	0	79.390	62.289
500	22.100	170.363	161.307	4.528	80.597	50.350
1000	21.266	185.362	170.038	15.324	82.403	19.317
2000	20.925	199.963	181.778	36.369	84.387	−44.635
			F_2(g)			
0	0	0		−8.825	0	0
298	31.302	202.789	202.789	0	0	0
500	34.255	219.738	206.452	6.743	0	0
1000	37.057	244.552	219.930	24.622	0	0
2000	38.846	270.904	239.531	62.745	0	0
			Fe(cr)			
0				−4.489		
298	25.10	27.28		0	0	0
			Fe^{2+}(ao)			
298		−137.7			−89.1	−78.90
			Fe^{3+}(ao)			
298		−315.9			−48.5	−4.7
			$Fe(OH)_3$(s)			
298		106.7			−823.0	−696.5
			$Fe(OH)_3$(ao)			
298						−659.3
			H_2(g)			
0	0	0		−8.467	0	0
298	28.836	130.680	130.680	0	0	0
500	29.260	145.737	133.973	5.882	0	0

(continued)

Table A.8 (*continued*)

Quantities						
T	$C^\circ_{V,m}$	S°_m	$-\dfrac{G^\circ_m - H^\circ_{m,298}}{T}$	$H^\circ_m - H^\circ_{m,298}$	$\Delta_f H^\circ$	$\Delta_f G^\circ$
Units						
K	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
1000	30.205	166.216	145.536	20.680	0	0
2000	34.280	188.418	161.943	52.951	0	0
			H(g)			
0	0	0		−6.197	216.35	216.035
298	20.786	114.713		0	217.965	203.247
500	20.786	125.463		5.928	219.254	192.957
			H^+(ao)			
298	0	0			0	0
			H_2CO_3(ao)			
298		187.4			−699.65	−623.08
			HBr(g)			
0	0	0		−8.648	−28.560	−28.560
298	29.142	198.695		0	−36.40	−53.45
500	29.453	213.812	202.006	5.903	−52.636	−57.026
1000	32.319	235.032		21.294	−54.018	−60.796
2000	36.109	258.824		55.838	−54.751	−67.196
			HCl(g)			
0	0	0		−8.640	−92.127	−92.127
298	29.136	186.901	186.901	0	−92.312	−95.300
500	29.304	201.898	190.205	5.892	−92.912	−97.166
1000	31.628	222.903	201.857	21.046	−94.388	−100.799
2000	35.600	246.246	218.769	54.953	−95.590	−106.631
			HF(g)			
298	29.138	173.780	173.780	0	−272.546	−274.646
			HI(g)			
0		0	0	−8.656	28.535	28.535
298	29.156	206.589	206.589	0	26.359	1.560
500	29.736	221.760	209.905	5.928	−5.622	−10.088
1000	33.135	243.404	221.763	21.641	−6.754	−14.006
2000	36.623	267.680	239.248	56.863	−7.589	−21.009
			HNO_3(g)			
0				−11.778	−125.27	
298	53.35	266.38		0	−135.06	−74.72
			HNO_3(ai)			
298	−86.6	146.4		0	−207.36	−111.25
			H_2O(g)			
0	0	0		−9.904	−238.921	−238.921
298	33.590	188.834	188.834	0	−241.826	−228.582

(*continued*)

Table A.8 (*continued*)

			Quantities			
T	$C^\circ_{\mathrm{V,m}}$	S°_{m}	$-\dfrac{G^\circ_{\mathrm{m}} - H^\circ_{\mathrm{m},298}}{T}$	$H^\circ_{\mathrm{m}} - H^\circ_{\mathrm{m},298}$	$\Delta_{\mathrm{f}} H^\circ$	$\Delta_{\mathrm{f}} G^\circ$
			Units			
K	$\mathrm{J\ K^{-1}\ mol^{-1}}$	$\mathrm{J\ K^{-1}\ mol^{-1}}$	$\mathrm{J\ K^{-1}\ mol^{-1}}$	$\mathrm{kJ\ mol^{-1}}$	$\mathrm{kJ\ mol^{-1}}$	$\mathrm{kJ\ mol^{-1}}$
500	35.226	206.534	192.685	6.925	−243.826	−219.051
1000	41.268	232.738	206.738	26.000	−247.857	−192.590
2000	51.180	264.769	228.374	72.790	−251.575	−135.528
			H_2O(l)			
298	75.351	69.950	69.950	0	−285.830	−237.141
500	83.694	109.898	78.579	15.659	−279.095	−206.002
			H_2S(g)			
298	34.192	205.757	205.757	0	−20.502	−33.329
500	37.192	224.102	209.726	7.188	−27.762	−40.179
1000	45.786	252.579	224.599	27.980	−90.024	−20.984
			H_2SO_4(l)			
298	83.761	298.796	298.796	0	−735.129	−653.366
			H_2SO_4(ai)			
298	−293	20.1		0	−909.27	−744.53
			He(g)			
0	0	0		−6.197	0	0
298	20.786	126.152	126.152	0	0	0
500	20.786	136.899	128.507	4.196	0	0
1000	20.786	151.306	136.718	14.589	0	0
2000	20.786	165.714	148.027	35.375	0	0
			Hg(l)			
298	27.978	76.028	0	0	0	0
			Hg(g)			
298	20.786	174.970	174.970	0	61.380	31.880
			Hg_2^{2+}(ao)			
298		84.5			172.4	153.52
			Hg^{2+}(ao)			
298		−32.2			171.1	164.4
			Hg_2Cl_2(cr)			
298	101.968	192.535	192.535	0	−264.927	−210.485
			$HgCl_2$(cr)			
298	73.906	144.494	144.494	0	−230.120	−184.022
			HgO(cr, red, orthorhombic)			
298	44.06	70.29			−90.83	−58.539
			HgS(cr, red)			
298	48.41	82.4			−58.2	−50.6

(*continued*)

Table A.8 (*continued*)

Quantities						
T	$C^\circ_{\mathrm{V,m}}$	S°_{m}	$-\dfrac{G^\circ_{\mathrm{m}} - H^\circ_{\mathrm{m,298}}}{T}$	$H^\circ_{\mathrm{m}} - H^\circ_{\mathrm{m,298}}$	$\Delta_{\mathrm{f}} H^\circ$	$\Delta_{\mathrm{f}} G^\circ$
Units						
K	$\mathrm{J\,K^{-1}\,mol^{-1}}$	$\mathrm{J\,K^{-1}\,mol^{-1}}$	$\mathrm{J\,K^{-1}\,mol^{-1}}$	$\mathrm{kJ\,mol^{-1}}$	$\mathrm{kJ\,mol^{-1}}$	$\mathrm{kJ\,mol^{-1}}$
			HgS(cr,black)			
298		88.3			−53.6	−47.7
			I_2(cr)			
298	54.436	116.142	116.142	0	0	0
			I_2(g)			
298	36.887	260.685	260.685	0	62.421	19.325
			I(g)			
0				−6.197	107.240	
298	20.786	180.791		0	106.838	70.250
			I^-(ao)			
298	−142.3	111.3			−55.19	−51.57
			K^+(ao)			
298	21.8	102.5			−252.38	−283.27
			KOH(cr)			
298	64.9	78.9		12.150	−424.764	−379.08
			Li^+(ao)			
298	68.6	13.4			−278.49	−293.31
			Mg(cr)			
0				−5.000		
298	24.89	32.68		0	0	0
			MgO(cr, macrocrystal)			
0				−5.167	−597.530	
298	37.15	26.74		0	−601.70	−569.43
			N_2(g)			
0	0	0		−8.670	0	0
298	29.124	191.609	191.609	0	0	0
500	29.580	206.739	194.917	5.911	0	0
1000	32.697	228.170	206.708	21.463	0	0
2000	35.971	252.074	224.006	56.137	0	0
			NH_3(g)			
0	0	0		−10.045	−38.907	−38.907
298	35.652	192.774	192.774	0	−45.898	−16.367
500	42.048	212.659	197.021	7.819	−49.857	4.800
1000	56.491	246.486	213.849	32.637	−55.013	61.910
2000	72.833	291.525	242.244	98.561	−54.833	179.447
			NH_3(ao)			
298		111.3			−80.29	−26.50
			$NH_4{}^+$(ao)			
298	79.9	113.4			−132.51	−79.31

(*continued*)

Table A.8 (*continued*)

			Quantities			
T	$C^\circ_{V,m}$	S°_m	$-\dfrac{G^\circ_m - H^\circ_{m,298}}{T}$	$H^\circ_m - H^\circ_{m,298}$	$\Delta_f H^\circ$	$\Delta_f G^\circ$
			Units			
K	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
			NO(g)			
298	29.845	210.758	210.758	0	90.291	86.600
			NO_2(g)			
298	36.874	240.034	240.034	0	33.095	51.258
			N_2O_4(g)			
0	0	0		−16.398	18.718	18.718
298	77.256	305.376	304.376	0	9.079	97.787
500	97.204	349.446	313.907	17.769	8.769	158.109
1000	119.208	425.106	352.127	72.978	15.189	305.410
2000	129.030	511.743	412.484	198.518	33.110	588.764
			N_2O(g)			
298	38.617	219.957	219.957	0	82.048	104.179
			NO_3^-(ao)			
298	−86.6	146.4			−205.0	−108.74
			N_2O_5(g)			
298	96.303	346.548	346.548	0	11.297	118.013
			NOCl(g)			
0				−11.364	53.60	
298	44.69	261.69			51.71	66.08
			Na^+(ao)			
298	46.4	59.0			−240.12	−261.905
			NaOH(cr)			
0	0	0		−10.487	−421.396	−421.396
298	59.530	64.445	64.445	0	−425.931	−379.741
500	75.157	98.172	71.595	13.288	−427.401	−347.767
			Ne(g)			
0	0	0		−6.197	0	0
298	20.786	146.327	146.327	0	0	0
500	20.786	157.074	148.683	4.196	0	0
1000	20.786	171.482	156.893	14.589	0	0
2000	20.786	185.889	168.202	35.375	0	0
			O(g)			
0	0	0		−6.725	246.790	246.790
298	21.911	161.058	161.058	0	249.173	231.736
500	21.257	172.197	163.511	4.343	250.474	219.549
1000	20.915	186.790	171.930	14.860	252.682	187.681
2000	20.826	201.247	183.391	35.713	255.299	121.552

(*continued*)

Table A.8 (*continued*)

			Quantities			
T	$C^\circ_{\mathrm{V,m}}$	S°_{m}	$-\dfrac{G^\circ_{\mathrm{m}} - H^\circ_{\mathrm{m,298}}}{T}$	$H^\circ_{\mathrm{m}} - H^\circ_{\mathrm{m,298}}$	$\Delta_{\mathrm{f}} H^\circ$	$\Delta_{\mathrm{f}} G^\circ$
			Units			
K	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
			O_2(g)			
0	0	0		−8.683	0	0
298	29.376	205.147	205.147	0	0	0
500	31.091	220.693	208.524	6.084	0	0
1000	34.870	243.578	220.875	22.703	0	0
2000	37.741	268.748	239.160	59.175	0	0
			O_3(g)			
0	0	0		−10.351	145.348	145.348
298	39.238	238.932	238.932	0	142.674	163.184
500	47.262	261.272	243.688	8.792	142.340	177.224
1000	55.024	297.048	262.228	34.819	143.439	211.759
2000	58.250	336.469	290.533	91.873	145.784	279.089
			OH^-(ao)			
298	−148.5	−10.75			−229.994	−157.244
			P(cr, white)			
298	23.840	41.09		5.360	0	0
			P(cr, red, triclinic)			
298	21.21	22.80		3.607	−17.6	−12.1
			P(cr, black)			
298					−39.3	
			P(am, red)			
298					−7.5	
			PCl_3(g)			
0	0	0		−15.932	−285.497	−285.497
298	71.581	311.682	311.682	0	−288.696	−269.610
500	78.370	350.656	320.107	15.274	−290.007	−256.102
1000	81.867	406.435	350.828	55.607	−290.528	−221.943
2000	82.819	463.583	394.530	138.107	−348.754	−110.631
			PCl_5(g)			
0	0	0		−22.852	−354.723	−354.723
298	111.890	364.288	364.288	0	−360.184	−290.271
500	124.332	425.745	377.544	24.100	−359.722	−242.799
1000	130.705	514.582	426.223	88.359	−354.829	−127.623
2000	132.439	605.912	495.804	220.215	−401.646	137.886
			Pb(cr)			
0				−6.878		
298	26.44	64.81		0	0	0
			Pb^{2+}(ao)			
298		10.5			−1.7	−24.43

(*continued*)

Table A.8 (*continued*)

Quantities						
T	$C^\circ_{\mathrm{V,m}}$	S°_{m}	$-\dfrac{G^\circ_{\mathrm{m}} - H^\circ_{\mathrm{m},298}}{T}$	$H^\circ_{\mathrm{m}} - H^\circ_{\mathrm{m},298}$	$\Delta_{\mathrm{f}} H^\circ$	$\Delta_{\mathrm{f}} G^\circ$
Units						
K	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
			PbO_2(cr)			
298	64.64	68.6			−277.4	−217.33
			PbS(cr)			
298	49.50	91.2			−100.4	−98.7
			$PbSO_4$(cr)			
0				−20.062		
298	103.207	148.57		0	−919.94	−813.14
			Pt(cr)			
0				−5.740		
298	25.86	41.63		0	0	0
			S(cr, rhombic)			
0				−4.410		
298	22.64	31.80		0	0	0
			S(cr, monoclinic)			
298					0.33	0.096
			S^{2-}(ao)			
298		−14.6			33.1	85.8
			SO_2(g)			
0	0	0		−10.552	−294.299	−294.299
298	39.878	248.212	248.212	0	−296.842	−300.125
500	46.576	270.495	252.979	8.758	−302.736	−300.871
1000	54.484	305.767	271.339	34.428	−361.940	−288.725
2000	58.229	345.007	299.383	91.250	−360.981	−215.929
			SO_3(g)			
0	0	0	−11.697	−390.025	−390.025	
298	50.661	256.769	256.769	0	−395.765	−371.016
500	63.100	286.152	262.992	11.580	−401.878	−352.668
1000	75.968	334.828	287.768	47.060	−459.581	−293.639
2000	81.140	389.616	326.421	126.390	−454.351	−129.768
			$SO_4{}^{2-}$(ao)			
298	−293	20.1			−909.27	−744.53

(*continued*)

Table A.8 (*continued*)

Quantities						
T	$C^\circ_{\mathrm{V,m}}$	S°_{m}	$-\dfrac{G^\circ_{\mathrm{m}} - H^\circ_{\mathrm{m},298}}{T}$	$H^\circ_{\mathrm{m}} - H^\circ_{\mathrm{m},298}$	$\Delta_{\mathrm{f}} H^\circ$	$\Delta_{\mathrm{f}} G^\circ$
Units						
K	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}	J K^{-1} mol^{-1}	kJ mol^{-1}	kJ mol^{-1}	kJ mol^{-1}
Sn^{2+}(ao) **(μ($NaClO_4$) = 3.0)**						
298		−17			−8.8	−27.2
Sn^{4+}(ao) **(in HCl + ∞H_2O)**						
298		−117			30.5	2.5
Zn(cr)						
0				−5.669		
298	25.287	41.717		0	0	0
Zn^{2+}(ao)						
298	46	−112.1			−153.89	−147.06
ZnO(cr)						
298	40.25	43.64			−348.28	−318.30
sphalerite, ZnS(cr)						
298	46.0	57.7			−205.98	−201.29
wurtzite, ZnS(cr)						
298					−192.63	

From M. W. Chase, Jr., C. A. Davies, J. R. Downey, Jr., D. J. Frurip, R. A. McDonald, and A. N. Syverud, *JANAF Thermochemical Tables*, 3rd ed., *J. Phys. Chem. Ref. Data*, Vol. 14, 1985, Supplement No. 1, published by the American Chemical Society and the American Institute of Physics for the National Bureau of Standards; D. D. Wagman, W. H. Evans, V. B. Parker, R. H. Schymm, I. Halow, S. M. Bailer, K. L. Churney, and R. L Nuttall, *The NBS Tables of Chemical Thermodynamic Properties—Selected Values for Inorganic and C_1 and C_2 Organic Substances in SI Units*, *J. Phys. Chem. Ref. Data*., Vol. 11, 1982, Supplement No. 2, published by the American Chemical Society and the American Institute of Physics for the National Bureau of Standards.

In the case of small discrepancies between Chase *et al*., and Wagman *et al*., the values from Chase *et al*., have been taken. Values for organic substances with more than two carbons are from D. R. Stull, E. F. Westrum, and G. C. Sinke, *The Chemical Thermodynamics of Organic Compounds*, Wiley, New York, 1969, or from M. Kh. Karapet'yants and M. L. Karapet'yants, *Thermodynamic Constants of Inorganic and Organic Compounds*, Humphrey Science Publishers, Ann Arbor, MI, 1970.

Abbreviations: cr = crystal; l = liquid; g = gas; ao = aqueous, molality standard state without (further) ionization; ai = aqueous, molality standard state with ionization; am = amorphous.

Table A.9 Average Bond Energies

Bond	Bond Energy/kJ mol^{-1}
Br—Br	193
C—C	343
C=C	615
C≡C	812
C—Cl	326
C—F	490
C—H	416
C—N	290
C≡N	891
C—O	351
C=O	724
C=O (in CO_2)	799
C≡O	1046
Cl—Cl	244
F—F	158
H—Br	366
H—Cl	432
H—H	436
H—F	568
H—I	298
H—N	391
H—S	367
N—N	160
N≡N	946
N—O	176
O—H	464
O—O	144
O=O (in O_2)	498

From F. T. Wall, *Chemical Thermodynamics*, 3rd ed., W. H. Freeman, San Francisco, 1974, p. 63.

Table A.10 Surface Tension Values

Substance	In Contact With	Temperature/°C	Value/N m^{-1}
Acetone	air	0	0.02621
	air	20	0.02370
	air	40	0.02116
Argon	vapor	−188	0.0132
Benzene	air	20	0.02885
	vapor	20	0.02889
Carbon dioxide	vapor	−25	0.00913
	vapor	20	0.00116
Carbon tetrachloride	vapor	20	0.02695
Ethanol	vapor	20	0.02275
Glycerol	air	20	0.0634
Gold	H_2,Ar	1120	1.128
Mercury	air	20	0.4355
Water	air	20	0.07275
	air	25	0.07197
	air	30	0.07118

From R. C. Weast, *Handbook of Chemistry and Physics*, 51st ed., CRC Publishing Co., Boca Raton, FL, 1970, p. F33ff.

Table A.11 Mean Ionic Activity Coefficients of Aqueous Electrolytes at 25°C

Molality	0.1	0.2	0.5	1.0	1.6	2.5
			1–1 Electrolytes			
Debye–Hückel	0.754	0.696	0.615	0.556	0.519	0.487
Davies	0.781	0.747	0.733	0.791	0.912	1.175
HCl	0.796	0.767	0.757	0.809	0.916	1.147
NaOH	0.764	0.725	0.688	0.677	0.690	0.741
NaCl	0.778	0.735	0.681	0.657	0.655	0.688
KCl	0.770	0.718	0.649	0.604	0.580	0.569
Sodium acetate	0.791	0.757	0.735	0.757	0.809	0.914
NH_4NO_3	0.740	0.677	0.582	0.504	0.447	0.391
			1–2 and 2–1 Electrolytes			
Debye–Hückel	0.436	0.359	0.275	0.226	0.199	0.179
Davies	0.538	0.547	0.790	1.868	5.865	35.27
$MgCl_2$	0.528	0.488	0.480	0.569	0.802	1.538
Na_2SO_4	0.452	0.371	0.270	0.204	0.168	0.144
K_2CrO_4	0.466	0.356	0.298	0.240	0.212	0.194
			2–2 Electrolytes			
Debye–Hückel	0.162	0.109	0.064	0.044	0.035	0.026
Davies	0.284	0.336	1.069	12.24	284.5	–
$CuSO_4$	0.150	0.104	0.0620	0.0432	–	–
$ZnSO_4$	0.150	0.104	0.0630	0.0435	0.0363	0.0367
$CdSO_4$	0.150	0.103	0.0615	0.0415	0.0338	0.0317

From R. A. Robinson and R. H. Stokes, *Electrolyte Solutions*, 2nd ed., Butterworths, London, 1968.

Table A.12 Partial Vapor Pressure of Hydrogen Halides in Aqueous Solution at 298.15 K

	Pressure/torr		
Molality/mol kg^{-1}	HCl	HBr	HI
4.0	0.0182		
5.0	0.0530		
6.0	0.140	0.00151	0.00057
7.0	0.348	0.00370	0.00182
8.0	0.844	0.0089	0.0065
9.0	1.93	0.0226	0.0295
10.0	4.20	0.059	0.132
11.0		0.151	

From S. J. Bates and H. D. Kirschman, *J. Am. Chem. Soc.*, **41**, 1991 (1919).

Table A.13 Some Standard Reduction Potentials in Aqueous Solution at 25°C and P° = 1 bar

Half-Cell Symbol	Half-Reaction	E°V
$\mathrm{F^- \mid F_2 \mid Pt}$	$\mathrm{F_2}(g) + 2e^- \rightarrow \mathrm{2F^-}$	+2.87
$\mathrm{H_2SO_4 \mid PbSO_4 \mid PbO_2}$	$\mathrm{PbO_2 + SO_4^{2-} + 4H^+ + 2}e^- \rightarrow \mathrm{PbSO_4 + 2H_2O}$	+1.685
$\mathrm{Ce^{3+},Ce^{4+} \mid Pt}$ (in 1M $\mathrm{HNO_3}$)	$\mathrm{Ce^{4+}} + e^- \rightarrow \mathrm{Ce^{3+}}$	+1.61
$\mathrm{Mn^{2+},MnO_4^- \mid Pt}$	$\mathrm{MnO_4^- + 8H^+ + 5}e^- \rightarrow \mathrm{Mn^{2+} + 4H_2O}$	+1.491
$\mathrm{Au^{3+} \mid Au}$	$\mathrm{Au^{3+} + 3}e^- \rightarrow \mathrm{Au}$	+1.42
$\mathrm{Cl^- \mid Cl_2 \mid Pt}$	$\mathrm{Cl_2 + 2}e^- \rightarrow \mathrm{2Cl^-}$	+1.3583
$\mathrm{O_2(g),H_2O \mid Pt}$	$\mathrm{O_2 + 4H^+ + 4}e^- \rightarrow \mathrm{2H_2O}$	+1.229
$\mathrm{Br^- \mid Br_2 \mid Pt}$	$\mathrm{Br_2 + 2}e^- \rightarrow \mathrm{2Br^-}$	+1.065
$\mathrm{Au \mid AuCl_4^- \mid Cl^-}$	$\mathrm{AuCl_4^- + 3}e^- \rightarrow \mathrm{Au(s) + 4Cl^-}$	+1.002
$\mathrm{Ag \mid Ag^+}$	$\mathrm{Ag^+} + e^- \rightarrow \mathrm{Ag}$	+0.7986
$\mathrm{Hg_2^{2+} \mid Hg(l) \mid Pt}$	$\mathrm{Hg_2^{2+}2}e^- \rightarrow \mathrm{2Hg(l)}$	+0.7961
$\mathrm{Fe^{2+} \mid Fe^{3+} \mid Pt}$	$\mathrm{Fe^{3+}} + e^- \rightarrow \mathrm{Fe^{2+}}$	+0.770
$\mathrm{MnO_2 \mid MnO_4^- \mid Pt}$	$\mathrm{MnO_4^- + 2H_2O + 3}e^- \rightarrow \mathrm{MnO_2 + 4OH^-}$	+0.588
$\mathrm{I^- \mid I_2(s) \mid Pt}$	$\mathrm{I_2(s) + 2}e^- \rightarrow \mathrm{2I^-}$	+0.535
$\mathrm{I^- \mid I_2(aq) \mid Pt}$	$\mathrm{I_2(aq) + 2}e^- \rightarrow \mathrm{2I^-}$	+0.6197
$\mathrm{I^-,I_3^- \mid Pt}$	$\mathrm{I_3^- + 2}e^- \rightarrow \mathrm{3I^-}$	+0.5338
$\mathrm{OH^- \mid O_2(g) \mid Pt}$	$\mathrm{O_2 + 2H_2O + 4}e^- \rightarrow \mathrm{4OH^-}$	+0.401
$\mathrm{Cu(s) \mid Cu^{2+}}$	$\mathrm{Cu^{2+} + 2}e^- \rightarrow \mathrm{Cu(s)}$	+0.3402
$\mathrm{Cl^- \mid Hg_2Cl_2(s) \mid Hg(l)}$	$\mathrm{Hg_2Cl_{2(s)} + 2}e^- \rightarrow \mathrm{2Hg(l) + 2Cl^-}$	+0.268
$\mathrm{Cl^- \mid AgCl(s) \mid Ag(s)}$	$\mathrm{AgCl(s)} + e^- \rightarrow \mathrm{Ag(s) + Cl^-}$	+0.2223
$\mathrm{Sn^{4+},Sn^{2+} \mid Pt}$	$\mathrm{Sn^{4+} + 2}e^- \rightarrow \mathrm{Sn^{2+}}$	+0.15
$\mathrm{Br^- \mid AgBr(s) \mid Ag(s)}$	$\mathrm{AgBr(s)} + e^- \rightarrow \mathrm{Ag(s) + Br^-}$	+0.0713
$\mathrm{H^+ \mid H_2 \mid Pt}$	$\mathrm{2H^+ + 2}e^- \rightarrow \mathrm{H_2}$	0.000
$\mathrm{Fe^{3+} \mid Fe(s)}$	$\mathrm{Fe^{3+} + 3}e^- \rightarrow \mathrm{Fe(s)}$	−0.036
$\mathrm{I^- \mid Hg_2I_2(s) \mid Hg(l)}$	$\mathrm{Hg_2I_{2(s)} + 2}e^- \rightarrow \mathrm{2Hg(l) + 2I^-}$	−0.0405
$\mathrm{Pb^{2+} \mid Pb(s)}$	$\mathrm{Pb^{2+} + 2}e^- \rightarrow \mathrm{Pb(s)}$	−0.1263
$\mathrm{I^- \mid AgI(s) \mid Ag(s)}$	$\mathrm{AgI(s)} + e^- \rightarrow \mathrm{Ag(s) + I^-}$	−0.1519
$\mathrm{Cd^{2+} \mid Cd(in\ Hg)}$	$\mathrm{Cd^{2+} + 2}e^- \rightarrow \mathrm{Cd(in\ Hg)}$	−0.3521
$\mathrm{SO_4^{2-} \mid PbSO_4(s) \mid Pb(s)}$	$\mathrm{PbSO_4(s) + 2}e^- \rightarrow \mathrm{Pb(s) + SO_4^{2-}}$	−0.356
$\mathrm{Cd^{2+} \mid Cd(s)}$	$\mathrm{Cd^{2+} + 2}e^- \rightarrow \mathrm{Cd(s)}$	−0.4026
$\mathrm{Fe^{2+} \mid Fe(s)}$	$\mathrm{Fe^{2+} + 2}e^- \rightarrow \mathrm{Fe(s)}$	−0.44
$\mathrm{S^{2-} \mid Ag_2S(s) \mid Ag(s)}$	$\mathrm{Ag_2S(s) + 2}e^- \rightarrow \mathrm{2Ag(s) + S^{2-}}$	−0.7051
$\mathrm{Zn^{2+} \mid Zn(s)}$	$\mathrm{Zn^{2+} + 2}e^- \rightarrow \mathrm{Zn(s)}$	−0.7628
$\mathrm{OH^- \mid H_2(g) \mid Pt}$	$\mathrm{2H_2O + 2}e^- \rightarrow \mathrm{H_2 + 2OH^-}$	−0.8277
$\mathrm{Mg^{2+} \mid Mg(s)}$	$\mathrm{Mg^{2+} + 2}e^- \rightarrow \mathrm{Mg(s)}$	−2.375
$\mathrm{Na^+ \mid Na(s)}$	$\mathrm{Na} + e^- \rightarrow \mathrm{Na(s)}$	−2.7109
$\mathrm{Ca^{2+} \mid Ca(s)}$	$\mathrm{Ca^{2+} + 2}e^- \rightarrow \mathrm{Ca(s)}$	−2.868
$\mathrm{K^+ \mid K(s)}$	$\mathrm{K^+} + e^- \rightarrow \mathrm{K(s)}$	−2.925
$\mathrm{Li^+ \mid Li(s)}$	$\mathrm{Li^+} + e^- \rightarrow \mathrm{Li(s)}$	−3.045

Table A.14 Parameters for the Lennard–Jones Potential

Substance	$\sigma \times 10^{10}/\text{m}$	$(\varepsilon/k_\text{B})/\text{K}$
Argon	3.40	120
Carbon dioxide	4.5	189
Helium	2.56	10.22
Krypton	3.60	58.8
Neon	2.75	35
Nitrogen	3.7	95
Oxygen	3.5	118
Xenon	4.1	87

From J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1954, p. 1110ff.

Table A.15 Effective Hard-Sphere Diameters

Substance	Temperature/K	$d \times 10^{10}/\text{m}$
Ammonia	293	4.38
Argon	273	3.65
	293	3.61
	373	3.48
	473	3.37
Carbon dioxide	293	4.53
Carbon monoxide	295	3.72
Chlorine	293	5.39
Ethane	293	5.26
Ethylene	293	4.90
Helium	293	2.17
Hydrogen	294	2.72
Iodine	397	6.35
Methane	293	4.10
Nitrogen	301	3.71
Oxygen	292	3.58
Water	373	4.18
Xenon	293	4.81

From R. C. Weast, ed., *Handbook of Chemistry and Physics*, 64th ed., CRC Press, Boca Raton, FL, 1983, p. F43ff.

Table A.16 Thermal Conductivities

Substance	Temperature/°C	κ/J s^{-1} m^{-1} K^{-1}
	Gases	
Air, 1 atm	20	0.02353
Argon, 1 atm	20	0.01625
Carbon dioxide, 1 atm	20	0.01409
Helium, 1 atm	20	0.13954
	Liquids	
Benzene	22.5	0.1582
Carbon tetrachloride	20	0.1033
Octane	30	0.1451
Water	27	0.6092
	Solids	
Aluminum	25	237
Iron	25	80.4

From R. C. Weast, ed., *Handbook of Chemistry and Physics*, 64th ed., CRC Press, Boca Raton, FL, 1983, pp. E2–E15.

Table A.17 Diffusion Coefficients for Dilute Solutes in Liquid Solutions

Solute	Solvent	Temperature/°C	$D \times 10^9$/m^2 s^{-1}
Acetylene	water	0	1.10
α-alanine	water	25	0.91
Carbon dioxide	n-pentanol	25	1.91
Ethane	n-heptane	30	5.60
Glucose	water	25	0.673
Glycine	water	25	1.064
Potassium chloride	water	25	1.917
Sodium chloride	water	25	1.545
Sucrose	water	25	0.5226

From R. C. Weast, ed., *Handbook of Chemistry and Physics*, 64th ed., CRC Press, Boca Raton, FL, 1983, pp. F45–F46.

Table A.18 Coefficients of Viscosity

Substance	State	Temperature/°C	$\eta \times 10^3/\mathrm{kg\,m^{-1}\,s^{-1}}$
Benzene	Liquid	20	0.652
Carbon tetrachloride	Liquid	20	0.969
Ethanol	Liquid	20	1.200
		40	0.834
Glycerol	Liquid	0	12, 110
		20	1490
Hexane	Liquid	0	0.401
		20	0.326
Mercury	Liquid	0	1.685
		20	1.554
Sulfuric acid	Liquid	20	25.4
Water	Liquid	0	1.787
		20	1.002
		25	0.8904
		100	0.2818
Argon	Gas	0	0.02096
		20	0.02217
Carbon dioxide	Gas	0	0.01390
		20	0.01480
Helium	Gas	20	0.01941
		100	0.02281
Nitrogen	Gas	27.4	0.01781
		127.2	0.02191
Oxygen	Gas	0	0.0189
		19.1	0.02018
Water	Gas	100	0.01255
		200	0.01635

From R. C. Weast, ed., *Handbook of Chemistry and Physics*, 64th ed., CRC Press, Boca Raton, FL, 1983, p. F38ff.

Table A.19 Self-Diffusion Coefficients at $P = 1.000$ atm

Substance	Temperature/K	$D \times 10^4/\mathrm{m^2\,s^{-1}}$
Argon	77.7	0.0134 ± 0.0002
	273.2	0.157 ± 0.0003
	353.2	0.249 ± 0.0003
Carbon dioxide	273.2	0.0970
Hydrogen	273	1.285 ± 0.002
Methane	273.2	0.206 ± 0.006
Nitrogen	353.2	0.287 ± 0.009
Oxygen	353.2	0.301 ± 0.004
Xenon	300.5	0.0576 ± 0.0009

Data from J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1954, p. 581.

Table A.20 Molar Conductivities and Ion Mobilities at Infinite Dilution in Water at 298.15 K

Ion	$\lambda_0 \times 10^3/\text{m}^2\ \text{ohm}^{-1}\ \text{mol}^{-1}$	$u \times 10^8/\text{m}^2\ \text{s}^{-1}\ \text{V}^{-1}$
H^+	34.982	36.25
K^+	7.352	7.619
Na^+	5.011	5.193
Li^+	3.869	4.010
${NH_4}^+$	7.34	7.61
Ca^{2+}	11.90	6.166
OH^-	19.8	20.5
Cl^-	7.634	7.912
Br^-	7.84	8.13
I^-	7.685	7.96
NO_3^+	7.144	7.404
Acetate, $C_2H_3O_2^-$	4.09	4.24
ClO_4^-	6.80	7.05
$SO_{4^{2-}}$	15.94	8.27

From A. J. Bard and L. R. Faulkner, *Electrochemical Methods*, Wiley, New York, 1980, p. 67.

Table A.21 Electronegativities on the Pauling Scale

Element	Value	Element	Value
H	2.1	K	0.8
He	–	Ca	1.0
Li	1.0	Sc	1.3
Be	1.5	Ti	1.5
B	2.0	V	1.6
C	2.5	Cr	1.6
N	3.0	Mn	1.5
O	3.5	Fe	1.8
F	4.0	Co	1.8
Ne	–	Ni	1.8
Na	0.9	Cu	1.9
Mg	1.2	Zn	1.6
Al	1.5	Ga	1.6
Si	1.8	Ge	1.8
P	2.1	As	2.0
S	2.5	Se	2.4
Cl	3.0	Br	2.8
Ar	–	Kr	–

Table A.22 Properties of Diatomic Molecules

Term/Unit:	D_e/hc cm^{-1}	$\tilde{\nu}_e$ cm^{-1}	$\tilde{\nu}_e x_e$ cm^{-1}	$\tilde{B}_e$ cm^{-1}	r_e Å	$\tilde{\alpha}_e$ cm^{-1}	$\tilde{\mathcal{D}}_e$ $10^{-4}\,\mathrm{cm}^{-1}$
$^{79}\mathrm{Br}_2/{}^1\Sigma_g^+$		325.32	1.077	0.0821	2.281	0.000319	0.00021
$^{12}\mathrm{C}^{16}\mathrm{O}/{}^1\Sigma^+$	90544	2169.8	13.29	1.931	1.128	0.0175	0.0612
$^{35}\mathrm{Cl}_2/{}^1\Sigma_g^+$		559.7	2.68	0.2440	1.988	0.0015	0.000186
$^{1}\mathrm{H}_2/{}^1\Sigma_g^+$	38297	4401.2	121.3	60.85	0.741	3.06	0.00471
$^{1}\mathrm{H}^{81}\mathrm{Br}/{}^1\Sigma^+$		2648.98	45.22	8.4649	1.414	0.233	3.46
$^{1}\mathrm{H}^{35}\mathrm{Cl}/{}^1\Sigma^+$	37240	2990.9	52.8	10.593	1.275	0.307	5.32
$^{1}\mathrm{H}^{19}\mathrm{F}/{}^1\Sigma^+$		4138.3	89.9	20.956	0.9168	0.798	21.51
$^{1}\mathrm{H}^{127}\mathrm{I}/{}^1\Sigma^+$		2309.01	39.64	6.4264	1.609	0.1689	2.069
$^{127}\mathrm{I}_2/{}^1\Sigma_g^+$	12550	214.5	0.615	0.03737	2.666	0.000114	0.000042
$^{14}\mathrm{N}_2/{}^1\Sigma_g^+$	79890	2358.6	14.3	1.998	1.098	14.3	0.0576
$^{14}\mathrm{N}^{16}\mathrm{O}/{}^2\Pi_{1/2}$		1904.20	14.075	1.67095	1.15077	0.0171	0.54
$^{16}\mathrm{O}_2/{}^3\Sigma_g^-$		1580.2	11.98	1.4456	1.208	0.0159	0.0048
$^{19}\mathrm{F}_2/{}^1\Sigma_g^+$		916.64	11.236	0.89019	1.41193	0.013847	0.033

Data primarily from K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure*, Vol. IV, *Constants of Diatomic Molecules*, Van Nostrand Reinhold, New York, 1979.

Table A.23 Properties of Some Nuclei in Their Ground States

Nuclide	I	g_N	Abundance/% (Earth's Crust)	Atomic Mass/amu
$^{1}\mathrm{H}$	1/2	5.5856	99.985	1.007825
$^{2}\mathrm{H}$	1	0.8574	0.015	2.014102
$^{7}\mathrm{Li}$	3/2	2.171	92.44	7.01600
$^{12}\mathrm{C}$	0	–	98.89	12.00000
$^{13}\mathrm{C}$	1/2	1.4048	1.11	13.00335
$^{14}\mathrm{N}$	1	0.403	99.63	14.003074
$^{15}\mathrm{N}$	1/2	−0.567	0.37	15.00011
$^{16}\mathrm{O}$	0	–	99.759	15.994915
$^{17}\mathrm{O}$	5/2	−0.757	0.037	16.99913
$^{19}\mathrm{F}$	1/2	5.257	100	18.99840
$^{23}\mathrm{Na}$	3/2	1.478	100	22.98977
$^{29}\mathrm{Si}$	1/2	−1.111	4.70	28.97650
$^{31}\mathrm{P}$	1/2	2.263	100	30.97376
$^{33}\mathrm{S}$	3/2	0.429	0.76	32.97146
$^{35}\mathrm{Cl}$	3/2	0.548	75.77	34.96885
$^{37}\mathrm{Cl}$	3/2	0.456	24.23	36.96590
$^{63}\mathrm{Cu}$	3/2	1.484	69.17	62.92959
$^{65}\mathrm{Cu}$	3/2	1.590	30.83	64.92779

Data on abundances and masses from Norman E. Holden and F. William Walker, *Chart of the Nuclides*, General Electric Co., Schenectady, NY, 1968.

Table A.24 Characteristic Vibrational Frequencies

Group	Frequency/cm^{-1}
C–H (stretch)	2850–3000
C–H (bend)	1350–1450
O–H (stretch)	3600–3700
C=C	1600–1680
C≡C	2200–2260
C=O	1660–1870
C–Cl	600–800
C≡N	*ca.* 2250

Table A.25 Characteristic Proton Chemical Shifts Relative to Tetramethyl Silane (TMS)

Group	δ/ppm
$-\mathrm{CO_2H}$	11–13
$-\mathrm{CHO}$	9–10
Ar–H	7–8
$-\mathrm{C{=}CH}$	5–7
ROH	3–5
$-\mathrm{CO_2CH_3}$	4
$\mathrm{RCOCH_3}$	3–4
$\mathrm{Ar{-}CH_3}$	2–3
$-\mathrm{CH_2}-$	1–5
$\mathrm{R{-}CH_3}$	1–2
$\mathrm{Si(CH_3)_4}$	0.00

R stands for an aliphatic radical, Ar stands for an aromatic radical.

Table A.26 Character Tables for a Few Common Point Groups

$C_{2\mathrm{v}}$	E	C_2	σ_{yz}	σ_{xz}	Function
$\mathrm{A_1}$	1	1	1	1	z, z^2
$\mathrm{A_2}$	1	1	−1	−1	xy, R_z
$\mathrm{B_1}$	1	−1	−1	1	xz, R_y
$\mathrm{B_2}$	1	−1	1	−1	yz, R_x

$C_{3\mathrm{v}}$	E	$2C_3$	$3\sigma_\mathrm{v}$	Function
$\mathrm{A_1}$	1	1	1	z^2
$\mathrm{A_2}$	1	1	−1	R_z
E	2	−1	0	x, y, R_x, R_y

$D_{2\mathrm{h}}$	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	
$\mathrm{A_g}$	1	1	1	1	1	1	1	1	z^2
$\mathrm{B_{1g}}$	1	1	−1	−1	1	1	−1	−1	xy

(*continued*)

Table A.26 (*continued*)

B_{2g}	1	−1	1	−1	1	−1	1	−1	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	yz
A_u	1	1	1	1	−1	−1	−1	−1	—
B_{1u}	1	1	−1	−1	−1	−1	1	1	—
B_{2u}	1	−1	1	−1	−1	1	−1	1	—
B_{3u}	1	−1	−1	1	−1	1	1	−1	—

D_{2d}	E	$2S_4$	C_2	C_2'	$2\sigma_d$	Function
A_1	1	1	1	1	1	z^2
A_2	1	1	1	−1	−1	—
B_1	1	−1	1	1	−1	$x^2 - y^2$
B_2	1	−1	1	−1	1	xy
E	2	0	−2	0	0	xz, yz

D_{6h}	E	$2C_6$	$2C_3$	C_2	$3C_2'$	$3C_2''$	i	$2S_3$	$2S_6$	σ_h	$3\sigma_d$	$3\sigma_v$	Function
A_{1g}	1	1	1	1	1	1	1	1	1	1	1	1	z^2
A_{2g}	1	1	1	1	−1	−1	1	1	1	1	−1	−1	R_z
B_{1g}	1	−1	1	−1	1	−1	1	−1	1	−1	1	−1	—
B_{2g}	1	−1	1	−1	−1	1	1	−1	1	−1	−1	1	—
E_{1g}	2	1	−1	−2	0	0	2	1	−1	−2	0	0	xz, yz
E_{2g}	2	−1	−1	2	0	0	2	−1	−1	2	0	0	xy
A_{1u}	1	1	1	1	1	1	−1	−1	−1	−1	−1	−1	—
A_{2u}	1	1	1	1	−1	−1	−1	−1	−1	−1	1	1	z
B_{1u}	1	−1	1	−1	1	−1	−1	1	−1	1	−1	1	—
B_{2u}	1	−1	1	−1	−1	1	−1	1	−1	1	1	−1	—
E_{1u}	2	1	−1	−2	0	0	−2	−1	1	2	0	0	x, y
E_{2u}	2	−1	−1	2	0	0	−2	1	1	−2	0	0	—

T_d	E	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
A_1	1	1	1	1	1
A_2	1	1	1	−1	−1
E	2	−1	2	0	0
T_1	3	0	−1	1	−1
T_2	3	0	−1	−1	1

O_h	E	$8C_3$	$6C_4$	$6C_2$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$
A_{1g}	1	1	1	1	1	1	1	1	1	1
A_{2g}	1	1	−1	−1	1	1	−1	1	1	−1
E_g	2	−1	0	0	2	2	0	−1	2	0
T_{1g}	3	0	−1	1	−1	3	1	0	−1	−1
T_{2g}	3	0	1	−1	−1	3	−1	0	−1	1
A_{1u}	1	1	1	1	1	−1	−1	−1	−1	−1
A_{2u}	1	1	1	1	1	−1	−1	−1	−1	−1
E_u	2	−1	0	0	2	−2	0	1	−2	0
T_{1u}	3	0	−1	1	−1	−3	−1	0	1	1
T_{2u}	3	0	1	−1	−1	−3	1	0	1	−1

From Arthur W. Adamson, *A Textbook of Physical Chemistry*, 3rd ed., Academic Press, 1986, p. 748ff. Other character tables can be found in this reference and in various other references.

B

Some Useful Mathematics

B.1 Differential Calculus with Several Variables

The fundamental equation of differential calculus for a function $f = f(x, y, z)$ is

$$df = \left(\frac{\partial f}{\partial x}\right)_{y,z} dx + \left(\frac{\partial f}{\partial y}\right)_{x,z} dy + \left(\frac{\partial f}{\partial z}\right)_{x,y} dz \tag{B-1}$$

The coefficients are partial derivatives. Each is obtained by the ordinary process of differentiation, treating the other independent variables as constants. The symbols for the variables that are held constant are written as subscripts to remind us what they are. If P is a function of T, V, and n,

$$dP = \left(\frac{\partial P}{\partial T}\right)_{V,n} dT + \left(\frac{\partial P}{\partial V}\right)_{T,n} dV + \left(\frac{\partial P}{\partial n}\right)_{T,V} dn \tag{B-2}$$

This represents an infinitesimal change in P produced by the corresponding infinitesimal changes in the independent variables T, V, and n. If finite changes are not too large, we can write an approximate version of this equation:

$$\Delta P \approx \left(\frac{\partial P}{\partial T}\right)_{V,n} \Delta T + \left(\frac{\partial P}{\partial V}\right)_{T,n} \Delta V + \left(\frac{\partial P}{\partial n}\right)_{T,V} \Delta n \tag{B-3}$$

Some Mathematical Identities An equation that is valid for any values of the variables involved is called an identity. The first task of this section is to obtain several identities involving partial derivatives.

An Identity for a Change of Variables. The expression for the differential of a function $U = U(T, V, n)$ is

$$dU = \left(\frac{\partial U}{\partial T}\right)_{V,n} dT + \left(\frac{\partial U}{\partial V}\right)_{T,n} dV + \left(\frac{\partial U}{\partial n}\right)_{T,V} dn \tag{B-4}$$

If T, P, and n are used as the independent variables, then dU is given by

$$dU = \left(\frac{\partial U}{\partial T}\right)_{P,n} dT + \left(\frac{\partial U}{\partial P}\right)_{T,n} dP + \left(\frac{\partial U}{\partial n}\right)_{T,P} dn \tag{B-5}$$

To obtain our identity, we "divide" Eq. (B-4) by dT and specify that P and n are fixed. Of course, you cannot correctly do this, since dT is infinitesimal, but it gives the correct relationship between the derivatives. Each "quotient" such as dU/dT is interpreted as a partial derivative with the same variables fixed in each "quotient." The result is, holding P and n fixed:

$$\left(\frac{\partial U}{\partial T}\right)_{P,n} = \left(\frac{\partial U}{\partial T}\right)_{V,n}\left(\frac{\partial T}{\partial T}\right)_{P,n} + \left(\frac{\partial U}{\partial V}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{P,n} + \left(\frac{\partial U}{\partial n}\right)_{T,V}\left(\frac{\partial n}{\partial T}\right)_{P,n} \tag{B-6}$$

The derivative of T with respect to T is equal to unity, and the derivative of n with respect to anything is equal to zero if n is fixed, so that:

$$\left(\frac{\partial U}{\partial T}\right)_{P,n} = \left(\frac{\partial U}{\partial T}\right)_{V,n} + \left(\frac{\partial U}{\partial V}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{P,n} \tag{B-7}$$

Equation (B-7) is an example of the *variable-change identity*. The version for any particular case can be obtained by systematically replacing each letter by the letter for any desired variable.

The Reciprocal Identity. If the roles of the independent and dependent variables are reversed, keeping the same variables held constant, the resulting derivative is the reciprocal of the original derivative. An example of this identity is:

$$\left(\frac{\partial V}{\partial P}\right)_{T,n} = \frac{1}{(\partial P/\partial V)_{T,n}} \tag{B-8}$$

This identity has the same form as though the derivatives were simple quotients, instead of limits of quotients.

The Chain Rule. If the independent variable of a function is itself a function of another variable, the chain rule can be used to obtain the derivative of the first dependent variable with respect to the second independent variable. For example, if U is considered to be a function of P, V, and n, while P is considered to be a function of T, V, and n, then

$$\left(\frac{\partial U}{\partial T}\right)_{V,n} = \left(\frac{\partial U}{\partial P}\right)_{V,n}\left(\frac{\partial P}{\partial T}\right)_{V,n} \tag{B-9}$$

The same quantities must be held fixed in all of the derivatives in the identity.

We can also obtain the differential of a quantity which is expressed as a function of one variable which is in turn given as a function of other variables. For example, if $f = f(u)$ and $u = u(x, y, z)$:

$$\left(\frac{\partial f}{\partial x}\right)_{y,z} = \left(\frac{df}{du}\right)\left(\frac{\partial u}{\partial x}\right)_{y,z} \tag{B-10}$$

The differential of f can be written:

$$df = \frac{df}{du}\left[\left(\frac{\partial u}{\partial x}\right)_{y,z} dx + \left(\frac{\partial u}{\partial y}\right)_{x,z} dy + \left(\frac{\partial u}{\partial z}\right)_{x,y} dz\right] \tag{B-11}$$

Euler's Reciprocity Relation. A second derivative is the derivative of a first derivative. If f is a differentiable function of two independent variables, x and y, there are four second derivatives:

$$\frac{\partial^2 f}{\partial y \partial x} = \left(\frac{\partial}{\partial y}\left(\frac{\partial f}{\partial x}\right)_y\right)_x \tag{B-12a}$$

$$\frac{\partial^2 f}{\partial x \partial y} = \left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial y} \right)_x \right)_y \tag{B-12b}$$

$$\left(\frac{\partial^2 f}{\partial x^2} \right)_y = \left(\frac{\partial}{\partial x} \left(\frac{\partial f}{\partial x} \right)_y \right)_y \tag{B-12c}$$

$$\left(\frac{\partial^2 f}{\partial y^2} \right)_x = \left(\frac{\partial}{\partial y} \left(\frac{\partial f}{\partial y} \right)_x \right)_x \tag{B-12d}$$

We refer to the second partial derivatives in Eqs. (B-12a) and (B-12b) as *mixed second partial derivatives*. The *Euler reciprocity relation* is a theorem of mathematics: If f is differentiable, then the two mixed second partial derivatives in Eq. (B-12a) and (B-12b) are the same function:

$$\frac{\partial^2 f}{\partial y \partial x} = \frac{\partial^2 f}{\partial x \partial y} \tag{B-13}$$

For a function of three variables, there are nine second partial derivatives, six of which are mixed derivatives. The mixed second partial derivatives obey relations exactly analogous to Eq. (B-13). For example,

$$\left(\frac{\partial^2 V}{\partial T \partial P} \right)_n = \left(\frac{\partial^2 V}{\partial P \partial T} \right)_n \tag{B-14}$$

The same third independent variable is held fixed in both derivatives, as shown by the subscript.

The Cycle Rule. If x, y, and z are related so that any two of them can be considered as independent variables we can write the cycle rule:

$$\left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x = -1 \tag{B-15}$$

We obtain this identity in a nonrigorous way. The differential dz can be written

$$dz = \left(\frac{\partial z}{\partial x} \right)_y dx + \left(\frac{\partial z}{\partial y} \right)_x dy \tag{B-16}$$

We consider the special case in which z is held fixed so that $dz = 0$, and "divide" Eq. (B-16) nonrigorously by dy. The "quotient" dx/dy at constant z is interpreted as a partial derivative at constant z, and the "quotient" dy/dy equals unity. We obtain

$$0 = \left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial x}{\partial y} \right)_z + \left(\frac{\partial z}{\partial y} \right)_x \tag{B-17}$$

We multiply by $(\partial y/\partial z)_x$ and apply the reciprocal identity to obtain

$$\left(\frac{\partial z}{\partial x} \right)_y \left(\frac{\partial x}{\partial y} \right)_z \left(\frac{\partial y}{\partial z} \right)_x = -1 \tag{B-18}$$

which is equivalent to Eq. (B-15).

Exact and Inexact Differentials Equation (B-1) gives the differential of a function, which is called an *exact differential*. We can also write a general differential in terms of dx, dy, and dz:

$$du = L(x, y, z)dx + M(x, y, z)dy + N(x, y, z)dz \tag{B-19}$$

where L, M, and N are some functions of x, y, and z. A general differential form like that of Eq. (B-19) is sometimes called a *Pfaffian form*. If the functions L, M, and N are not the appropriate partial derivatives of the same function, then the differential du is an *inexact differential*, and has some different properties from an exact differential.

To test the differential du for exactness, we can see if the appropriate derivatives of L, M, and N are mixed second derivatives of the same function and obey the Euler reciprocity relation:

$$\left(\frac{\partial L}{\partial y}\right)_{x,z} = \left(\frac{\partial M}{\partial x}\right)_{y,z} \quad \text{(exact differential)} \qquad \text{(B-20a)}$$

$$\left(\frac{\partial L}{\partial z}\right)_{x,y} = \left(\frac{\partial N}{\partial x}\right)_{y,z} \quad \text{(exact differential)} \qquad \text{(B-20b)}$$

$$\left(\frac{\partial M}{\partial z}\right)_{x,y} = \left(\frac{\partial N}{\partial y}\right)_{x,z} \quad \text{(exact differential)} \qquad \text{(B-20c)}$$

If any one of the conditions of Eq. (B-20) is not obeyed then du is an inexact differential, and if all of them are obeyed then du is an exact differential.

B.2 Integral Calculus with Several Variables

There are two principal types of integrals of functions of several variables, the line integral and the multiple integral.

Line Integrals For a differential with two independent variables,

$$du = M(x, y)dx + N(x, y)dy$$

a line integral is denoted by

$$\int_c du = \int_c \left[M(x, y)dx + N(x, y)dy\right] \qquad \text{(B-21)}$$

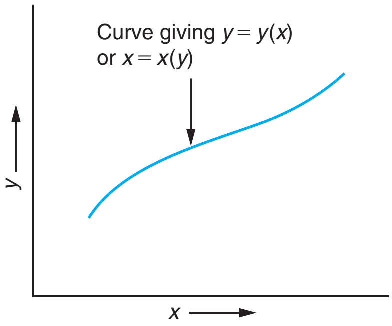

Figure B.1 A Curve Giving *y* as a Function of *x* or giving *x* as a Function of *y*.

where the letter c denotes a curve in the xy plane. This curve gives y as a function of x and x as a function of y, as in Figure B.1. We say that the integral is carried out along this curve (or path). To carry out the integral, we replace y in M by the function of x given by the curve and replace x in N by the function of y given by the curve. If these functions are represented by $y(x)$ and $x(y)$:

$$\int_c du = \int_{x_1}^{x_2} M(x, y(x))dx + \int_{y_1}^{y_2} N(x(y), y)dy \qquad \text{(B-22)}$$

where x_1 and y_1 are the coordinates of the initial point of the line integral and x_2 and y_2 are the coordinates of the final point. Each integral is an now an ordinary integral and can be carried out in the usual way. If the differential form has three or more independent variables, the procedure is analogous. The curve must be a curve in a space of all independent variables, giving each one of the other independent variables as a function of one variable.

There is an important theorem of mathematics concerning the line integral of an exact differential: If dz is an exact differential it is the differential of a function z.

If T, V, and n are the independent variables in the exact differential then z is a function of T, V, and n. The theorem states that a line integral of dz is equal to the value of z at the end point of the integration minus the value of z at the starting point:

$$\begin{aligned}\int_c dz &= \int_c \left[\left(\frac{\partial z}{\partial T}\right)_{V,n} dT + \left(\frac{\partial z}{\partial V}\right)_{T,n} dV + \left(\frac{\partial z}{\partial n}\right)_{T,V} dn\right] \\ &= z(T_2, V_2, n_2) - z(T_1, V_1, n_1) \qquad \text{(B-23)}\end{aligned}$$

where T_2, V_2, and n_2 are the values of the independent variables at the final point of the curve, and T_1, V_1, and n_1 are the values at the initial point of the curve. Since many different curves can have the same initial and final points, Eq. (B-23) means that the line integral depends only on the initial point and the final point, and is independent of the curve between these points. It is said to be *path-independent*. The line integral of an inexact differential is generally *path-dependent*. That is, one can always find two or more paths between a given initial point and a given final point for which the line integrals are not equal.

Multiple Integrals If $f = f(x, y, z)$ is an integrand function, a multiple integral with constant limits is denoted by

$$I(a_1, a_2, b_1, b_2, c_1, c_2) = \int_{a_1}^{a_2} \int_{b_1}^{b_2} \int_{c_1}^{c_2} f(x, y, z) dz dy dx \qquad \text{(B-24)}$$

The integrations are carried out sequentially. The leftmost differential and the rightmost integral sign belong together, and this integration is done first, and so on. Variables not yet integrated are treated as constants during the integrations. In Eq. (B-24), z is first integrated from c_1 to c_2, treating x and y as constants during this integration. The result is a function of x and y, which is the integrand when y is then integrated from b_1 to b_2, treating x as a constant. The result is a function of x, which is the integrand when x is then integrated from a_1 to a_2. In this multiple integral the limits of the z integration can be replaced by functions of x and y, and the limits of the y integration can be replaced by functions of x. The limit functions are substituted into the indefinite integral in exactly the same way as are constants when the indefinite integral is evaluated at the limits.

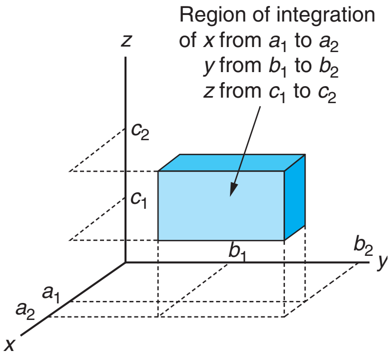

Figure B.2 An Integration Region in Cartesian Coordinates with Constant Limits.

If the variables are Cartesian coordinates and the limits are constants, the region of integration is a rectangular parallelepiped (box) as shown in Figure B.2. If the limits for the first two integrations are not constants, the region of integration can have a more complicated shape.

The integration process can be depicted geometrically as follows: The product *dxdydz* is a *volume element* and is depicted in Figure B.3 (although the box pictured has finite dimensions and the volume element *dxdydz* is infinitesimal). This volume element is also denoted as $d^3\mathbf{r}$. If (x, y, z) represents a point in the volume element, then the contribution of the element of volume to the integral is equal to the value of the function at (x, y, z) times the volume of the volume element:

$$(\text{contribution of the volume element } dxdydz) = f(x, y, z) dxdydz \qquad \text{(B-25)}$$

The integral is the sum of the contributions of all the volume elements in the region of integration.

If an integral over a volume in three-dimensional space is needed and spherical polar coordinates are used, the volume element is as depicted in Figure B.4. The length

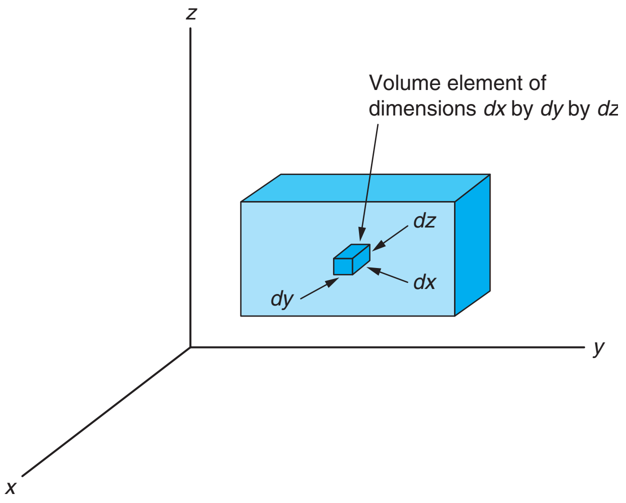

Figure B.3 An Infinitesimal Volume Element in Cartesian Coordinates.

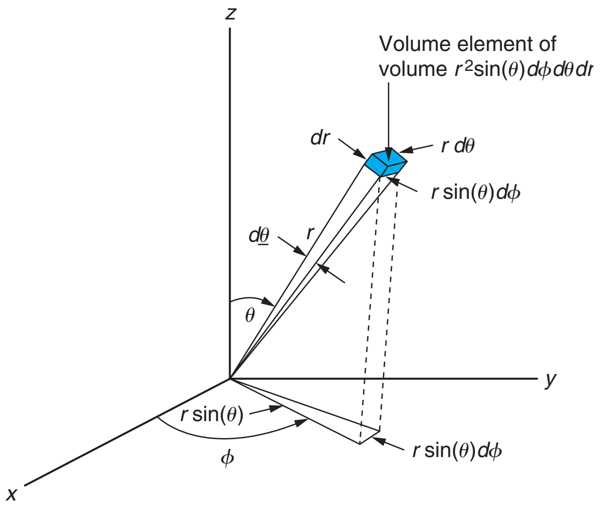

Figure B.4 An Infinitesimal Volume Element in Spherical Polar Coordinates.

of the volume element in the r direction is equal to dr. The length of the box in the θ direction (the direction in which an infinitesimal change in θ carries a point in space) is equal to $rd\theta$ if θ is measured in radians, since the measure of an angle in radians is the ratio of the arc length to the radius. The length of the volume element in the ϕ direction is $r\sin(\theta)d\phi$, which comes from the fact that the projection of r in the xy plane has length $r\sin(\theta)$, as shown in the figure. The volume of the element of volume is thus

$$d^3\mathbf{r} = r^2\sin(\theta)d\phi d\theta dr \tag{B-26}$$

where $d^3\mathbf{r}$ is a general abbreviation for a volume element in any coordinate system. An integral of an integrand function f over all of space using spherical polar coordinates is

$$I = \int_0^\infty \int_0^\pi \int_0^{2\pi} f(r, \theta, \phi) r^2 \sin(\theta) d\phi d\theta dr \tag{B-27}$$

Since the limits are constants, this integral is carried out in the same way as that of Eq. (B-24), with the ϕ integration done first and the θ integration done next.

For other coordinate systems, a factor analogous to the factor $r^2 \sin(\theta)$ must be used. This factor is called a *Jacobian*. For example, for cylindrical polar coordinates, where the coordinates are z, ϕ (the same angle as in spherical polar coordinates, and ρ (the projection of r into the xy plane), the Jacobian is the factor ρ, so that the element of volume is $\rho d\rho dz d\phi$. We use the symbol $d^3\mathbf{r}$ for the three-dimensional volume element in any coordinate system, so that $dxdydz$, $r^2 \sin(\theta) d\phi d\theta dr$, $\rho d\phi d\rho dz$, and so on are all denoted by $d^3\mathbf{r}$.

B.3 Vectors

A vector is a quantity with both magnitude and direction. The vector **A** can be represented by its Cartesian components, A_x, A_y, and A_z:

$$\mathbf{A} = \mathbf{i}A_x + \mathbf{j}A_y + \mathbf{k}A_z \tag{B-28}$$

where **i**, **j**, and **k** are unit vectors that point in the x, y, and z directions, respectively, and A_x, A_y, and A_z are the Cartesian components of the vector. The product of the unit vector **i** and the scalar A_x is a vector of length A_x pointing in the positive x direction if A_x is positive and in the negative x direction if A_x is negative. The other two products in Eq. (B-28) are analogous. The sum of two vectors can be obtained by moving the second vector so that its tail coincides with the head of the first vector without rotating it or changing its length. The sum vector is then drawn from the tail of the first vector to the head of the second. Figure B.5 indicates how the three vectors in the x, y, and z directions add in the case that all three components are positive. The sum of $\mathbf{i}A_x$ and $\mathbf{j}A_y$ lies in the xy plane and the $\mathbf{k}A_z$ vector is added to it by bringing its tail to the head of the first sum and constructing the final sum as shown.

The sum of two arbitrary vectors is obtained in the same way. If $\mathbf{A} + \mathbf{B} = \mathbf{C}$, then **C** is obtained by moving the tail of **B** to the head of **A** and drawing **C** from the tail of **A** to the head of **B**. The sum vector is then drawn from the tail of the first vector to the head of the second. Figure B.6 shows the sum $\mathbf{A} + \mathbf{B} = \mathbf{C}$. Vector addition is commutative, so that $\mathbf{A} + \mathbf{B} = \mathbf{B} + \mathbf{A}$, as shown in the figure. The vector sum is also obtained by adding the components. If $\mathbf{A} + \mathbf{B} = \mathbf{C}$, then

$$\begin{aligned} C_x &= A_x + B_x \\ C_y &= A_y + B_y \\ C_z &= A_z + B_z \end{aligned} \tag{B-29a}$$

The *dot product* or *scalar product* of two vectors is a scalar quantity equal to the product of the magnitudes of the two vectors times the cosine of the angle between them:

$$\mathbf{A} \cdot \mathbf{B} = |\mathbf{A}||\mathbf{B}|\cos(\alpha) = AB\cos(\alpha) \tag{B-30}$$

where α is the angle between the vectors and where the magnitude of the vectors **A** and **B** are denoted either by $|\mathbf{A}|$ and $|\mathbf{B}|$ or by A and B. The scalar product is commutative:

$$\mathbf{A} \cdot \mathbf{B} = \mathbf{B} \cdot \mathbf{A} \tag{B-31}$$

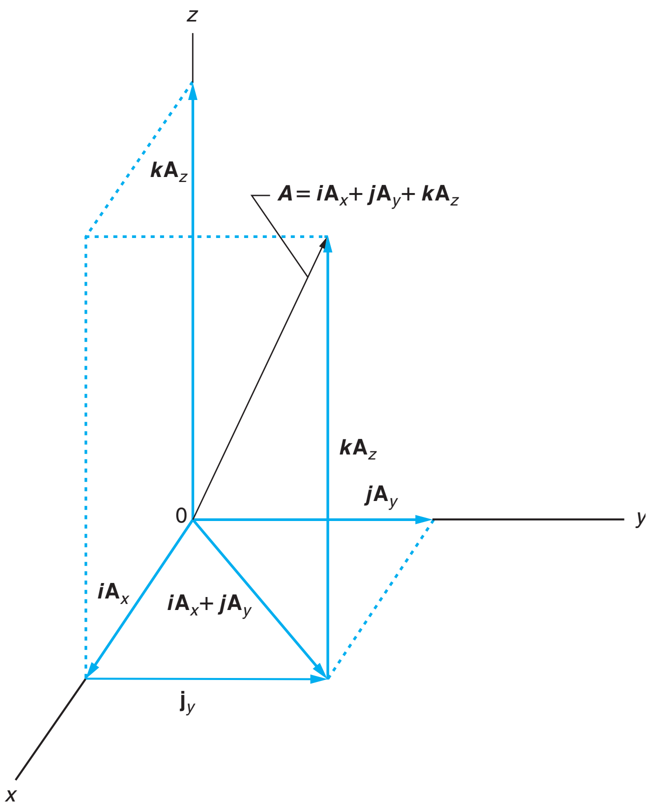

Figure B.5 The Vector A Represented by the Sum of Three Components.

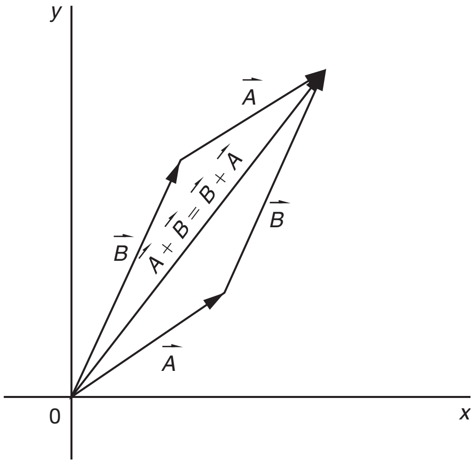

Figure B.6 The Sum of Two Vectors.

The scalar product of a vector with itself is the square of the magnitude of the vector:

$$\mathbf{A}\cdot\mathbf{A} = |\mathbf{A}|^2 = A^2 \tag{B-32}$$

The scalar products of the unit vectors are

$$\mathbf{i}\cdot\mathbf{j} = \mathbf{i}\cdot\mathbf{k} = \mathbf{j}\cdot\mathbf{k} = 0 \tag{B-33}$$

$$\mathbf{i}\cdot\mathbf{i} = \mathbf{j}\cdot\mathbf{j} = \mathbf{k}\cdot\mathbf{k} = 1 \tag{B-34}$$

If the vectors **A** and **B** are represented by Cartesian components as in Eq. (B-28), Eq. (B-33) implies that six of the nine terms in the product $\mathbf{A}\cdot\mathbf{B}$ vanish, leaving

$$\mathbf{A}\cdot\mathbf{B} = A_xB_x + A_yB_y + A_zB_z \tag{B-35}$$

The scalar product of a vector with itself is the square of the magnitude of the vector:

$$\mathbf{A}\cdot\mathbf{A} = |\mathbf{A}|^2 = A_x^2 + A_y^2 + A_z^2 \tag{B-36}$$

$$|\mathbf{A}| = A = \sqrt{A_x^2 + A_y^2 + A_z^2} \tag{B-37}$$

The *cross product* or *vector product* of two vectors is a vector quantity that is perpendicular to the plane containing the two vectors with magnitude equal to the product of the magnitudes of the two vectors times the sine of the angle between them:

$$|\mathbf{A}\times\mathbf{B}| = |\mathbf{A}||\mathbf{B}|\sin(\alpha) \tag{B-38}$$

The direction of the product vector is the direction in which an ordinary (right-handed) screw moves if it is rotated in the direction which the vector on the left must be rotated to coincide with the vector on the right, rotating through an angle less than or equal to 180°. The cross product is not commutative:

$$\mathbf{A}\times\mathbf{B} = -\mathbf{B}\times\mathbf{A} \tag{B-39}$$

The cross products of the unit vectors are

$$\mathbf{i}\times\mathbf{i} = 0,\quad \mathbf{j}\times\mathbf{j} = 0,\quad \mathbf{k}\times\mathbf{k} = 0 \tag{B-40}$$

$$\mathbf{i}\times\mathbf{j} = \mathbf{k},\quad \mathbf{i}\times\mathbf{k} = -\mathbf{j},\quad \mathbf{j}\times\mathbf{k} = \mathbf{i} \tag{B-41}$$

In terms of Cartesian components, we can deduce from Eqs. (B-40) and (B-41) that

$$\mathbf{A}\times\mathbf{B} = \mathbf{i}[A_yB_z - A_zB_y] + \mathbf{j}[A_zB_x - A_xB_z] + \mathbf{k}[A_xB_y - A_yB_x] \tag{B-42}$$

Vector Derivatives The *gradient* is a vector derivative of a scalar function. If f is a function of x, y, and z, its gradient is given by

$$\nabla f = \mathbf{i}\frac{\partial f}{\partial x} + \mathbf{j}\frac{\partial f}{\partial y} + \mathbf{k}\frac{\partial f}{\partial z} \tag{B-43}$$

The symbol for the gradient operator, ∇, is called "del." At a given point in space, the gradient points in the direction of most rapid increase of the function, and its magnitude is equal to the rate of change of the function in that direction. The gradient of a vector function is also defined, and the gradient of each component is as defined in Eq. (B-43). The gradient of a vector quantity therefore has nine components, and is called a *dyadic* or a *Cartesian tensor*. Each of its components is multiplied by a product of two unit vectors.

The *divergence* of a vector function **F** is denoted by $\nabla \cdot \mathbf{F}$ and is defined by

$$\nabla \cdot \mathbf{F} = \left(\frac{\partial F_x}{\partial x}\right) + \left(\frac{\partial F_y}{\partial y}\right) + \left(\frac{\partial F_z}{\partial z}\right) \tag{B-44}$$

The divergence is a scalar quantity. If the vector function represents the flow velocity of a fluid, the divergence is a measure of the spreading out of the streaming curves along which small elements of the fluid flow. A positive value of the divergence corresponds to a decrease in density along a curve following the flow. See the discussion of the equation of continuity in Section 11.2.

The divergence of the gradient of a scalar function is called the *Laplacian*. The Laplacian of a scalar function f is given in Cartesian coordinates by

$$\nabla^2 f = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} \tag{B-45}$$

The Laplacian is sometimes called "del squared."

The vector derivative operators can be expressed in other coordinate systems. In spherical polar coordinates, the gradient of the scalar function f is

$$\nabla f = \mathbf{e}_r \frac{\partial f}{\partial r} + \mathbf{e}_\theta \frac{1}{r}\frac{\partial f}{\partial \theta} + \mathbf{e}_\phi \frac{1}{r\sin(\theta)}\frac{\partial f}{\partial \phi} \tag{B-46}$$

where $\mathbf{e}_r$ is the unit vector in the r direction (the direction of motion if r is increased by a small amount, keeping θ and ϕ fixed), $\mathbf{e}_\theta$ is the unit vector in the θ direction, and $\mathbf{e}_\phi$ is the unit vector in the ϕ direction. In spherical polar coordinates, the Laplacian is

$$\nabla^2 f = \frac{1}{r^2}\left[\frac{\partial}{\partial r}\left[r^2 \frac{\partial f}{\partial r}\right] + \frac{1}{\sin(\theta)}\frac{\partial}{\partial \theta}\left[\sin(\theta)\frac{\partial f}{\partial \theta}\right] + \frac{1}{\sin^2(\theta)}\frac{\partial^2 f}{\partial \phi^2}\right] \tag{B-47}$$

In cylindrical polar coordinates the three coordinates are z (same as in Cartesian coordinates), ϕ (same as in spherical polar coordinates), and ρ, equal to $\sqrt{x^2 + y^2}$. The gradient of a scalar function f is given by

$$\nabla f = \mathbf{e}_\rho \frac{\partial f}{\partial \rho} + \mathbf{e}_\phi \frac{1}{\rho}\frac{\partial f}{\partial \phi} + \mathbf{k}\frac{\partial f}{\partial z} \tag{B-48}$$

where $\mathbf{e}_\rho$ is the unit vector in the ρ direction, $\mathbf{e}_\phi$ is the unit vector in the ϕ direction, and **k** is the unit vector in the z direction.

For example, the liquid in a pipe with radius R has a velocity that depends on ρ, the distance from the center of the pipe such that

$$\mathbf{u} = \mathbf{k}u_z(\rho) = \mathbf{k}A(\rho^2 - R^2) \tag{B-49}$$

where A is a constant. All of the nine components of the gradient of this velocity will vanish except for $\partial u_z/\partial \rho$:

$$\nabla u_z = \mathbf{e}_\rho \frac{\partial u_z}{\partial_\rho} = \mathbf{e}_\rho 2A\rho \tag{B-50}$$

The gradient of the flow velocity points at right angles to the velocity.

B.4 Solution of a Differential Equation from the Two-Step Mechanism of Chapter 11

Equation (11.5-5) is

$$\frac{d[\mathrm{B}]}{dt} = k_1[A]_0 e^{-k_1 t} - k_2[\mathrm{B}] \tag{B-51}$$

We will see that it can be put into the form

$$dz = M d[\mathrm{B}] + N dt = 0 \tag{B-52}$$

where M and N are functions of t and [B], the concentration of substance B. The equation shown in Eq. (B-52) represents a class of equations called *Pfaffian differential equations*. An equation of this type is called an *exact differential equation* if dz is an exact differential. If dz is exact, M and N must be derivatives of the function z and must obey the Euler reciprocity relation shown in Eq. (B-13):

$$\frac{\partial M}{\partial t} = \frac{\partial^2 z}{\partial t \partial[\mathrm{B}]} = \frac{\partial^2 z}{\partial[\mathrm{B}]\partial t} = \frac{\partial N}{\partial[\mathrm{B}]} \tag{B-53}$$

We multiply Eq. (B-51) by dt and recognize that $(d[\mathrm{B}]/dt)dt = d[\mathrm{B}]$ to obtain an equation in Pfaffian form:

$$d[B] + \left(k_2[B] - k_1[A]_0 e^{-k_1 t}\right) dt = 0 \tag{B-54}$$

This equation corresponds to $M = 1$ and $N = (k_2[\mathrm{B}] - k_1[\mathrm{A}]_0 e^{-k_1 t})$. The differential is not exact since the derivative of M with respect to t equals zero and the derivative of N with respect to [B] equals k_2. However, if the equation is multiplied by the factor $e^{k_2 t}$, we get the exact differential equation

$$e^{k_2 t} d[\mathrm{B}] + \left(k_2[\mathrm{B}]e^{k_2 t} - k_1[\mathrm{A}]_0 e^{(k_2 - k_1)t}\right) dt = 0 \tag{B-55}$$

as can be checked by differentiation. A factor that converts an inexact Pfaffian differential equation into an exact differential equation is called an *integrating factor*. Multiplication of any equation on both sides by the same nonzero factor yields a valid equation with the same solution as the original equation.

We consider the special case that no B or F is present at time $t = 0$. We denote the differential in Eq. (B-55) by dz and perform a line integral of dz on the path shown in Figure B.7. The result of the integration must equal zero, since the differential equals zero if it satisfies the differential equation. That is, the function z must have the same value at the two ends of the path.

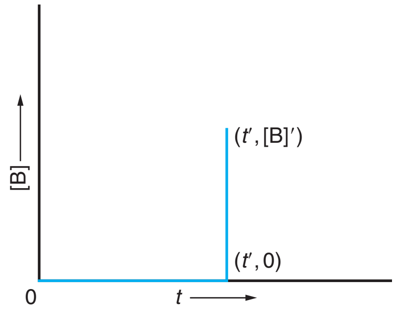

Figure B.7 The Path of Integration to Solve Eq. (11.5-5).

The d[B] term in dz gives no contribution on the first leg of the path. On the second leg t is equal to t' so that

$$\int_0^{[\mathrm{B}]_{t'}} e^{k_2 t'} d[\mathrm{B}] = e^{k_2 t'} [\mathrm{B}]_{t'} \tag{B-56}$$

On the first leg of the path we replace [B] by zero, and the result is

$$-\int_0^{t'} k_1[\mathrm{A}]_0 e^{(k_2 - k_1)t} dt = -\frac{k_1[\mathrm{A}]_0}{k_2 - k_1}\left(e^{(k_2 - k_1)t'} - 1\right) \tag{B-57}$$

The dt term gives no contribution on the second leg of the path since t is constant and dt vanishes on this leg.

The contributions of Eqs. (B-56) and (B-57) are combined and set equal to zero:

$$z(t', [\mathrm{B}]_{t'}) - z(0,0) = e^{-k_2 t'}[\mathrm{B}]_{t'} - \frac{K_1[\mathrm{A}]_0}{k_2 - k_1}\left(e^{(k_2-k_1)t'} - 1\right) = 0 \qquad \text{(B-58)}$$

Our only interest in the function z is that it furnishes us with this equation, which is an algebraic equation that can be solved for [B] as a function of t', giving the desired solution:

$$[\mathrm{B}]_t = \frac{k[\mathrm{A}]_0}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \qquad \text{(B-59)}$$

where we omit the prime symbol on t'.

B.5 Complex and Imaginary Quantities

Any complex quantity z can be written in the form

$$z = x + iy \qquad \text{(B-60)}$$

where x and y are real quantities and where i is the *imaginary unit,* defined to equal $\sqrt{-1}$. Do not confuse the imaginary unit i with the unit vector $\mathbf{i}$. The real quantity x is called the *real part* of z and the real quantity y is called the *imaginary part* of z. The *complex conjugate* of z is denoted by z^* (or sometimes by $\bar{z}$), and is defined to have the same real part as z and an imaginary part that is the negative of that of z.

$$z^* = x - iy \quad \text{(definition of } z^*\text{)} \qquad \text{(B-61)}$$

A real quantity is equal to its complex conjugate.

Any complex expression can be turned into its complex conjugate by changing the sign in front of every i in the expression, although we do not prove this fact. For example,

$$\left(e^{i\alpha}\right)^* = e^{-i\alpha} \qquad \text{(B-62)}$$

This can be shown by using the identity

$$e^{i\alpha} = \cos(\alpha) + i\sin(\alpha) \qquad \text{(B-63)}$$

and the fact that the cosine is an even function and the sine is an odd function.

The product of any complex number and its complex conjugate is equal to the square of the magnitude of that complex number, denoted by $|z|^2$, and is always a real quantity. The *magnitude* or *absolute value* of z is the positive square root of z^*z.

$$r = |z| = \sqrt{|z|^2} = \sqrt{z^*z} \qquad \text{(B-64)}$$

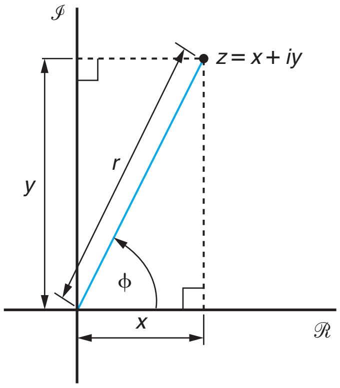

Figure B.8 The Argand Plane. A point in this diagram represents a complex number in the form $x + iy$ or $re^{i\phi}$.

where we use the common symbol r for the magnitude of z. If a complex number is written in the form of Eq. (B-61),

$$\begin{aligned} r^2 &= |z|^2 = z^* z = (x - iy)(x + iy) = x^2 + iyx - ixy + y^2 \\ &= x^2 + y^2 \end{aligned} \tag{B-65}$$

Complex numbers are sometimes represented by a point in the *Argand plane*, in which the real part is plotted on the horizontal axis, and the imaginary part is plotted on the vertical axis, as shown in Figure B.8. By the theorem of Pythagoras, the magnitude of a complex number is the length of the directed line segment from the origin to the point representing the number in the Argand plane. The angle ϕ is the angle between the positive x axis and this directed line segment:

$$\phi = \arctan(y/x) \tag{B-66}$$

By using the identity in Eq. (B-63), we can show that a complex number can be represented in terms of r and ϕ:

$$z = x + iy = re^{i\phi} \tag{B-67}$$

where $r = \sqrt{x^2 + y^2}$. From this equation, we obtain

$$|z|^2 = z^* z = \left(re^{-i\phi} re^{i\phi}\right) = r^2 \tag{B-68}$$

B.6

Some Properties of Hermitian Operators

In Chapter 16 we asserted several properties of hermitian operators. We provide proofs of two of these properties here.

Property 4: The eigenvalues of a hermitian operator are real.

To establish this property, we take the eigenvalue equation for an arbitrary hermitian operator

$$\widehat{A} f_j(q) = a_j f_j(q) \tag{B-69}$$

We multiply both sides by the complex conjugate of the eigenfunction f_j and integrate over all values of the coordinates, factoring the constant eigenvalue out of the integral:

$$\int f_j^* \widehat{A} f_j dq = a_j \int f_j^* f_j dq \tag{B-70}$$

We now apply the definition of a hermitian operator, Eq. (16.3-28) to the left-hand side of this equation:

$$\int f_j^* \widehat{A} f_j dq = \int (\widehat{A}^* f_j^*) f_j dq \tag{B-71}$$

From the complex conjugate of the eigenvalue equation, Eq. (B-69), we can replace $\widehat{A}^* f_j^*$ by $a_j^* f_j^*$, and by using Eq. (B-70) we obtain

$$\int f_j^* \widehat{A} f_j dq = a_j \int f_j^* f_j dq = \int (\widehat{A}^* f_j^*) f_j dq = a_j^* \int f_j^* f_j dq \tag{B-72}$$

Therefore

$$a_j \int f_j^* f_j dq = a_j^* \int f_j^* f_j dq \tag{B-73}$$

and

$$a_j^* = a_j \tag{B-74}$$

A quantity equals its complex conjugate if and only if it is real, so that a_j must be real.

Property 5. Two eigenfunctions of a hermitian operator with different eigenvalues are orthogonal to each other.

Two functions f and g are *orthogonal* to each other if

$$\int f^* g dq = \int g^* f dq = 0 \quad \left(\begin{matrix}\text{definition of}\\ \text{orthogonality}\end{matrix}\right) \tag{B-75}$$

where f^* is the complex conjugate of f and g^* is the complex conjugate of g. The two integrals in Eq. (B-75) are the complex conjugates of each other, so that if one vanishes, so does the other.

We prove property 5 as follows: Multiply the eigenvalue equation, Eq. (B-69), by f_k^*, the complex conjugate of a different eigenfunction, and integrate, factoring the constant eigenvalue out of the integral:

$$\int f_k^* \widehat{A} f_j dq = a_j \int f_k^* f_j dq \tag{B-76}$$

Now apply the hermitian property to the left-hand side of this equation:

$$\int f_k^* \widehat{A} f_j dq = \int (\widehat{A}^* f_k^*) f_j dq = a_k^* \int f_k^* f_j dq = a_k \int f_k^* f_j dq \tag{B-77}$$

where we have replaced a_k^* by a_k because we know a_k to be real. The left-hand sides of Eqs. (B-76) and (B-77) are equal, so the difference of the right-hand sides vanishes:

$$(a_j - a_k) \int f_k^* f_j dq = 0 \tag{B-78}$$

If the two eigenvalues are not equal to each other, the integral must vanish, and we have proved the orthogonality of f_k and f_j:

$$\int f_k^* f_j dq = 0 \tag{B-79}$$

If two eigenfunctions have equal eigenvalues, they are not necessarily orthogonal to each other, but linear combinations of the eigenfunctions can be constructed that are orthogonal to each other.

B.7 Matrices and Determinants

A *matrix* is an array or list of quantities arranged in rows and columns. If the matrix **A** has m rows and n columns, it is called an m by n matrix and is written in the form:

$$\mathbf{A} = \begin{bmatrix} A_{11} & A_{12} & A_{13} & \cdots & A_{1n} \\ A_{21} & A_{22} & A_{23} & \cdots & A_{2n} \\ A_{31} & A_{32} & A_{33} & \cdots & A_{3n} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ A_{m1} & A_{m2} & A_{m3} & \cdots & A_{mn} \end{bmatrix} \tag{B-80}$$

where the ellipses (. . .) indicate additional entries. The entries in the two-dimensional list are called *elements* of the matrix. If $m = n$, the matrix is a *square matrix*. Two matrices are equal to each other if both have the same number of rows and the same number of columns and if every element of one is equal to the corresponding element of the other. Three-dimensional (and higher) matrices also exist, but we will not need to use them.

Matrix Algebra If the matrix **C** is the sum of **A** and **B**, it is defined by

$$C_{ij} = A_{ij} + B_{ij} \quad \text{for every } i \text{ and } j \tag{B-81}$$

The matrices **A**, **B**, and **C** must have the same number of rows and the same number of columns for the addition to be valid.

The product of a matrix **A** and a scalar c is denoted by $\mathbf{B} = c\mathbf{A}$ and defined by

$$B_{ij} = cA_{ij} \quad \text{for every } i \text{ and } j \tag{B-82}$$

The product of two matrices is similar to the scalar product of two vectors as written in Eq. (B-35). Let the components of two vectors be called F_1, F_2, F_3, and G_1, G_2, G_3. instead of F_x, F_y, etc. Eq. (B-35) is the same as

$$\mathbf{F} \cdot \mathbf{G} = F_1G_1 + F_2G_2 + F_3G_3 = \sum_{k=1}^{3} F_kG_k \tag{B-83}$$

We define matrix multiplication in a similar way. If **A**, **B**, and **C** are matrices such that **C** is the product **AB**, then

$$C_{ij} = \sum_{k=1}^{n} A_{ik}B_{kj} \tag{B-84}$$

where n is the number of columns in **A**, which must equal the number of rows in the matrix **B**. The matrix **C** will have as many rows as **A** and as many columns as **B**.

We can think of the vector **F** in Eq. (B-83) as a matrix with one row and three columns (a *row vector*) and the vector **G** as being a matrix with three rows and one column (a *column vector*). Equation (B-83) is then a special case of Eq. (B-84):

$$\mathbf{F} \cdot \mathbf{G} = [F_1 \quad F_2 \quad F_3] \begin{bmatrix} G_1 \\ G_2 \\ G_3 \end{bmatrix} \tag{B-85}$$

If two matrices are square, they can be multiplied together in either order. However, the multiplication is not always commutative. It is possible that

$$\mathbf{AB} \neq \mathbf{BA} \quad \text{(in some cases)} \tag{B-86}$$

Matrix multiplication is *associative*:

$$\mathbf{A(BC)} = \mathbf{(AB)C} \tag{B-87}$$

Matrix multiplication and addition are *distributive*:

$$\mathbf{A(B + C)} = \mathbf{AB} + \mathbf{AC} \tag{B-88}$$

Matrix multiplication is similar to operator multiplication in that both are associative and distributive but not necessarily commutative.

We define an identity matrix **E** such that

$$\mathbf{EA} = \mathbf{AE} = \mathbf{A} \tag{B-89}$$

The symbol **E** is taken from the German word *Einheit* (unity). The fact that we require **E** to be the identity matrix when multiplied on either side of **A** requires both **A** and **E** to be square matrices, but **E** can have any number of rows and columns. It has the form

$$\mathbf{E} = \begin{bmatrix} 1 & 0 & 0 & \cdots & 0 \\ 0 & 1 & 0 & \cdots & 0 \\ 0 & 0 & 1 & \cdots & 0 \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ 0 & 0 & 0 & \cdots & 1 \end{bmatrix} \tag{B-90}$$

The *diagonal elements* of any square matrix are those with both indices equal. The diagonal elements of **E** are all equal to 1 and are the only nonzero elements. This can be written in the form:

$$E_{ij} = \delta_{ij} = \begin{cases} 1 & \text{if} \quad i = j \\ 0 & \text{if} \quad i \neq j \end{cases} \tag{B-91}$$

The quantity δ_{ij} is called the *Kronecker delta* and is defined by the second equality.

Division by a matrix is not defined, but we define the *inverse* of a square matrix. We denote the inverse of **A** by $\mathbf{A}^{-1}$ and require that

$$\mathbf{A}^{-1}\mathbf{A} = \mathbf{A}\mathbf{A}^{-1} = \mathbf{E} \tag{B-92}$$

This multiplication of a matrix and its inverse is commutative, so that **A** is the inverse of $\mathbf{A}^{-1}$.

Associated with each square matrix is a determinant (see below). If the determinant of a square matrix vanishes, the matrix is said to be *singular*. A singular matrix has no inverse. The *trace* of a square matrix is the sum of the diagonal elements of the matrix:

$$\mathrm{Tr}(\mathbf{A}) = \sum_{i=1}^{n} A_{ii} \tag{B-93}$$

The trace of the n by n identity matrix is equal to n. The trace is sometimes called the *spur*, from a German word that means track or trace.

A matrix in which all the elements below the diagonal elements vanish is called an *upper triangular matrix*. A matrix in which all the elements above the diagonal elements vanish is called a *lower triangular matrix*, and a matrix in which all the elements except the diagonal elements vanish is called a *diagonal matrix*. The matrix in which all of the elements vanish is called the *null matrix* or the *zero matrix*. The *transpose* of a matrix is obtained by replacing the first column by the first row of the original matrix, the second column by the second row of the original matrix, and so on. The transpose of **A** is denoted by $\tilde{\mathbf{A}}$ (pronounced "A tilde").

$$(\tilde{A})_{ij} = A_{ji} \tag{B-94}$$

If a matrix is equal to its transpose, it is a *symmetric matrix*.

The *hermitian conjugate* of a matrix is obtained by taking the complex conjugate of each element and then taking the transpose of the matrix. If a matrix has only real elements, the hermitian conjugate is the same as the transpose. The hermitian conjugate is also called the *adjoint* (mostly by physicists) and the *associate* (mostly by mathematicians, who use the term "adjoint" for something else). The hermitian conjugate is denoted by $\mathbf{A}^{\dagger}$.

$$(A^{\dagger})_{ij} = A_{ji}^{*} \tag{B-95}$$

A matrix that is equal to its hermitian conjugate is said to be a *hermitian matrix*. An *orthogonal matrix* is one whose inverse is equal to its transpose. If **A** is orthogonal, then

$$\mathbf{A}^{-1} = \tilde{\mathbf{A}} \quad \text{(orthogonal matrix)} \tag{B-96}$$

A *unitary matrix* is one whose inverse is equal to its hermitian conjugate. If **A** is unitary, then

$$\mathbf{A}^{-1} = \mathbf{A}^{\dagger} = \tilde{\mathbf{A}}^{*} \quad \text{(unitary matrix)} \tag{B-97}$$

Determinants A square matrix has a quantity associated with it that is called a determinant. If **A** is a square matrix, we denote its determinant by det(**A**). When explicitly written, it contains the same elements as the matrix, but is written with vertical lines at the left and right. If the elements of a matrix are constant, its determinant is equal to a constant, which can be evaluated as follows: A 2 by 2 determinant has the value

$$\begin{vmatrix} A_{11} & A_{12} \\ A_{21} & A_{22} \end{vmatrix} = A_{11}A_{22} - A_{12}A_{21} \tag{B-98}$$

Larger determinants can be evaluated by *expanding by minors*, as follows:

1. Pick a row or a column of the determinant. Any row or column will do, but one with zeros in it will minimize the work.
2. The determinant equals a sum of terms, one for each element in the row or column. Each term consists of an element of the chosen row or column times the *minor* of that element, with an assigned sign that is either positive or negative. The minor of an element in a determinant is the determinant that is obtained by deleting the row and the column containing that element. The minor of an n by n determinant is an

$n-1$ by $n-1$ determinant. To determine the sign of a given term in the expansion, count the number of steps of one row or one column required to get from the upper left element to the element whose minor is desired. If the number of steps is odd, the sign is negative. If the number of steps is even (including zero), the sign is positive.

3. Repeat the entire process with each determinant in the expansion until you have a sum of 2 by 2 determinants, which can be evaluated by Eq. (B-98).

Expanding a 3 by 3 determinant gives six terms, as follows:

$$\begin{aligned}\begin{vmatrix}A_{11} & A_{12} & A_{13}\\ A_{21} & A_{22} & A_{23}\\ A_{31} & A_{32} & A_{33}\end{vmatrix} &= A_{11}\begin{vmatrix}A_{22} & A_{23}\\ A_{32} & A_{33}\end{vmatrix} - A_{12}\begin{vmatrix}A_{21} & A_{23}\\ A_{31} & A_{33}\end{vmatrix} + A_{13}\begin{vmatrix}A_{21} & A_{22}\\ A_{31} & A_{32}\end{vmatrix}\\ &= A_{11}(A_{22}A_{33} - A_{23}A_{32}) - A_{12}(A_{21}A_{33} - A_{23}A_{31})\\ &\quad + A_{13}(A_{21}A_{32} - A_{22}A_{31})\\ &= A_{11}A_{22}A_{33} - A_{11}A_{23}A_{32} + A_{12}A_{21}A_{33} - A_{12}A_{23}A_{31}\\ &\quad + A_{13}A_{21}A_{32} - A_{13}A_{22}A_{31} \end{aligned} \tag{B-99}$$

Expanding larger determinants by hand can be tedious. Computer programs such as Mathematica perform the manipulations automatically.

Determinants have a number of useful properties:

Property 1. If two rows of a determinant are interchanged, the result is a determinant whose value is the negative of the original determinant. The same is true if two columns are interchanged.

Property 2. If two rows or two columns of a determinant are identical, the determinant has value zero. This property follows from Property 1, since only zero is equal to its own negative.

Property 3. If each element in one row or one column of a determinant is multiplied by the same quantity c the value of the new determinant is c times the value of the original determinant. Therefore, if an n by n determinant has every element multiplied by c, the new determinant is c^n times the original determinant.

Property 4. If every element in any one row or in any one column of a determinant is equal to zero, the value of the determinant is equal to zero.

Property 5. If any row is replaced, element by element, by that row plus a constant times another row, the value of the determinant is unchanged. The same is true for two columns. For example,

$$\begin{vmatrix}a_{11} + ca_{12} & a_{12} & a_{13}\\ a_{21} + ca_{22} & a_{22} & a_{23}\\ a_{31} + ca_{32} & a_{32} & a_{33}\end{vmatrix} = \begin{vmatrix}a_{11} & a_{12} & a_{13}\\ a_{21} & a_{22} & a_{23}\\ a_{31} & a_{32} & a_{33}\end{vmatrix} \tag{B-100}$$

Property 6. The determinant of a triangular matrix (a *triangular determinant*) is equal to the product of the diagonal elements. For example,

$$\begin{vmatrix}a_{11} & 0 & 0\\ a_{21} & a_{22} & 0\\ a_{31} & a_{32} & a_{33}\end{vmatrix} = a_{11}a_{22}a_{33} \tag{B-101}$$

A diagonal determinant is a special case of a triangular determinant, so it also obeys this relation.

Property 7. The determinant of a matrix is equal to the determinant of the transpose of that matrix.

$$\det(\tilde{\mathbf{A}}) = \det(\mathbf{A}) \tag{B-102}$$

These properties can be verified using the expansion of a determinant by minors.

B.8 Fourier Series

Fourier series are important examples of representations of functions as linear combinations of basis functions. The basis functions in Fourier series are sine and cosine functions, which are periodic functions. A *periodic function* of x with period $2L$ has the property that

$$\boxed{f(x + 2L) = f(x) \quad \text{(definition of a periodic function)}} \tag{B-103}$$

for all values of x. A Fourier series that represents a periodic function of period $2L$ is

$$\boxed{f(x) = a_0 + \sum_{n=1}^{\infty} a_n \cos\left(\frac{n\pi x}{L}\right) + \sum_{n=1}^{\infty} b_n \sin\left(\frac{n\pi x}{L}\right)} \tag{B-104}$$

Different functions are represented by having different a and b coefficients.

Fourier proved the following facts about Fourier series: (1) Any Fourier series in x is uniformly convergent for all real values of x; (2) the set of sine and cosine basis functions in Eq. (B-104) is a *complete set* for the representation of periodic functions of period $2L$. This means that any periodic function obeying certain conditions such as integrability can be accurately represented by the appropriate Fourier series. It is not necessary that the function be continuous.

To find the coefficients in a Fourier series, we use the *orthogonality* of the basis functions. Orthogonality means that if m and n are integers,

$$\int_{-L}^{L} \cos(m\pi x/L)\cos(n\pi x/L)dx = L\delta_{mn} = \begin{cases} L & \text{if} \quad m = n \neq 0 \\ 0 & \text{if} \quad m \neq 0 \end{cases} \tag{B-105}$$

$$\int_{-L}^{L} \sin(m\pi x/L)\sin(n\pi x/L)dx = L\delta_{mn} = \begin{cases} L & \text{if} \quad m = n \\ 0 & \text{if} \quad m \neq 0 \end{cases} \tag{B-106}$$

$$\int_{-L}^{L} \cos(m\pi x/L)\sin(n\pi x/L)dx = 0 \tag{B-107}$$

To find a_m for $m \neq 0$ we multiply both sides of Eq. (B-104) by $\cos(m\pi x/L)$ and integrate from $-L$ to L.

$$\begin{aligned}\int_{-L}^{L} f(x)\cos(m\pi x/L)dx &= \sum_{n=0}^{\infty} a_n \int_{-L}^{L} \cos(n\pi x/L)\cos(m\pi x/L)dx \\ &\quad + \sum_{n=0}^{\infty} b_n \int_{-L}^{L} \sin(n\pi x/L)\cos(m\pi x/L)dx\end{aligned} \tag{B-108}$$

We have incorporated the a_0 term into the first sum, using the fact that $\cos(0) = 1$. We have also used the fact that the integral of a sum is equal to the sum of the integrals of the terms if the series is uniformly convergent.

We now apply the orthogonality facts to find that all of the integrals on the right-hand side of Eq. (B-108) vanish except for the term with two cosines in which $n = m$. The result is, for $m \neq 0$:

$$\int_{-L}^{L} f(x)\cos(m\pi x/L)dx = a_m L \tag{B-109}$$

or

$$a_m = \frac{1}{L}\int_{-L}^{L} f(x)\cos(m\pi x/L)dx \quad (m \neq 0) \tag{B-110}$$

To find a_0, we use the fact that

$$\int_{-L}^{L} \cos(0)\cos(0)dx = \int_{-L}^{L} dx = 2L \tag{B-111}$$

which leads to

$$a_0 = \frac{1}{2L}\int_{-L}^{L} f(x)dx \tag{B-112}$$

A similar procedure consisting of multiplication by $\sin(m\pi x/L)$ and integration from $-L$ to L yields

$$b_m = \frac{1}{L}\int_{-L}^{L} f(x)\sin(m\pi x/L)dx \tag{B-113}$$

A function must be integrable in order to be represented by a Fourier series, but it does not have to be continuous. It can have step discontinuities, as long as the step in the function is finite. At a step discontinuity, a Fourier series will converge to a value halfway between the value just to the right of the discontinuity and the value just to the left of the discontinuity.

If the function $f(x)$ is an even function of x, all of the b_n coefficients will vanish, and only the cosine terms will appear in the series. Such a series is called a *Fourier cosine series*. If $f(x)$ is an odd function of x, only the sine terms will appear, and the series is called a *Fourier sine series*. We can represent a function that is not necessarily periodic by a Fourier series if we are only interested in representing the function in the interval $-L < x < L$. The Fourier series will be periodic with period $2L$, and the series will be equal to the function inside the interval, but not necessarily equal to the function outside the interval. If we want to represent a function only in the interval $0 < x < L$ we can regard it as the right half of an odd function or the right half of an even function, and can therefore represent it either with a sine series or a cosine series. These two series would have the same value in the interval $0 < x < L$ but would be the negatives of each other in the interval $-L < x < 0$.

It is a necessary condition for the convergence of Fourier series that the coefficients become smaller and smaller and approach zero as n becomes larger and larger. If a Fourier series is convergent, it will be uniformly convergent for all values of x.

If convergence is fairly rapid, it is possible to approximate a Fourier series by one of its partial sums.

The sine and cosine basis functions are closely related to complex exponential functions, as shown in Eq. (B-63). One can write

$$b_n \sin\left(\frac{n\pi x}{L}\right) + a_n \cos\left(\frac{n\pi x}{L}\right) = \frac{1}{2}(a_n - ib_n)e^{in\pi x/L} + \frac{1}{2}(a_n + ib_n)e^{-in\pi x/L} \tag{B-114}$$

It is therefore possible to rewrite Eq. (B-104) as an *exponential Fourier series*:

$$f(x) = \sum_{n=-\infty}^{\infty} c_n e^{in\pi x/L} \tag{B-115}$$

We have incorporated the terms with negative exponents into the same sum with the other terms by allowing the summation index to take on negative as well as positive values. The function that is represented by a Fourier series does not have to be a real function. However, if it is a real function, the coefficients a_n and b_n will be real, so that c_n will be complex.

B.9 Fourier Integrals (Fourier Transforms)

Fourier series are designed to represent periodic functions with period $2L$. If we allow L to become larger and larger without bound, the values of $n\pi x/L$ become closer and closer together. We let

$$k = \frac{n\pi}{L} \tag{B-116}$$

As the limit $L \to \infty$ is taken, k becomes a continuously variable quantity if the limit $n \to \infty$ is taken in the proper way. In this limit the exponential Fourier series of Eq. (B-115) becomes an integral, which is called a *Fourier integral* or a *Fourier transform*.

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(k)e^{ikx}dk \tag{B-117}$$

where the coefficient c_n in Eq. (B-115) is replaced by a function of k that is denoted by $F(k)/\sqrt{2\pi}$. The equation for determining $F(k)$ is analogous to Eqs. (B-109), (B-112), and (B-113)

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x)e^{-ikx}dx \tag{B-118}$$

We have introduced a factor of $1/\sqrt{2\pi}$ in front of the integral in Eq. (B-117) in order to have the same factor in front of this integral and the integral in Eq. (B-118).

The function $F(k)$ is called the *Fourier transform* of $f(x)$ and the function $f(x)$ is also called the Fourier transform of $F(k)$. The function $f(x)$ is no longer required to be periodic, because the period $2L$ has been allowed to become infinite. Since we now have improper integrals, the functions $f(x)$ and $F(k)$ must have properties such that the integrals converge. For the integral of Eq. (B-118) to converge, the following integral must converge:

$$\int_{-\infty}^{\infty} |f(x)|^2 dx < \infty \tag{B-119}$$

We say that the function $f(x)$ must be *square integrable*. The function $f(x)$ must approach zero as $x \to -\infty$ and as $x \to \infty$ to be square integrable. If the Fourier transform $F(k)$ exists, it will also be square integrable.

If the function $f(x)$ is an even function, its Fourier transform is a *Fourier cosine transform*:

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x)\cos(kx)dx = \sqrt{\frac{2}{\pi}} \int_{0}^{\infty} f(x)\cos(kx)dx \tag{B-120}$$

The second version of the transform is called a *one-sided cosine transform*. If $f(x)$ is an odd function, its Fourier transform is a *Fourier sine transform*:

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x)\sin(kx)dx = \sqrt{\frac{2}{\pi}} \int_{0}^{\infty} f(x)\sin(kx)dx \tag{B-121}$$

There is a useful theorem for the Fourier transform of a product of two functions, called the *convolution theorem* or the *Faltung theorem* (*Faltung* is German for "folding"). The *convolution* of two functions $f(x)$ and $g(x)$ is defined as the integral

$$\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x)g(x-y)dy \tag{B-122}$$

This integral is a function of x, and its Fourier transform is equal to $F(k)G(k)$ where $F(k)$ is the Fourier transform of $f(x)$ and $G(k)$ is the Fourier transform of $g(x)$.[1] Since the Fourier transform is nearly the same going in both directions, the analogous convolution

$$\frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(1)G(k-1)dl \tag{B-123}$$

has as its Fourier transform the product $f(x)g(x)$.

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[1] Philip M. Morse and Herman Feshbach, *Methods of Theoretical Physics*, Part I, McGraw-Hill, New York, 1953, p. 464ff.

C

A Short Table of Integrals

C.1 Indefinite Integrals

$$\int \sin^2(x)dx = \frac{x}{2} - \frac{\sin(2x)}{4}$$

$$\int \cos^2(x)dx = \frac{x}{2} + \frac{\sin(2x)}{4}$$

$$\int \cos^n(x)\sin(x)dx = \frac{-1}{n+1}\cos^{n+1}(x) \quad n = 1, 2, \ldots$$

$$\int \sin^n(x)\cos(x)dx = \frac{1}{n+1}\sin^{n+1}(x) \quad n = 1, 2, \ldots$$

$$\int x\sin(x)dx = \sin(x) - x\cos(x)$$

$$\int x\sin^2(x)dx = \frac{x^2}{4} - \frac{x\sin(2x)}{4} - \frac{\cos(2x)}{8}$$

$$\int x^2\sin(x)dx = 2x\sin(x) - (x^2 - 2)\cos(x)$$

$$\int x\cos^2(x)dx = \frac{x^2}{4} + \frac{x\sin(2x)}{4} + \frac{\cos(2x)}{8}$$

$$\int x^2\sin^2(x)dx = \frac{x^3}{6} - \left(\frac{x^2}{4} - \frac{1}{8}\right)\sin(2x) - \frac{x\cos(2x)}{4}$$

$$\int e^{ax}dx = \frac{1}{a}e^{ax}$$

$$\int a^x dx = \frac{a^x}{\ln(a)}$$

$$\int xe^{ax}dx = e^{ax}\left(\frac{x}{a} - \frac{1}{a^2}\right)$$

$$\int x^2e^{ax}dx = e^{ax}\left(\frac{x^2}{a} - \frac{2x}{a^2} + \frac{2}{a^3}\right)$$

$$\int \ln(x)dx = x\ln(x) - x$$

$$\int \ln(ax)dx = x\ln(ax) - x$$

$$\int x\ln(x)dx = \frac{x^2}{2}\ln(x) - \frac{x^2}{4}$$

C.2 Definite Integrals

$$\int_0^\pi \sin(mx)\sin(nx)dx = \begin{cases} \frac{\pi}{2} & \text{if } m = n \\ 0 & \text{if } m \neq n \end{cases} \qquad (m \text{ and } n \text{ integers})$$

$$\int_0^\pi \cos(mx)\cos(nx)dx = \begin{cases} \frac{\pi}{2} & \text{if } m = n \\ 0 & \text{if } m \neq n \end{cases} \qquad (m \text{ and } n \text{ integers})$$

$$\int_0^\pi \sin(mx)\cos(nx)dx = \begin{cases} 0 & \text{if } m = n \\ 0 & \text{if } m \neq n\ (m+n \text{ even}) \\ \frac{2m}{m^2 - n^2} & \text{if } m \neq n\ (m+n \text{ odd}) \end{cases}$$

$$\int_0^\infty e^{-ax}dx = \frac{1}{a}, \qquad a > 0$$

$$\int_0^\infty x^n e^{-ax}dx = \frac{1}{a^{n+1}}n! \qquad a > 0,\ n = 0, 1, 2, \ldots$$

$$\int_0^\infty e^{-ax^2}dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}, \qquad a > 0$$

$$\int_0^\infty xe^{-ax^2}dx = \frac{1}{2a}, \qquad a > 0$$

$$\int_0^\infty x^2 e^{-ax^2} dx = \frac{1}{4}\sqrt{\frac{\pi}{a^3}}, \qquad a > 0$$

$$\int_0^\infty x^3 e^{-ax^2} dx = \frac{1}{2a^2}, \qquad a > 0$$

$$\int_0^\infty x^{2n} e^{-ax^2} dx = \frac{(1)(3)(5)\ldots(2n-1)}{2^{n+1}a^{n+1/2}}\sqrt{\pi}, \quad a > 0$$

$$\int_0^\infty x^{2n+1} e^{-ax^2} dx = \frac{n!}{2a^{n+1}}, \qquad a > 0$$

C.3 The Error Function

The error function is defined by

$$\operatorname{erf}(z) = \frac{2}{\sqrt{\pi}}\int_0^z e^{-t^2} dt$$

So that

$$\operatorname{erf}(0) = 0$$
$$\operatorname{erf}(1/\sqrt{2}) = 0.683\ldots$$
$$\operatorname{erf}(\infty) = 1$$
$$\operatorname{erf}(-1/\sqrt{2}) = -0.683\cdots$$
$$\operatorname{erf}(-\infty) = -1$$

The following identity is sometimes useful:

$$\int_0^z t^2 e^{-at^2} dt = \frac{\sqrt{\pi}}{4a^{3/2}}\operatorname{erf}(\sqrt{a}\, z) - \frac{z}{2a}e^{-az^2}$$

The error function cannot be expressed in closed form (as a formula with a finite number of terms) for values of z other than 0 or ∞. The following asymptotic formula[2] gives values of the error function for large arguments:

$$\operatorname{erf}(z) = 1 - \frac{e^{-z^2}}{\sqrt{\pi}\, z}\left(1 + \sum_{m=1}^{\infty}\frac{(-1)^m(1)(3)\ldots(2m-1)}{(2z^2)^m}\right)$$

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[2] M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, National Bureau of Standards, Washington, DC, 1964, p. 298.

Table C.1 Table of Values of erf(z)

z		0	1	2	3	4	5	6	7	8	9
0.0	0.0	000	113	226	338	451	564	676	789	901	*013
1	0.1	125	236	348	459	569	680	790	900	*009	*118
2	0.2	227	335	443	550	657	763	869	974	*079	*183
3	0.3	286	389	491	593	694	794	893	992	*090	*187
4	0.4	284	380	475	569	662	755	847	937	*027	*117
5	0.5	205	292	379	465	549	633	716	798	879	959
6	0.6	039	117	194	270	346	420	494	566	638	708
7		778	847	914	981	*047	*112	*175	*238	*300	*361
8	0.7	421	480	538	595	651	707	761	814	867	918
9		969	*019	*068	*116	*163	*209	*254	*299	*342	*385
1.0	0.8	427	468	508	548	586	624	661	698	733	768
1		802	835	868	900	931	961	991	*020	*048	*076
2	0.9	103	130	155	181	205	229	252	275	297	319
3		340	361	381	400	419	438	456	473	490	507
4	0.95	23	39	54	69	83	97	*11	*24	*37	*49
5	0.96	61	73	84	95	*06	*16	*26	*36	*45	*55
6	0.97	63	72	80	88	96	*04	*11	*18	*25	*32
7	0.98	38	44	50	56	61	67	72	77	82	86
8		91	95	99	*03	*07	*11	*15	*18	*22	*25
9	0.99	28	31	34	37	39	42	44	47	49	51
2.0	0.995	32	52	72	91	*09	*26	*42	*58	*73	*88
1	0.997	02	15	28	41	53	64	75	85	95	*05
2	0.998	14	22	31	39	46	54	61	67	74	80
3		86	91	97	*02	*06	*11	*15	*20	*24	*28
4	0.999	31	35	38	41	44	47	50	52	55	57
5		59	61	63	65	67	69	71	72	74	75
6		76	78	79	80	81	82	83	84	85	86
7		87	87	88	89	89	90	91	91	92	92
8	0.9999	25	29	33	37	41	44	48	51	54	56
9		59	61	64	66	68	70	72	73	75	77

The value of the error function is obtained by taking the first digits from the column after the vertical rule and the later digits from the appropriate column under the digits 0 through 9. Entries marked with an asterisk take the first digits from the next lower line.

D

Some Derivations of Formulas and Methods

This appendix expands on some of the things presented without derivation.

D.1 Caratheodory's Theorem

Caratheodory devised a three-part proof that the mathematical statement of the second law follows from a physical statement of the second law.[3] The first part is to establish that in the state space of the system only one reversible adiabat passes through any given point. This was shown in Chapter 3. The second part of the argument is to show that this fact implies that a function S exists whose differential vanishes along the reversible adiabat on which dq_{rev} also vanishes. This implies that dq_{rev} possesses an *integrating factor*, which is a function y that produces an exact differential dS when it multiplies an inexact differential:

$$dS = y\, dq_{\text{rev}} \tag{D-1}$$

The third part of the proof is to show that $y = 1/T$ is a valid choice for an integrating factor.

We will give only a nonrigorous outline of Caratheodory's proof.[4] We represent the state of a simple closed system by a point in the state space with T on the vertical axis and V on the horizontal axis. The main idea is that if there is a single curve in this space along which dq_{rev} vanishes there is also a differential of a function, dS, which vanishes on the same curve. Consider reversible adiabatic processes of a closed simple system starting from a particular initial state. Since no two adiabats can cross the reversible adiabat can be represented mathematically by a function

$$T = f(V) \tag{D-2}$$

Equation (2.4-21b) is an example of such a function, holding for an ideal gas with constant heat capacity, but for another system it would be whatever function applies to that system. Equation (D-2) is the same as

$$0 = f(V) - T \quad \text{(valid only on the curve)} \tag{D-3}$$

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[3] C. Caratheodory, *Math. Ann.*, **67**, 335 (1909).

[4] J. G. Kirkwood and I. Oppenheim, *Chemical Thermodynamics*, McGraw-Hill, New York, 1961, p. 31ff; J. deHeer, *Phenomenological Thermodynamics*, Prentice-Hall, Englewood Cliffs, NJ, 1986, p. 123ff.

Let a function S be defined by

$$S = S(T, V) = f(V) - T + C \tag{D-4}$$

where C is a constant. Equation (D-4) applies for all values of T and V, not just values on the curve. Since f is a function of V, S is a function of T and V for our closed system, and is therefore a state function. Now we need to show that dS vanishes on the reversible adiabat. For reversible adiabatic processes T is equal to $f(V)$, and S is equal to the constant C. Therefore, for reversible adiabatic processes

$$dS = 0 \qquad \text{(reversible adiabatic processes)} \tag{D-5}$$

Since reversible adiabatic processes cannot lead away from the curve, dq_{rev} vanishes only on the curve. Since $f(V)$ represents a unique curve, dS vanishes only on the curve, and we can write

$$dS = y\,dq_{\text{rev}} \tag{D-6}$$

where y is a function that is nonzero in the vicinity of the curve. Since S is a function, dS is exact and y is an integrating factor. We have shown in Chapter 3 that $y = 1/T$ is a valid integrating factor.

D.2 Proof That the Liquid and Vapor Curves Are Tangent at an Azeotrope

To show this fact we write the Gibbs–Duhem relation, Eq. (4.6-10), for the liquid phase containing two components at constant temperature and pressure. Using Eq. (6.3-6) for the activity and dividing by RT, we obtain the following version of the Gibbs–Duhem relation:

$$x_1 d[\ln(a_1)] + x_2 d[\ln(a_2)] = 0 \qquad (T \text{ and } P \text{ constant}) \tag{D-7}$$

where x_1 and x_2 are the mole fractions in the liquid and a_1 and a_2 are the activities in the liquid.

We assume that an ideal gas phase is at equilibrium with the solution. Using convention I, we equate the chemical potential of the solvent in the two phases:

$$\mu_1^{\circ(I)} + RT\ln(a_1) = \mu_1^{\circ(\text{gas})} + RT\ln(P_1/P^\circ) \tag{D-8}$$

For an infinitesimal equilibrium change in state at constant T and P

$$RTd[\ln(a_1)] = RTd[\ln(P_1/P^\circ)] \tag{D-9}$$

When Eq. (D-9) and the analogous equation for substance 2 are substituted in Eq. (D-8), we obtain for the vapor at equilibrium with the solution

$$x_1 d[\ln(P_1/P^\circ)] + x_2 d[\ln(P_2/P^\circ)] = 0 \tag{D-10}$$

$$x_1 \frac{1}{P_1} dP_1 + x_2 \frac{1}{P_2} dP_2 = 0 \tag{D-11}$$

where the mole fractions are those in the liquid solution. We convert this equation into a derivative equation:

$$\frac{x_1}{P_1}\left(\frac{\partial P_1}{\partial x_1}\right)_{T,P}+\frac{x_2}{P_2}\left(\frac{\partial P_2}{\partial x_1}\right)_{T,P}=0 \tag{D-12}$$

The total vapor pressure is the sum of the partial vapor pressures.

$$P_{\text{vap}}=P_1+P_2 \tag{D-13}$$

At the azeotrope, the total vapor pressure is at a maximum or a minimum with respect to x_1, so that

$$\left(\frac{\partial P_{\text{vap}}}{\partial x_1}\right)_{T,P}=\left(\frac{\partial P_1}{\partial x_1}\right)_{T,P}+\left(\frac{\partial P_2}{\partial x_1}\right)_{T,P}=0 \tag{D-14}$$

When this equation is substituted into Eq. (D-12),

$$\frac{x_1}{P_1}=\frac{x_2}{P_2} \tag{D-15}$$

or

$$\frac{x_1}{x_2}=\frac{P_1}{P_2}=\frac{y_1}{y_2} \tag{D-16}$$

where we denote the mole fraction in the gas phase by y and where we have used the fact that in an ideal gas mixture the mole fraction is proportional to the partial pressure (Dalton's law). Each mole fraction has the same value in the solution and in the gas phase, since they have the same ratio and must add to unity. The two curves must coincide at the azeotrope. They are tangent to each other since they cannot cross.

D.3 Euler's Theorem[5]

A function f that depends on $n_1, n_2, n_3, \ldots n_c$, is said to be *homogeneous of degree m* in the n's if

$$f(\lambda n_1,\lambda n_2,\ldots,\lambda n_c)=\lambda^m f(n_1,n_2,\ldots,n_c) \tag{D-17}$$

for every positive real value of λ. Euler's theorem states that for such a function

$$mf=\sum_{i=1}^{c} n_1\left(\frac{\partial f}{\partial n_i}\right)_{n'} \tag{D-18}$$

where the subscript n' means that all of the n''s are held fixed except for n_i.

To prove the theorem, we differentiate Eq. (D-17) with respect to λ, using the chain rule:

$$\sum_{i=1}^{c}\left(\frac{\partial f}{\partial(\lambda n_i)}\right)_{n'}\left(\frac{\partial(\lambda n_i)}{\partial(\lambda)}\right)_{n'}=m\lambda^{m-1}f(n_1,n_2,\ldots,n_c) \tag{D-19}$$

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[5] E. A. Desloge, *Statistical Physics*, Holt Rinehart and Winston, New York, 1966, Appendix 10.

The subscript n' means that all of the n''s are held fixed in the differentiation except for n_i. We use the fact that

$$\left(\frac{\partial(\lambda n_i)}{\partial(\lambda)}\right)_{n'} = n_i \tag{D-20}$$

and set λ equal to unity in Eq. (D-19) to obtain Eq. (D-18), and the theorem is proved.

D.4 The Method of Intercepts

The value of the derivative $(\partial Y_m/\partial x_1)_{T,P}$ gives the slope of the desired tangent line when evaluated at $x_1 = x_1'$. We write the analogue of Eq. (4.6-15) for a general extensive quantity Y and differentiate with respect to x_1:

$$\left(\frac{\partial Y_m}{\partial x_1}\right)_{T,P} = \bar{Y}_1 + x_1\left(\frac{\partial \bar{Y}_1}{\partial x_1}\right)_{T,P} - \bar{Y}_2 + x_2\left(\frac{\partial \bar{Y}_2}{\partial x_1}\right)_{T,P} \tag{D-21}$$

where we have used the fact that $(\partial x_2/\partial x_1) = -1$, which follows from the fact that $x_1 + x_2 = 1$. The second and fourth terms on the right-hand side of Eq. (D-21) sum to zero by the analogue of Eq. (4.6-13), giving

$$\left(\frac{\partial Y_m}{\partial x_1}\right)_{T,P} = \bar{Y}_1 - \bar{Y}_2 \tag{D-22}$$

If this derivative is evaluated at $x_1 = x_1'$, it gives the slope of the tangent line at that point. If we let y stand for the ordinate of a point on the line, then

$$y = [\bar{Y}_1(x_1') - \bar{Y}_2(x_1')]\, x_1 + b \tag{D-23}$$

where b is the intercept of the tangent line at $x_1 = 0$, and where we consider both of the partial molar quantities to be functions of x_1, and omit mention of the dependence on P and T.

The line and the curve must coincide at $x_1 = x_1'$, so that from Eqs. (D-21) and (D-23)

$$\bar{Y}_2(x_1') + x_1'[\bar{Y}_1(x_1') - \bar{Y}_2(x_1')] = [\bar{Y}_1(x_1') - \bar{Y}_2(x_1')]\, x_1' + b \tag{D-24}$$

Canceling equal terms on both sides of the equation, we get

$$\bar{Y}_2(x_1') = b \tag{D-25}$$

One can repeat the entire argument with the roles of components 1 and 2 reversed to show that the intercept at the right side of the figure is equal to the value of $\bar{Y}_1$ at $x_1 = x_1'$. However, it can more easily be shown by evaluating the function represented by the line at $x_1 = 1$.

$$y(1) = [\bar{Y}_1(x_1') - \bar{Y}_2(x_1')] + \bar{Y}_2(x_1') = \bar{Y}_1(x_1') \tag{D-26}$$

Thus, the intercept at $x_1 = 1$ is equal to $\bar{Y}_1(x_1')$.

D.5 An Integration for the Collision Theory of Bimolecular Reactions

In Section 12.3 we stated the result of an integration over all relative velocities satisfying the constant that $v < v_c$. In order to carry out this integration, we change variables, expressing the kinetic energy of the pair of particles in terms of the velocity $\mathbf{v}_c$ of the center of mass and the relative velocity $\mathbf{v}$ of the two molecules. The kinetic energy is expressed in terms of the kinetic energy of the center of mass and the kinetic energy of relative motion, as shown in Appendix E:

$$\mathscr{K} = \frac{1}{2}Mv_c^2 + \frac{1}{2}\mu v^2 \tag{D-27}$$

where $M = m_1 + m_2$, where $\mu = m_1 m_2/M$ is the reduced mass of the two particles, where v_c is the speed of the center of mass of the two particles, and where v is the relative speed of one particle relative to the other. Using Eq. (9.3-40) for the probability distributions, we write

$$dZ_{12} = \pi d_{12}^2 \mathscr{N}_1 \mathscr{N}_2 \left(\frac{m_1}{2\pi k_B T}\right)^{3/2} \left(\frac{m_2}{2\pi k_B T}\right)^{3/2} v e^{-MV^2/2k_B T} e^{-\mu v^2/2k_B T} d^3\mathbf{v}_{cx} d^3\mathbf{v} \tag{D-28}$$

We integrate Eq. (D-28) over all values of v_{cx}, v_{cy}, and v_{cz}. Integration over $\mathbf{v}_{cx}$ is just like the integration in Eq. (9.3-20), and gives a factor of $(2\pi k_B T/M)^{3/2}$:

$$Z_{12}(\text{reactive}) = \pi d_{12}^2 \mathscr{N}_1 \mathscr{N}_2 \left(\frac{2\pi k_B T}{M}\right)^{3/2} \left(\frac{m_1}{2\pi k_B T}\right)^{3/2} \left(\frac{m_2}{2\pi k_B T}\right)^{3/2} \int v e^{-\mu v^2/2k_B T} d^3\mathbf{v} \tag{D-29}$$

We now integrate over the values of $\mathbf{v}$ that satisfy the condition that the relative speed exceeds the critical value v_c. The integration in this equation is carried out in spherical polar coordinates in the relative velocity space of v, θ, and ϕ. Integration over the angles θ and ϕ gives a factor of 4π. The integration must include only values of v satisfying the condition that $v < v_c$. We use a tabulated indefinite integral to obtain

$$\int_{v_c}^{\infty} e^{-\mu v^2/2k_B T} v^3 dv = \frac{1}{2} e^{-\mu v_c^2/2k_B T} \left(\frac{2k_B T}{\mu}\right) \left(v_c^2 + \frac{2k_B T}{\mu}\right) \tag{D-30}$$

The final result is

$$Z_{12}(\text{reactive}) = \pi d_{12}^2 \mathscr{N}_1 \mathscr{N}_2 (8k_B T/\pi\mu)^{1/2} (1 + \mu v_c^2/2k_B T) e^{-\mu v_c^2/2k_B T} \tag{D-31}$$

E

Classical Mechanics

Classical mechanics was the accepted version of mechanics prior to the discovery of relativistic mechanics and quantum mechanics. It is valid for large energies, large masses, and speeds that are small compared with the speed of light. It is often called *Newtonian mechanics*, since it was largely discovered by Isaac Newton.

E.1 Newton's Laws of Motion

Classical mechanics is based on Newton's three laws. The first law is the *law of inertia*: *If not acted upon by a force, a stationary object remains stationary, and a moving object continues to move in a straight line at a constant speed.*

Newton's second law is the *law of acceleration*, which states that a force on an object produces an acceleration inversely proportional to its mass:

$$\mathbf{F} = m\mathbf{a} = m\frac{d\mathbf{v}}{dt} = \frac{d^2\mathbf{r}}{dt^2} \tag{E-1a}$$

or

$$\mathbf{i}F_x + \mathbf{j}F_y + \mathbf{k}F_z = m\left(\mathbf{i}\frac{d^2x}{dt^2} + \mathbf{j}\frac{d^2y}{dt^2} + \mathbf{k}\frac{d^2z}{dt^2}\right) \tag{E-1b}$$

where m is the mass of the particle and where $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ are unit vectors in the direction of the x, y, and z coordinate axes, respectively. The acceleration $\mathbf{a}$ is the time derivative of the velocity $\mathbf{v}$ and the second time derivative of the position vector.

Newton's third law is the *law of action and reaction*: *If one object exerts a force on a second object, the second object exerts a force on the first object that is equal in magnitude to the first force and opposite in direction.*

If the force on a particle is a known function of position, Eq. (E-1) is an *equation of motion*, which determines the particle's position and velocity for all values of the time if the position and velocity are known for a single time. Classical mechanics is thus said to be *deterministic*. The state of a system in classical mechanics is specified by giving the position and velocity of every particle in the system. All mechanical quantities such as kinetic energy and potential energy have values that are determined by the values of these coordinates and velocities, and are mechanical state functions. The kinetic energy of a point-mass particle is a state function that depends on its velocity:

$$\mathscr{K} = \frac{1}{2}mv^2 = \frac{1}{2}m(v_x^2 + v_y^2 + v_z^2) \tag{E-2}$$

If the forces on the particles of a system depend only on the particles' positions, these forces can be derived from a potential energy. Consider motion in the z direction. If z' and z'' are two values of z, the difference in the potential energy $\mathscr{V}$ between these two locations is defined to equal the reversible work done on the system by an external agent to move the particle from z' to z''.

$$\Delta\mathscr{V} = \mathscr{V}(z'') - \mathscr{V}(z') = \int_{z_1}^{z_2} F_{\text{ext(rev)}}(z)dz \tag{E-3}$$

Since only the difference in potential energy is defined in Eq. (E-3), we have the option of deciding at what state of the system we want to set the potential energy equal zero. We accomplish this by adding an appropriate constant to a formula for the potential energy.

The external force $\mathrm{F}_{\text{ext(rev)}}$ must exactly balance the force due to the other particles in order for the process to be reversible:

$$F_{\text{ext(rev)}}(z) = -F_z \tag{E-4}$$

By the principles of calculus, the integrand in Eq. (E-3) is equal to the derivative of the function $\mathscr{V}$, so that

$$F_z = -\frac{d\mathscr{V}}{dz} \tag{E-5}$$

In the case of motion in three dimensions, analogous equations for the x and y components can be written, and the vector force is given by

$$\mathbf{F} = \mathbf{i}F_x + \mathbf{j}F_y + \mathbf{k}F_z = -\mathbf{i}\frac{\partial\mathscr{V}}{\partial x} - \mathbf{j}\frac{\partial\mathscr{V}}{\partial y} - \mathbf{k}\frac{\partial\mathscr{V}}{\partial z} = -\nabla\mathscr{V} \tag{E-6}$$

where the symbols **i**, **j**, and **k** stand for unit vectors in the x, y, and z directions, respectively, and where the symbol ∇ ("del") stands for the three-term *gradient operator* expressed in the right-hand side of the first line of Eq. (E-6). A system in which no forces occur except those derivable from a potential energy is called a *conservative system*. It is a theorem of mechanics that the energy of such a system is constant, or *conserved*.

E.2 Derivation of the Wave Equation for a Flexible String

The wave equation for the flexible string was stated in Section 14.3. We now derive this equation. Consider a small portion of the string lying between x and $x + \Delta x$, as shown in Figure E.1. The tension force on the left end of the string segment is denoted by $\mathbf{F}_1$, and the force on the right end is denoted by $\mathbf{F}_2$. Since the string is perfectly flexible, no force can be put on the string by bending it. The force exerted on one portion of the string by an adjacent portion is tangent to the string at the point dividing the portions, and has a magnitude equal to T, the tension force at each end of the string. If the string is straight, the forces at the ends of a given segment will cancel. If the string is curved, the forces at the two ends of a portion of the string will not cancel.

Consider the segment of the string lying between $x = x'$ and $x = x + dx$. We denote the angles between the x axis and the two tangent lines at the ends of the segment by

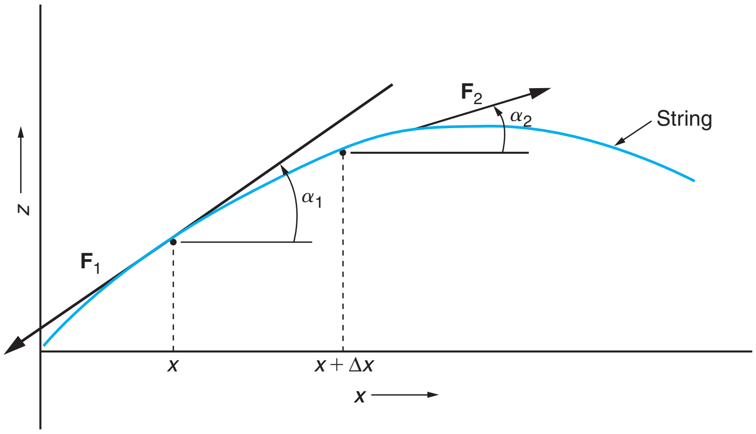

Figure E.1 The Position of a Flexible String and the Forces on a Segment of the String. This arbitrary conformation of the string as a function of length along the string is used to describe the forces on a small segment of the string.

α_1 and α_2. For small displacements, the net force on the string segment will lie in the z direction:

$$F_z = F_{2z} + F_{1z} = T\sin(\alpha_2) - T\sin(\alpha_1) \approx T[\tan(\alpha_2) - \tan(\alpha_1)]$$

$$\approx T\left[\left(\frac{\partial z}{\partial x}\right)\bigg|_{x'+\Delta x} - \left(\frac{\partial z}{\partial x}\right)\bigg|_{x'}\right] \tag{E-7}$$

where the subscripts on the derivatives denote the positions at which they are evaluated. We have used the fact that the sine and the tangent are nearly equal for small angles, which corresponds to our case of small displacements. We have also used the fact that the first derivative is equal to the tangent of the angle between the horizontal and the tangent line.

The mass of the string per unit length is ρ and the mass of the segment is $\rho\Delta x$. Its acceleration is $(\partial^2 z/\partial t^2)$, so that from Newton's second law

$$T\left[\left(\frac{\partial z}{\partial x}\right)\bigg|_{x+\Delta x} - \left(\frac{\partial z}{\partial x}\right)\bigg|_{x}\right] = \rho\Delta x\frac{\partial^2 z}{\partial t^2} \tag{E-8}$$

We divide both sides of this equation by $\rho\Delta x$ and then take the limit as Δx is made to approach zero. In this limit, the quotient of differences becomes a second derivative:

$$\lim_{\Delta x\to 0}\left[\frac{\left(\frac{\partial z}{\partial x}\right)\Big|_{x+\Delta x} - \left(\frac{\partial z}{\partial x}\right)\Big|_{x}}{\Delta x}\right] = \frac{\partial^2 z}{\partial x^2} \tag{E-9}$$

This equation is substituted into Eq. (E-8) to obtain the classical wave equation:

$$\frac{\partial^2 z}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 z}{\partial t^2} \tag{E-10}$$

where $c^2 = T/\rho$. We show in Chapter 14 that c is the speed of propagation of a traveling wave in the string.

E.3 Lagrangian Mechanics

Lagrangian mechanics is a way of writing the classical mechanics of Newton in a way that has the same form in any coordinate system. It is convenient for problems in which Cartesian coordinates cannot conveniently be used. We specify the positions of the particles in a system by the coordinates $q_1, q_2, q_3, \ldots, q_n$, where n is the number of coordinates, equal to three times the number of particles if they are point-mass particles that move in three dimensions. These coordinates can be any kind of coordinates, such as spherical polar coordinates, cylindrical polar coordinates, and so on. To specify the state of the system, some measures of the particles' velocities are needed in addition to coordinates. The Lagrangian method uses the time derivatives of the coordinates:

$$\dot{q}_i = \frac{dq_i}{dt} \quad (i = 1, 2, \ldots, n) \tag{E-11}$$

We use a symbol with a dot over it to represent a time derivative.

The Lagrangian function is defined by

$$\mathscr{L} = \mathscr{K} - \mathscr{V} \quad \text{(definition of the Lagrangian)} \tag{E-12}$$

where $\mathscr{K}$ and $\mathscr{V}$ are the kinetic and potential energy expressed in terms of the qs and the $\dot{q}$s. The *Lagrangian equations of motion* are:

$$\frac{d}{dt}\left(\frac{\partial \mathscr{L}}{\partial \dot{q}_i}\right) - \frac{\partial \mathscr{L}}{\partial q_i} = 0 \quad (i = 1, 2, \ldots, n) \tag{E-13}$$

These equations are equivalent to Newton's second law and we present them without derivation. These equations have exactly the same form for all coordinate systems, so that the work of transforming Newton's second law into a particular coordinate system can be avoided, once we have expressed the kinetic and potential energy in terms of the appropriate coordinates.[6]

One application of Lagrange's equations of motion is to a particle orbiting about a fixed point in a plane. We use plane polar coordinates ρ and ϕ (with ϕ measured in radians), and place the origin of coordinates at the fixed point. The component of the velocity parallel to the position vector is $\dot{\rho}$, and the component perpendicular to this direction is $\rho\dot{\phi}$, so that the Lagrangian is

$$\mathscr{L} = \frac{1}{2}m\dot{\rho}^2 + \frac{1}{2}m\rho^2\dot{\phi}^2 - \mathscr{V}(\rho, \phi) \tag{E-14}$$

The Lagrangian equations of motion are

$$\frac{d(2m\dot{\rho})}{dt} - m\rho\dot{\phi}^2 + \frac{\partial \mathscr{V}}{\partial \rho} = 0 \tag{E-15}$$

$$\frac{d(m\rho^2\dot{\phi})}{dt} + \frac{\partial \mathscr{V}}{\partial \phi} = 0 \tag{E-16}$$

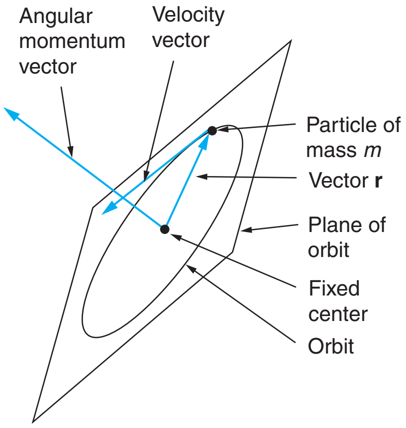

Figure E.2 Diagram to Illustrate the Definition of the Angular Momentum Vector. The angular momentum vector, **L**, is perpendicular to the vector **r** and the vector **v**, and has magnitude equal to $m|\mathbf{r}||\mathbf{v}|$.

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[6] This fact is proved in J. C. Slater and N. Frank, *Mechanics*, McGraw-Hill, New York, 1947, p. 69ff, or in any other book on the same subject.

The second term in Eq. (E-15) produces a rate of change in $\dot{\rho}$ if $\mathscr{V}$ does not depend on ρ. This represents the *centrifugal force*, which is not a force, but an expression of the natural tendency of an orbiting particle to move off in a straight line. To maintain a circular orbit about the origin of coordinates, the second term must be canceled by a *centripetal force*:

$$F(\text{centripetal}) = -\frac{\partial \mathscr{V}}{\partial \rho} = -m\rho\dot{\phi}^2 = -\frac{mv^2}{\rho} \tag{E-17}$$

where the speed v in a circular orbit equals $\rho\dot{\phi}$.

An important variable for an orbiting object is the *angular momentum* around a fixed center. This is the vector

$$\mathbf{L} = m\mathbf{r} \times \mathbf{v} \tag{E-18}$$

where $\mathbf{r}$ is the position vector from the fixed center to the particle, $\mathbf{v}$ is its velocity vector, and × stands for the cross product of two vectors, discussed in Appendix B. Figure E.2 illustrates the angular momentum of a single orbiting particle. In a circular orbit, $\mathbf{r}$ and $\mathbf{v}$ are perpendicular to each other and the angular momentum vector has the magnitude

$$L = |\mathbf{L}| = m\rho v = m\rho^2\dot{\phi} \tag{E-19}$$

For any moving mass not subject to friction or forces other than a centripetal force, the angular momentum about a fixed center remains constant. We say that it is *conserved*. The orbit of the moving mass remains in the same plane, and the angular momentum has a fixed direction and a fixed magnitude. If a system consists of several interacting particles, the vector sum of their angular momenta (the total angular momentum) is conserved. If the set of particles constitutes a rotating rigid body such as a gyroscope spinning on its axis, the total angular momentum remains constant if no forces act on the body. Figure E.3 shows a simple gyroscope. If a gyroscope stands on one end of its axis at an angle in a gravitational field, the gravitational force produces a torque (a turning force) in the direction that would make the gyroscope fall on its side if it were not rotating. If it is rotating, instead of making the gyroscope fall on its side, it makes the axis move (precess) around a vertical cone, as shown in the figure.

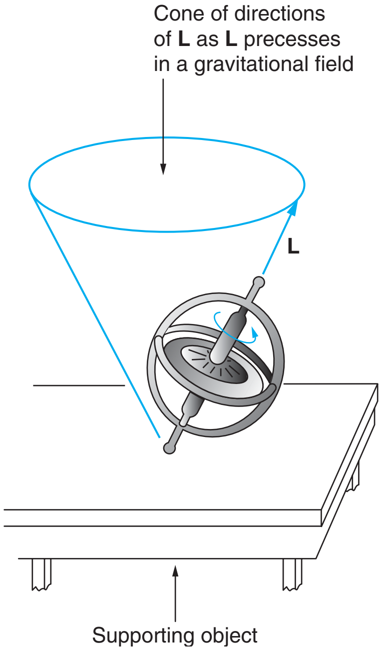

Figure E.3 A Simple Gyroscope. If a torque is placed on a gyroscope, as by supporting one end of the gyroscope in a gravitational field, the gyroscope will precess, which means that its axis of rotation will move around a cone with a vertical axis.

E.4 Hamiltonian Mechanics

Hamilton's method is similar to that of Lagrange in that it provides equations of motion that have the same form in any coordinate system. It uses *conjugate momenta* instead of time derivatives of coordinates as state variables. The conjugate momentum to the coordinate q_i is defined by

$$p_i = \frac{\partial \mathscr{L}}{\partial \dot{q}_i} \quad (i = 1, 2, \ldots, n) \quad \text{(definition)} \tag{E-20}$$

where $\mathscr{L}$ is the Lagrangian. The momentum conjugate to a Cartesian coordinate is a component of the ordinary (linear) momentum:

$$p_x = mv_x, \quad p_y = mv_y, \quad p_z = mv_z \tag{E-21}$$

As with the angular momentum, the vector sum of the momenta of a set of interacting particles is conserved if no external forces act on the particles.

The *Hamiltonian function*, also called *Hamilton's principal function* or the *classical Hamiltonian*, is defined by

$$\mathscr{H} = \sum_{i=1}^{n} p_i \dot{q}_i - \mathscr{L} \tag{E-22}$$

The Hamiltonian function must be expressed as a function of coordinates and conjugate momenta. It is equal to the total energy of the system (kinetic plus potential).[7]

$$\mathscr{H} = \mathscr{K} + \mathscr{V} \tag{E-23}$$

The Hamiltonian equations of motion are

$$\dot{q}_i = \frac{\partial \mathscr{H}}{\partial p_i}, \quad \dot{p}_i = -\frac{\partial \mathscr{H}}{\partial q_i} \quad (i = 1, 2, \ldots, n) \tag{E-24}$$

There is one pair of equations for each value of i, as indicated.

E.5 The Two-Body Problem

Consider a two-particle system with a potential energy that depends only on the distance between the particles. This case applies to the hydrogen atom and to the nuclei of a rotating diatomic molecule in the Born–Oppenheimer approximation. The equation of motion of such a system can be separated into two separate equations. We first treat the case in which there is motion only in the x direction and apply the Lagrangian method. The Lagrangian of the system is

$$\mathscr{L} = \mathscr{K} - \mathscr{V} = \frac{1}{2} m_1 \dot{x}_1^{\,2} + \frac{1}{2} m_2 \dot{x}_2^{\,2} - \mathscr{V}(x_2 - x_1) \tag{E-25}$$

We now change to a different set of coordinates:

$$x_c = \frac{m_1 x_1 + m_2 x_2}{m_1 + m_2} \tag{E-26}$$

$$x = x_2 - x_1 \tag{E-27}$$

The coordinate x_c is the *center of mass coordinate*, and the coordinate x is the *relative coordinate*. We now show that these two coordinates obey separate equations of motion. We solve Eqs. (E-26) and (E-27) for x_1 and x_2:

$$x_1 = x_c - \frac{m_2 x}{M} \tag{E-28}$$

$$x_2 = x_c + \frac{m_1 x}{M} \tag{E-29}$$

where $M = m_1 + m_2$.

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[7] J. C. Slater and N. H. Frank, *op. cit.*, p. 74ff (note 1).

Taking the time derivatives of Eqs. (E-28) and (E-29), we can write the Lagrangian as

$$\mathscr{L} = \frac{1}{2}m_1\left(\dot{x}_c - \frac{m_2\dot{x}}{M}\right)^2 + \frac{1}{2}m_2\left(\dot{x}_c + \frac{m_1\dot{x}}{M}\right)^2 - \mathscr{V}(x)$$

$$= \frac{1}{2}m_1\left[\dot{x}_c^{\,2} - 2m_2\frac{\dot{x}_c\dot{x}}{M} + \left(\frac{m_2\dot{x}}{M}\right)^2\right] + \frac{1}{2}m_2\left[\dot{x}_c^2 + 2m_1\frac{\dot{x}_c\dot{x}}{M} + \left(\frac{m_1\dot{x}}{M}\right)^2\right] - \mathscr{V}(x) \tag{E-30}$$

The terms containing $\dot{x}_c\dot{x}$ cancel, so that

$$\mathscr{L} = \frac{1}{2}(m_1 + m_2)\dot{x}_c^2 + \frac{1}{2}\frac{m_1m_2(m_1+m_2)}{M^2}\dot{x}^2 - \mathscr{V}(x)$$

$$= \frac{1}{2}M\dot{x}_c^2 + \frac{1}{2}\mu\dot{x}^2 - \mathscr{V}(x) \tag{E-31}$$

The *reduced mass* of the pair of particles is denoted by μ and is defined by

$$\mu = \frac{m_1m_2}{m_1+m_2} = \frac{m_1m_2}{M} \tag{E-32}$$

The kinetic energy is

$$\mathscr{K} = \frac{1}{2}M\dot{x}_c^2 + \frac{1}{2}\mu\dot{x}^2 \tag{E-33}$$

Since the variables are separated in the Lagrangian, we obtain separate equations of motion for x_c and x:

$$M\frac{d\dot{x}_c}{dt} = \frac{\partial\mathscr{L}}{\partial x_c} = 0 \tag{E-34}$$

$$\mu\frac{d\dot{x}}{dt} = \frac{\partial\mathscr{L}}{\partial x} = -\frac{d\mathscr{V}}{dx} \tag{E-35}$$

If there are no external forces, the center of mass of the two particles moves like a particle of mass M that has no forces acting on it, while the relative coordinate changes like the motion of a particle of mass μ moving at a distance x from a fixed origin and subject to the potential energy $\mathscr{V}(x)$. The motion of two particles moving in the x direction has been separated into two one-body problems. The motion in the y and z directions is completely analogous, so that in three dimensions we can assert: *The fictitious particle of mass* μ *moves around the origin of its coordinate in the same way that particle 1 moves relative to particle 2, while the center of mass moves like a free particle of mass* M.

The separation is the same in Hamiltonian mechanics. In three dimensions, the kinetic energy is

$$\mathscr{K} = \frac{1}{2}M(\dot{x}^2{}_c + \dot{y}^2{}_c + \dot{z}^2{}_c) + \frac{1}{2}\mu(\dot{x}^2 + \dot{y}^2 + \dot{z}^2) \tag{E-36}$$

The classical Hamiltonian is expressed in coordinates and momentum components. If the potential energy depends only on the relative coordinates,

$$\mathscr{H} = \frac{1}{2M}(p_{cx}^2 + p_{cy}^2 + p_{cz}^2) + \frac{1}{2\mu}(p_x^2 + p_y^2 + p_z^2) + \mathscr{V}(x, y, z) \tag{E-37}$$

where p_{cx} is the momentum component that is conjugate to x_c, p_x is the momentum component that is conjugate to x, and so on. The Hamiltonian equations of motion are separated so that the center-of-mass motion and the relative motion are separated.

F

Some Mathematics Used in Quantum Mechanics

F.1

The Classical Wave Equations for Electromagnetic Radiation

In 1865, Maxwell developed a mathematical theory of electromagnetism. In this theory, there are four important vector quantities, the *electric field* **E**, the *electric displacement* **D**, the *magnetic field strength* **H**, and the *magnetic induction* **B**. The magnetic induction **B** is generally called the *magnetic field* by chemists. The dependence of these quantities on time and position is described by *Maxwell's equations*, which Maxwell deduced from empirical laws. He found that the electric and magnetic fields can oscillate like waves, constituting electromagnetic radiation. All other waves known at the time of Maxwell were oscillations of some physical object, so it was thought that light consisted of oscillations in a medium called the "luminiferous ether." The assumption that such a medium exists was abandoned after Michelson and Morley demonstrated that the speed of light has the same value for observers moving with different velocities. We now think of electromagnetic waves as oscillations that do not require any supporting medium.

A *plane polarized* electromagnetic wave traveling in the y direction can have an electric field that oscillates in the yz plane and a magnetic field that oscillates in the xy plane. In a medium with zero electrical conductivity (a perfect insulator or a vacuum), the following equations for such a wave follow from Maxwell's equations.[8]

$$\frac{\partial^2 E_z}{\partial y^2} + \frac{1}{c^2}\frac{\partial^2 E_z}{\partial t^2} = 0 \tag{F-1}$$

$$\frac{\partial^2 H_x}{\partial y^2} + \frac{1}{c^2}\frac{\partial^2 H_x}{\partial t^2} = 0 \tag{F-2}$$

where

$$c = \frac{1}{\sqrt{\varepsilon\mu}} \tag{F-3}$$

The *permittivity* of the medium is denoted by ε and the *permeability* of the medium is denoted by μ. The values of these quantities for a vacuum are denoted by ε_0 and μ_0. In SI units

$$\varepsilon_0 = 8.8542 \times 10^{-12}\ \mathrm{C^2\,N^{-1}\,m^{-2}} \tag{F-4}$$

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[8] See J. C. Slater and N. H. Frank, *Electromagnetism*, McGraw-Hill, New York, 1947, p. 90ff, or any other textbook on electricity and magnetism.

and

$$\mu_0 = 4\pi \times 10^{-7}\ \text{newton ampere}^{-2} = 4\pi \times 10^{-7}\ \mathrm{N\,A^{-2}}\ \text{(exact value by definition)}$$
$$= 12.566370614 \times 10^{-7}\ \mathrm{N\,A^{-2}} \qquad \text{(F-5)}$$

The quantity c is the speed of propagation of the wave. The theory of Maxwell correctly predicts the value of the speed of light in a vacuum:

$$c = \frac{1}{\sqrt{(8.8542 \times 10^{-12}\ \mathrm{C^2\,N^{-1}\,m^{-2}})(12.56637\ldots \times 10^{-7}\ \mathrm{N\,A^{-2}})}}$$
$$= 2.9979 \times 10^{8}\ \mathrm{m\,s^{-1}}$$

There is an additional condition from Maxwell's equations that makes Eqs. (F-1) and (F-2) interdependent:

$$\frac{E_z}{H_x} = \pm\sqrt{\frac{\mu}{\varepsilon}} \qquad \text{(F-6)}$$

The electric field cannot oscillate without oscillation of the magnetic field, and vice versa.

A traveling-wave solution to Eqs. (F-1) and (F-2) is

$$E_z(y,t) = E_0 \sin[2\pi(y - ct)/\lambda] \qquad \text{(F-7)}$$

$$H_x(y,t) = H_0 \sin[2\pi(y - ct)/\lambda] \qquad \text{(F-8)}$$

where E_0 and H_0 are constants that obey Eq. (F-6). The wavelength λ can take on any real value.

An electromagnetic wave cannot penetrate a perfect conductor (one with zero resistance) since a finite electric field would produce an infinite current. Electromagnetic waves must have nodes at perfectly conducting walls, and will approximately vanish at a real conducting wall. Reflection between walls in a conducting cavity can produce standing electromagnetic waves.

F.2 The Particle in a Three-Dimensional Box

In Section 15.3 we discussed a model system consisting of a single point-mass particle absolutely confined in a three-dimensional rectangular box. We now go through the mathematics of the Schrödinger equation for this system. We choose the potential energy function:

$$\mathcal{V} = \begin{cases} 0 & \text{if } 0 < x < a \text{ and } 0 < y < b \text{ and } 0 < z < c \\ \mathcal{V}_0 & \text{otherwise (outside the box)} \end{cases} \qquad \text{(F-9)}$$

and then take the limit that $\mathcal{V}_0$ approaches $+\infty$.

We divide our space into two regions: region I, inside the box, and region II, outside the box. For reasons exactly the same as in the one-dimensional case, the coordinate wave function vanishes in region II. The time-independent Schrödinger equation for the interior of the box is

$$\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) = -\frac{2mE}{\hbar^2}\psi \qquad \text{(F-10)}$$

We assume the trial solution:

$$\psi(x, y, z) = X(x)Y(y)Z(z) \tag{F-11}$$

Substitution of the trial function into the Schrödinger Eq. (F-10) and division by XYZ completes the separation of variables:

$$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{1}{Z}\frac{d^2Z}{dz^2} = -\frac{2mE}{\hbar^2} \tag{F-12}$$

Since x, y, and z are independent variables, we can keep two of these variables fixed while allowing the other to vary. Every term must be a constant function:

$$\frac{1}{X}\frac{d^2X}{dx^2} = -\frac{2mE_x}{\hbar^2} \tag{F-13}$$

$$\frac{1}{Y}\frac{d^2Y}{dy^2} = -\frac{2mE_y}{\hbar^2} \tag{F-14}$$

$$\frac{1}{Z}\frac{d^2Z}{dz^2} = -\frac{2mE_z}{\hbar^2} \tag{F-15}$$

where E_x, E_y, and E_z are newly defined constants that obey

$$E = E_x + E_y + E_z \tag{F-16}$$

We multiply Eq. (F-13) by the function X:

$$\frac{d^2X}{dx^2} = -\frac{2mE_x}{\hbar^2}X \tag{F-17}$$

This equation is identical with Eq. (15.3-4) except for the symbols used, and has the same boundary conditions, so that we can transcribe the solution of the one-dimensional problem with appropriate replacement of symbols:

$$X_{n_x}(x) = C_x \sin\left(\frac{n_x \pi x}{a}\right) \tag{F-18}$$

$$E_x = \frac{h^2}{8ma^2}n_x^2 \tag{F-19}$$

where we use the symbol n_x for the quantum number and where C_x is a constant.

The Y and Z equations are identical except for the symbols used, so we can write their solutions:

$$Y_{n_y}(y) = C_y \sin\left(\frac{n_y \pi y}{b}\right) \tag{F-20}$$

$$Z_{n_z}(z) = C_z \sin\left(\frac{n_z \pi z}{c}\right) \tag{F-21}$$

$$E_y = \frac{h^2}{8mb^2}n_y^2 \tag{F-22}$$

$$E_z = \frac{h^2}{8mc^2}n_z^2 \tag{F-23}$$

Here n_y and n_z are positive integers that are not necessarily equal to n_x.

The energy eigenfunction is

$$\psi_{n_x n_y n_z}(x, y, z) = C\sin\left(\frac{n_x \pi x}{a}\right)\sin\left(\frac{n_y \pi y}{b}\right)\sin\left(\frac{n_z \pi z}{c}\right) \tag{F-24}$$

where we let $C = C_x C_y C_z$. The energy eigenvalue is

$$E_{n_x n_y n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \tag{F-25}$$

We attach the three quantum numbers n_x, n_y, and n_z to the symbols ψ and E. A particular energy eigenfunction is specified by giving the values of the three quantum numbers, which we sometimes denote by writing the three quantum numbers in parentheses: (n_x, n_y, n_z).

F.3 The Time-Independent Schrödinger Equation for the Harmonic Oscillator (the Hermite Equation)

The Schrödinger equation for the harmonic oscillator is given in Eq. (15.4-3):

$$\frac{d^2\psi}{dx^2} + (b - a^2x^2)\psi = 0 \tag{F-26}$$

The first step of Hermite's solution to this equation is to find an *asymptotic solution*, which is a solution that applies for very large magnitudes of x. In this case b will be negligible compared with a^2x^2, so that

$$\frac{d^2\psi}{dx^2} - a^2x^2\psi \approx 0 \quad \text{(for large magnitudes of } x\text{)} \tag{F-27}$$

The asymptotic solution is

$$\psi_\infty \approx e^{\pm ax^2/2} \quad \text{(for large magnitudes of } x\text{)} \tag{F-28}$$

We must choose the negative sign in the exponent to keep the solution finite as $|x|$ becomes large.

To represent the solution for all values of x, we choose a trial solution of the form

$$\psi(x) = \psi_\infty(x)S(x) = e^{-ax^2/2}S(x) \tag{F-29}$$

where $S(x)$ is a power series

$$S(x) = c_0 + c_1x + c_2x^2 + c_3x^3 + \ldots = \sum_{n=0}^{\infty} c_n x^n \tag{F-30}$$

with constant coefficients $c_1, c_2, c_3, \ldots$. We might have tried to represent the solution by a power series instead of by a power series multiplied by the asymptotic solution, but this leads to a solution that violates the condition that the wave function remains finite for all values of x.[9]

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[9] Ira N. Levine, *Quantum Chemistry*, 5th ed., Prentice-Hall, Englewood Cliffs, NJ, 1991, p. 64ff.

The second derivative of our trial solution is

$$\frac{d^2\psi}{dx^2} = e^{-ax^2/2}\left(\frac{d^2S}{dx^2} - 2ax\frac{dS}{dx} + (a^2x^2 - a)S\right) \tag{F-31}$$

Substitution of this expression into Eq. (F-26) gives (after cancellation of two terms)

$$e^{-ax^2/2}\left[\frac{d^2S}{dx^2} - 2ax\frac{dS}{dx} + (b - a)S\right] = 0 \tag{F-32}$$

The exponential factor does not vanish for any finite real value of x, so the quantity in square brackets must vanish. From Eq. (F-30), the first two derivatives of S are

$$\frac{dS}{dx} = \sum_{n=1}^{\infty} nc_n x^{n-1} = \sum_{n=0}^{\infty} nc_n x^{n-1} \tag{F-33}$$

$$\frac{d^2S}{dx^2} = \sum_{n=2}^{\infty} n(n-1)c_n x^{n-2} = \sum_{j=0}^{\infty}(j+2)(j+1)c_{j+2}x^j = \sum_{n=0}^{\infty}(n+2)(n+1)c_{n+2}x^n \tag{F-34}$$

where we let $j = n - 2$. The index n or the index j can be called a "dummy index." The symbol used for it is unimportant, since it just stands for successive integral values. We can therefore replace j by n without changing the sum, even though n now has a different meaning than in the original sum. Also, we can add an $n = 0$ term to the expression for dS/dx without any change, since the $n = 0$ term has a factor of zero. We substitute Eq. (F-33) and (F-34) into Eq. (F-32) and cancel a common factor of $e^{-ax^2/2}$. The result is

$$\sum_{n=0}^{\infty}[(n+2)(n+1)c_{n+2} - 2anc_n + (b-a)c_n]x^n = 0 \tag{F-35}$$

The quantity in the square brackets must vanish for each value of n, since every power of x on the right-hand side of the equation has a zero coefficient, and every power of x must have the same coefficient on both sides of the equation. Therefore, we have the recursion relation of Eq. (15.4-6):

$$c_{n+2} = \frac{2an + a - b}{(n+2)(n+1)}c_n \quad (n = 0, 1, 2, \ldots) \tag{F-36}$$

This recursion relation leads to the termination of the series as discussed in Section 15.4 and to the energy eigenfunctions shown in Eqs. (15.4-10)–(15.4-13). The first three energy eigenfunctions correspond to the first three Hermite polynomials:

$$H_0(y) = 1 \tag{F-37}$$

$$H_1(y) = 2y \tag{F-38}$$

$$H_2(y) = 4y^2 - 2 \tag{F-39}$$

where in order to correspond with our wave functions, $y = \sqrt{a}x$. All of the Hermite polynomials can be generated by the formula:

$$H_n(y) = (-1)^n e^{y^2}\frac{d^n}{dy^n}\left(e^{-y^2}\right) \tag{F-40}$$

or the formula[10]

$$H_n(y) = n! \sum_{m=0}^{[n/2]} \frac{(-1)^m (2y)^{n-2m}}{m!(n-2m)!} \tag{F-41}$$

The sum contains only even powers of y if n is even or only odd powers of y if n is odd. The symbol $[n/2]$ stands for $n/2$ if n is even and for $(n-1)/2$ if n is odd.

There are a number of identities obeyed by Hermite polynomials.[11] One useful identity is

$$yH_n(y) = nH_{n-1}(y) + \frac{1}{2}H_{n+1}(y) \tag{F-42}$$

An important fact is that if n is even, then $H_n(y)$ is an even function of y, and if n is odd, then $H_n(y)$ is an odd function of y:

$$H_n(-y) = H_n(y) \quad (n \text{ even}) \tag{F-43}$$

$$H_n(-y) = -H_n(y) \quad (n \text{ odd}) \tag{F-44}$$

F.4 The Hydrogen Atom Energy Eigenfunctions

The energy eigenfunctions are written as products of three factors

$$\psi_{nlm} = R_{nl}(r)Y_{lm}(\theta,\phi) = R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\phi) \tag{F-45}$$

The Φ functions are discussed in Chapter 17. The Θ_{lm} functions obey Eq. (17.2-22). With a change of variables, $y = \cos(\theta)$, $P(y) = \Theta(\theta)$, the equation becomes, after some manipulation

$$(1-y^2)\frac{d^2P}{dy^2} - 2y\frac{dP}{dy} - \frac{m^2}{1-y^2}P + KP = 0 \tag{F-46}$$

Equation (F-46) is the same as the *associated Legendre equation* if $K = l(l+1)$, where l is an integer that must be at least as large as $|m|$. The set of solutions is known as the *associated Legendre functions*, given for non-negative values of m by[12]

$$P_l^m(y) = (1-y^2)^{m/2}\frac{d^m P_l(y)}{dy^m} \tag{F-47}$$

where $P_l(y)$ is the Legendre polynomial

$$P_l(y) = \frac{1}{2^l l!}\frac{d^l}{dy^l}(y^2-1)^l \tag{F-48}$$

With suitable normalization,

$$\Theta = \Theta_{lm} = \left(\frac{(2l+1)(l-m)!}{2(l+m)!}\right)^{1/2} P_l^m(\cos(\theta)) \tag{F-49}$$

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[10] A. Erdelyi *et al.*, eds., *Higher Transcendental Functions*, Vol. II, McGraw-Hill, New York, 1953, p. 192ff.

[11] A. Erdelyi *et al.*, *op. cit.* (note 3).

[12] J. C. Davis, Jr., *Advanced Physical Chemistry*, Ronald Press, New York, 1965, p. 596ff.

This equation is valid only for non-negative values of the integer m, but Eq. (F-47) contains only the square of m, so that we can replace a negative value of m by $|m|$ when using this equation. This equation leads to the Θ functions discussed in Chapter 17.

The radial function R obeys Eq. (17.3-5), the associated Laguerre equation:

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{dr} - \frac{R}{4} + \frac{\beta R}{\rho} - \frac{l(l+1)R}{\rho^2} = 0 \tag{F-50}$$

The solution to this equation can be written in the form

$$R(\rho) = G(\rho)e^{-\rho/2} \tag{F-51}$$

where $G(\rho)$ is a polynomial related to the associated Laguerre functions $L_j^k(\rho)$:

$$G(\rho) = N_{nl}\rho^l L_{n+1}^{2l+1}(\rho) \tag{F-52}$$

where N_{nl} is a normalizing factor, given by

$$N_{nl} = \left[\left(\frac{2Z}{na}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{1/2} \tag{F-53}$$

The associated Laguerre functions are

$$L_u^s(\rho) = \frac{d^s}{d\rho^s}L_u(\rho) \tag{F-54}$$

where L_u is the Laguerre polynomial

$$L_u(\rho) = e^\rho \frac{d^u}{d\rho^u}(\rho^u e^{-\rho}) \tag{F-55}$$

These equations lead to the radial factors discussed in Chapter 17.

G

The Perturbation Method

The perturbation method is applied to a problem in which the Hamiltonian operator can be written in the form

$$\widehat{H} = \widehat{H}^{(0)} + \widehat{H}' \tag{G-1}$$

such that $\widehat{H}^{(0)}$ gives a time-independent Schrödinger equation that can be solved:

$$\widehat{H}^{(0)}\Psi^{(0)} = E^{(0)}\Psi^{(0)} \tag{G-2}$$

The $\widehat{H}'$ term is called the perturbation. We assume that the perturbation term is spin-independent, so that spin functions and integrations over spins can be omitted. We now construct a new Hamiltonian operator by multiplying the perturbation term by a fictitious parameter, λ:

$$\widehat{H}(\lambda) = \widehat{H}^{(0)} + \lambda\widehat{H}' \tag{G-3}$$

The actual Hamiltonian is recovered when $\lambda = 1$.

G.1 The Nondegenerate Case

In the nondegenerate case each energy eigenvalue corresponds to a single eigenfunction. We assume that the energy eigenvalues and energy eigenfunctions of state number n can be represented by a power series in λ, as in Eqs. (19.3-5) and (19.3-6). When these power series are substituted into the time-independent Schrödinger equation we obtain

$$\begin{aligned}(\widehat{H}^{(0)} + \lambda\widehat{H}')(\Psi_n^{(0)} + \Psi_n^{(1)}\lambda + \Psi_n^{(2)}\lambda^2 + \cdots)\\ = (E_n^{(0)} + E_n^{(1)}\lambda + E_n^{(2)}\lambda^2 + \cdots)(\Psi_n^{(0)} + \Psi_n^{(1)}\lambda + \Psi_n^{(2)}\lambda^2 + \cdots)\end{aligned} \tag{G-4}$$

We multiply out the products in Eq. (G-4) and use the fact that if two power series are equal to each other for all values of the independent variables, the corresponding coefficients in the two series are then equal to each other. We equate the terms that are independent of λ on the two sides of the equation, after which we equate the coefficients of the terms proportional to λ, and so on. The terms independent of λ (zero-order terms) produce the same equation as Eq. (G-2):

$$\widehat{H}^{(0)}\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)} \tag{G-5}$$

The coefficients of the linear (first-degree) terms obey the relation:

$$\widehat{H}'\Psi_n^{(0)} + \widehat{H}^{(0)}\Psi_n^{(1)} = E_n^{(1)}\Psi_n^{(0)} + E_n^{(0)}\Psi_n^{(1)} \tag{G-6}$$

We represent the first-order correction to the wave function by a linear combination of the unperturbed (zero-order) wave functions:

$$\Psi_n^{(1)} = \sum_{j=1}^{\infty} a_{nj}\Psi_j^{(0)} \tag{G-7}$$

This representation is substituted into Eq. (G-6), giving

$$\widehat{H}'\Psi_n^{(0)} + \widehat{H}^{(0)}\sum_{j=1}^{\infty} a_{nj}\Psi_j^{(0)} = E_n^{(1)}\Psi_n^{(0)} + E_n^{(0)}\sum_{j=1}^{\infty} a_{nj}\Psi_j^{(0)} \tag{G-8}$$

Since $\Psi_j^{(0)}$ is an eigenfunction of $\widehat{H}^{(0)}$ with eigenvalue $E_j^{(0)}$,

$$\widehat{H}'\Psi_n^{(0)} + \sum_{j=1}^{\infty} a_{nj}E_j^{(0)}\Psi_j^{(0)} = E_n^{(1)}\Psi_n^{(0)} + E_n^{(0)}\sum_{j=1}^{\infty} a_{nj}\Psi_j^{(0)} \tag{G-9}$$

We now multiply each term of Eq. (G-9) by $\Psi_n^{(0)*}$ and integrate over all values of the coordinates on which the wave function depends. Since the zero-order energy eigenfunctions are orthogonal to each other if belonging to different eigenvalues, every integral in the sums vanishes except the one for which $n = j$. We assume that the zero-order wave functions are normalized, so that this integral equals unity. There is only one term surviving in each sum, and we now have

$$\int \Psi_n^{(0)*}\widehat{H}'\Psi_n^{(0)}dq + a_{nn}E_n^{(0)} = E_n^{(1)} + a_{nn}E_n^{(0)} \tag{G-10}$$

where we abbreviate the coordinates of the system by q. The second term on each side cancels so that we obtain the result given in Eq. (19.3-8):

$$E_n^{(1)} = \int \Psi_n^{(0)*}\widehat{H}'\Psi_n^{(0)}dq \tag{G-11}$$

The first-order correction to the wave function and the second-order correction to the energy eigenvalue involve sums over all of the unperturbed wave functions and energy eigenvalues. We do not derive these formulas, but present them here. The formula for the coefficient a_{nj} in Eq. (G-7) is

$$\Psi_n^{(1)} = -\sum_{j=1}^{\infty} \frac{<n|H'|j>}{E_n^{(0)} - E_j^{(0)}}\Psi_j^{(0)} \qquad (j \neq n) \tag{G-12}$$

where we introduce the "bracket" notation for the integral

$$<n|H'|j> = \int \Psi_n^{(0)*}\widehat{H}'\Psi_j^{(0)}dq \tag{G-13}$$

This integral is called a *matrix element* of $\widehat{H}'$, and is also denoted by H'_{nj}. The second-order correction for the energy is given by

$$E_n^{(2)} = \sum_{j=1}^{\infty} \frac{< n|H'|\, j >< j|H'|\, n >}{E_n^{(0)} - E_j^{(0)}} \tag{G-14}$$

These corrections cannot generally be computed exactly since they contain an infinite number of terms, but various approximation schemes have been worked out. The higher-order corrections are even more difficult to work with, but a number of approximate calculations of higher-order corrections to the energy of the helium atom have been published.

G.2 The Degenerate Case

We must modify perturbation theory to apply it to an energy level that is degenerate in zero order. For example, the two configurations $(1s)(2s)$ and $(1s)(2p)$ of the helium atom correspond to several states that have the same energy in zero order. We assume the same kind of Hamiltonian as in Eq. (G-1) and consider a zero-order energy level with a degeneracy equal to g. We have g zero-order wave functions. We call them the "initial" zero-order functions. Unfortunately, there is no guarantee that each of these functions would turn smoothly into one of the exact wave functions if λ is increased from 0 to 1.

The first task is to find the "correct" zero-order wave functions, which means that there is a one-to-one correspondence between each of these functions and one of the exact wave functions. Since there are no other zero-order wave functions corresponding to the energy eigenvalue being considered, it must be possible to express each correct zero-order wave functions as a linear combination of the g initial zero-order wave functions:

$$\Psi_{n,\text{corr}}^{(0)} = \sum_{j=1}^{g} c_{nj} \Psi_{j,\text{init}}^{(0)} \qquad (n = 1, 2, \ldots, g) \tag{G-15}$$

where we denote the nth correct zero-order wave function by $\Psi_{n,\text{corr}}^{(0)}$ and the jth initial zero-order wave function by $\Psi_{j,\text{init}}^{(0)}$.

Since the initial zero-order functions all correspond to the same zero-order energy eigenvalue, the correct zero-order functions correspond to the same zero-order energy eigenvalue. We assume that the exact energy eigenfunctions and energy eigenvalues can be represented by power series in λ as in Eqs. (19.3-5) and (19.3-6). For state number n,

$$\Psi_n = \Psi_{n,\text{corr}}^{(0)} + \Psi_n^{(1)}\lambda + \Psi_n^{(2)}\lambda^2 + \cdots \tag{G-16}$$

$$E_n = E^{(0)} + E_n^{(1)}\lambda + E_n^{(2)}\lambda^2 + \cdots \tag{G-17}$$

where we must include the correct zero-order function as the first term in Eq. (G-16), not the initial function.

We now substitute the expressions of Eqs. (G-16) and (G-17) into the time-independent Schrödinger equation:

$$\widehat{H}(\lambda)\Psi_n(\lambda) = E_n(\lambda)\Psi_n(\lambda) \tag{G-18}$$

$$(\widehat{H}^{(0)} + \lambda\widehat{H}')(\Psi_{n,\text{corr}}^{(0)} + \Psi_n^{(1)}\lambda + \Psi_n^{(2)}\lambda^2 + \cdots)$$
$$= (E^{(0)} + E_n^{(1)}\lambda + E_n^{(2)}\lambda^2 + \cdots)(\Psi_n^{(0)} + \Psi_n^{(1)}\lambda + \Psi_n^{(2)}\lambda^2 + \cdots) \quad \text{(G-19)}$$

The coefficients of any power of λ on the two sides of the equation must be equal. For the terms proportional to λ we have

$$\widehat{H}^{(0)}\Psi_n^{(1)} + \widehat{H}'\Psi_{n,\text{corr}}^{(0)} = E^{(0)}\Psi_n^{(1)} + E_n^{(1)}\Psi_{n,\text{corr}}^{(0)} \quad \text{(G-20)}$$

or

$$(\widehat{H}^{(0)} - E^{(0)})\Psi_n^{(1)} = (E_n^{(1)} - \widehat{H}')\Psi_{n,\text{corr}}^{(0)} \quad \text{(G-21)}$$

We now multiply by the complex conjugate of one of the initial wave functions, $\Psi_{m,\text{init}}^{(0)*}$, and integrate:

$$\int \Psi_{m,\text{init}}^{(0)*}\widehat{H}^{(0)}\Psi_n^{(1)}dq - E^{(0)}\int \Psi_{m,\text{init}}^{(0)*}\Psi_n^{(1)}dq$$
$$= E_n^{(1)}\int \Psi_{m,\text{init}}^{(0)*}\Psi_{n,\text{corr}}^{(0)}dq - \int \Psi_{m,\text{init}}^{(0)*}\widehat{H}'\Psi_{n,\text{corr}}^{(0)}dq \quad \text{(G-22)}$$

We now apply the hermitian property to the first term on the left-hand side of this equation and use the fact that the eigenvalues of a hermitian operator are real:

$$\int \Psi_{m,\text{init}}^{(0)*}\widehat{H}^{(0)}\Psi_n^{(1)}dq = \int (\widehat{H}^{(0)*}\Psi_{m,\text{init}}^{(0)*})\Psi_n^{(1)}dq = E^{(0)}\int \Psi_{m,\text{init}}^{(0)*}\Psi_n^{(1)}dq \quad \text{(G-23)}$$

We omit any subscript on $E^{(0)}$ since all of the zero-order wave functions correspond to the same value of $E^{(0)}$. The two terms on the left side of Eq. (G-22) cancel and we have

$$0 = E_n^{(1)}\int \Psi_{m,\text{init}}^{(0)*}\Psi_{n,\text{corr}}^{(0)}dq - \int \Psi_{m,\text{init}}^{(0)*}\widehat{H}'\Psi_{n,\text{corr}}^{(0)}dq \quad \text{(G-24)}$$

We use the expression in Eq. (G-15):

$$0 = E_n^{(1)}\int \Psi_{m,\text{init}}^{(0)*}\sum_{j=1}^{g} c_{nj}\Psi_{j,\text{init}}^{(0)}dq - \int \Psi_{m,\text{init}}^{(0)*}\widehat{H}'\sum_{j=1}^{g} c_{nj}\Psi_{j,\text{init}}^{(0)}dq \quad \text{(G-25)}$$

We interchange the order of integration and summation to obtain

$$0 = E_n^{(1)}\sum_{j=1}^{g} c_{nj}\int \Psi_{m,\text{init}}^{(0)*}\Psi_{j,\text{init}}^{(0)}dq - \sum_{j=1}^{g} c_{nj}\int \Psi_{m,\text{init}}^{(0)*}\widehat{H}'\Psi_{j,\text{init}}^{(0)}dq \quad \text{(G-26)}$$

Since the initial zero-order functions are assumed to be normalized and orthogonal to each other, the integral in the first sum vanishes if $m \neq j$ and equals unity if $m = j$:

$$\int \Psi_{m,\text{init}}^{(0)*}\Psi_{j,\text{init}}^{(0)}dq = \delta_{mj} = \begin{cases} 1 & \text{if} \quad m = j \\ 0 & \text{if} \quad m \neq j \end{cases} \quad \text{(G-27)}$$

where δ_{mj} is called the Kronecker delta. We now can write

$$0 = E_n^{(1)}\sum_{j=1}^{g} c_{nj}\delta_{mj} - \sum_{j=1}^{g} c_{nj}H'_{mj} \quad \text{(G-28)}$$

where we define the *matrix element* of $\widehat{H}'$

$$H'_{mj} = \int \Psi^{(0)*}_{m,\text{init}} \widehat{H}' \Psi^{(0)}_{j,\text{init}} dq \tag{G-29}$$

We can rewrite Eq. (G-27) as

$$0 = \sum_{j=1}^{g} (H'_{mj} - E^{(1)}_n \delta_{mj}) c_{nj} \qquad (m = 1, 2, \ldots, g) \tag{G-30}$$

Equation (G-29) represents a set of simultaneous equations, one for each value of m. The number of equations is g, and the number of unknown coefficients c_{nj} for which we can solve is g. These are homogeneous linear equations, which can be satisfied by setting each of the c_{nj} coefficients equal to zero. This is called the *trivial solution*. If we divide all of the c_{nj} coefficients by c_{11} it is clear that we really have only $g - 1$ independent coefficients. We have one equation too many and the set of g equations is overdetermined, which means that unless some condition is satisfied, the trivial solution is the only solution.

The condition that must be satisfied is that the determinant of the factors multiplying the c_{nj} coefficients must vanish. We illustrate this condition with the case that $g = 2$. The simultaneous equations are

$$(H'_{11} - E^{(1)}_n) c_{n1} + H'_{12} c_{n2} = 0 \tag{G-31a}$$

$$H'_{21} c_{n1} + (H'_{22} - E^{(1)}_n) c_{n2} = 0 \tag{G-31b}$$

and the condition that must be satisfied is

$$\begin{vmatrix} (H'_{11} - E^{(1)}_n) & H'_{12} \\ H'_{21} & H'_{22} - E^{(1)}_n \end{vmatrix} = 0 \tag{G-32}$$

Equation (G-31) is called a *secular equation*. Since the matrix elements contain the zero-order functions, they can be calculated. When the determinant is multiplied out, we obtain a quadratic equation for $E^{(1)}_n$. This equation can be solved to give two values of $E^{(1)}_n$. Each of these values is substituted into the set of equations in Eq. (G-30), and two different sets of c_{nj} coefficients can be obtained, producing two different correct zero-order wave functions, one corresponding to each value of $E^{(1)}_n$.

For values of g larger than 2, the secular equation is a g by g determinant, yielding an algebraic equation of degree g. The solution of the secular equation provides g values of $E^{(1)}_n$, some of which might be equal to each other. If two or more of the values of $E^{(1)}_n$ are equal to each other, we say that the perturbation has not completely lifted the degeneracy of the level. In any case, there is a different correct zero-order wave function for each of the g values of $E^{(1)}_n$. The coefficients for one of the zero-order wave functions are found by solving the simultaneous equations after substituting one of the values of $E^{(1)}_n$ into the equations. As in the nondegenerate case, formulas for the first-order corrections to the wave functions and second-order corrections to the energies can be found. We do not discuss these corrections.

H

The Hückel Method

The Hückel method is a simple semi-empirical method for determining approximate LCAO molecular orbitals to represent delocalized bonding in planar molecules. It treats only pi electrons and assumes that the framework of sigma bonds has been treated separately. As an example we consider the allyl radical, $CH_2 = CH - CH_2\cdot$. If the plane of the molecule is the xy plane, each carbon atom has an unhybridized $2p_z$ orbital that is not involved in the sigma bonds, which are made from the $2sp^2$ hybrids in the xy plane with the appropriate rotation of the coordinate system at each atom to provide maximum overlap. We construct linear combinations from the three $2p_z$ orbitals, as in Eq. (21.6-2).

$$\varphi_i = c_1^{(i)}\psi_1 + c_2^{(i)}\psi_2 + c_3^{(i)}\psi_3 \qquad (i = 1, 2, 3) \tag{H-1}$$

where i is an index specifying which LCAOMO is meant, and where Ψ_1 is the $2p_z$ orbital on carbon number 1, and so on. From three independent atomic orbitals, three LCAOMOs can be made.

We assume that there is an effective one-electron Hamiltonian operator, $\widehat{H}_{\text{eff}}$, in which all attractions and repulsions are expressed in an approximate way such that each electron moves independently of the other electrons. We apply the variational method, seeking the lowest value of the variational orbital energy,

$$W_i = \frac{\int \varphi_i^* \widehat{H}_{\text{eff}}\, \varphi_i d^3\mathbf{r}}{\int \varphi_i^* \varphi_i d^3\mathbf{r}} \tag{H-2}$$

When the linear combination of Eq. (H-1) is substituted into this expression we have

$$W_i = \frac{\sum_{a=1}^{3}\sum_{b=1}^{3} c_a^{(i)} c_b^{(i)} H_{ab}}{\sum_{a=1}^{3}\sum_{b=1}^{3} c_a^{(i)} c_b^{(i)} S_{ab}} = \frac{N}{D} \tag{H-3}$$

where we abbreviate the numerator of this expression by N and the denominator by D. This expression contains two types of integrals:

$$S_{ab} = \int \psi_a^* \psi_b d^3\mathbf{r} \tag{H-4}$$

$$H_{ab} = \int \psi_a^* \widehat{H}_{\text{eff}} \psi_b d^3\mathbf{r} \tag{H-5}$$

where ψ_a and ψ_b are two of the $2p_z$ atomic orbitals. The integral S_{ab} is an *overlap integral* if $a \neq b$, and is a *normalization integral* if $a = b$. The integral H_{ab} is a matrix element of the effective Hamiltonian. We assume that the c coefficients are real, as are the Ψ functions, so that $H_{ab} = H_{ba}$ and $S_{ab} = S_{ba}$.

We now need to minimize this variational energy with respect to all of the c coefficients. To do this, we differentiate W_i with respect to each of the c coefficients and set each derivative equal to zero. This gives us three simultaneous equations for the three c coefficients. The derivative of W with respect to c_j is (where we temporarily omit the superscript (i) and the limits on the sums):

$$\begin{aligned}\frac{\partial W}{\partial c_j} &= \frac{1}{D}\left(\sum_b c_b H_{jb} + \sum_a c_a H_{aj}\right) - \frac{N}{D^2}\left(\sum_b c_b S_{jb} + \sum_a c_a S_{aj}\right)\\ &= \frac{2}{D}\left(\sum_b c_b H_{jb}\right) - \frac{2N}{D^2}\left(\sum_b c_b S_{jb}\right)\\ &= \frac{2}{D}\left(\sum_b c_b H_{jb}\right) - \frac{2W}{D}\left(\sum_b c_b S_{jb}\right) \qquad \text{(H-6)}\end{aligned}$$

We have used the facts that $H_{ab} = H_{ba}$ and $S_{ab} = S_{ba}$, and have replaced the summation index a by b in one sum (this makes no difference after summation). We set the expression in Eq. (H-5) equal to zero to find the minimum. We multiply by $D/2$ and obtain

$$0 = \sum_{a=1}^{3}(H_{aj} - WS_{aj})c_a \qquad (j = 1, 2, 3) \qquad \text{(H-7)}$$

This is a set of three simultaneous linear homogeneous equations, one for each value of j. The equations are satisfied by the "trivial solution" in which all the c's vanish, but this is not the solution that we seek.

The situation is similar to that in the degenerate perturbation theory. If we divide each equation by c_1, we have only two unknown variables, c_2/c_1 and c_3/c_1. If W is arbitrary, the system of equations is therefore overdetermined, with three equations for two variables. In order for a nontrivial solution to exist, a condition must be satisfied that makes the equations equivalent to two independent equations. This condition is that the determinant of the matrix of the coefficients must vanish.[13] Determinants are discussed in Appendix B. We write the condition

$$\det(H_{ab} - WS_{ab}) = 0 \qquad \text{(H-8)}$$

Equation (H-8) is called a *secular equation*. It is similar to but not identical to the secular equation in degenerate perturbation theory. For each value of W that satisfies this equation there is a usable set of simultaneous equations, so that for each value of W there is a delocalized molecular orbital.

We assume that the $2p_z$ orbitals are normalized, so that the normalization integrals (S_{aa}) equal unity. We now introduce some additional assumptions and approximations that define the Hückel method: (1) we approximate the overlap integrals (S_{ab} with $a \neq b$) by zero; (2) we assume that H_{aa} has the same value, called α, for every atom;

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[13] I. N. Levine, *op. cit.*, pp. 220ff, 629ff (note 6).

(3) we assume that for $a \neq b$ H_{ab} has one value, called β, when a and b represent atoms that are bonded to each other and that H_{ab} vanishes when orbitals a and b represent atoms that are not bonded to each other. The secular equation for the allyl radical now becomes

$$\begin{vmatrix} \alpha - W & \beta & 0 \\ \beta & \alpha - W & \beta \\ 0 & \beta & \alpha - W \end{vmatrix} = 0 \tag{H-9}$$

We divide each element of the determinant by β and let

$$x = \frac{\alpha - W}{\beta} \tag{H-10}$$

The secular equation becomes

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \tag{H-11}$$

This determinant is expanded by minors using the top row:

$$x \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} - 1 \begin{vmatrix} 1 & 1 \\ 0 & x \end{vmatrix} + 0 = 0 \tag{H-12a}$$

$$x(x^2 - 1) - 1(x - 0) = x^3 - x - x + 0 = x(x^2 - 2) = 0 \tag{H-12b}$$

There are three roots, which we call x_1, x_2, and x_3:

$$x_1 = -\sqrt{2}, \quad x_2 = 0, \quad x_3 = \sqrt{2} \tag{H-13}$$

corresponding to

$$W_1 = \alpha + \sqrt{2}\beta \tag{H-14a}$$

$$W_2 = \alpha \tag{H-14b}$$

$$W_3 = \alpha - \sqrt{2}\beta \tag{H-14c}$$

Since β turns out to be negative, W_1 is the lowest energy. For each of these roots, there is a set of three equations for the three c coefficients. Expressing these simultaneous equations in terms of x, we obtain

$$xc_1 + c_2 = 0 \tag{H-15a}$$

$$c_1 + xc_2 + c_3 = 0 \tag{H-15b}$$

$$c_2 + xc_3 = 0 \tag{H-15c}$$

This represents one set of equations for each value of x, so that we obtain one molecular orbital for each value of x. The resulting orbitals are

$$\varphi_1 = c_1^{(1)}(\psi_1 + \sqrt{2}\psi_2 + \psi_3) \tag{H-16a}$$

$$\varphi_2 = c_1^{(2)}(\psi_1 - \psi_3) \tag{H-16b}$$

$$\varphi_3 = c_1^{(3)}(\psi_1 - \sqrt{2}\psi_2 + \psi_3) \tag{H-16c}$$

The c coefficients in these orbitals can be determined so that the orbitals are normalized. We omit this step. These orbitals follow the pattern that we have come to expect: The lowest-energy orbital has no nodes between the carbon atoms, the next lowest has a single node that passes through the center carbon atom, and the highest-energy orbital has two nodes that pass between carbon atoms. Since there are three pi electrons, the lowest-energy orbital is occupied by two electrons and the next orbital is occupied by one electron.

The results of the Hückel method for benzene are summarized in Chapter 21. The delocalized pi orbitals in benzene are linear combinations of six unhybridized $2p_z$ orbitals:

$$\varphi_i = c_1^{(i)}\psi_1 + c_2^{(i)}\psi_2 + c_3^{(i)}\psi_3 + c_4^{(i)}\psi_4 + c_5^{(i)}\psi_5 + c_6^{(i)}\psi_6 \tag{H-17}$$

The treatment is exactly analogous to that of the allyl radical except that we must deal with six simultaneous equations and a 6 by 6 secular equation:

$$\begin{vmatrix} \alpha - W & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - W & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - W & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - W & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - W & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - W \end{vmatrix} = 0 \tag{H-18}$$

Note that there is a β in the upper right and lower left corners, corresponding to the carbons being bonded in a ring. With the same replacement as before, the secular equation is

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0 \tag{H-19}$$

We do not go through the solution of this secular equation, but it gives the six values of W and the six delocalized orbitals of Figure 21.9.

I

Matrix Representations of Groups

Matrix multiplication is completely analogous to operator multiplication: It is distributive but not necessarily commutative, and the product of two matrices is another matrix. Because of this similarity it is possible to find a set of matrices that has the same multiplication table as any group of symmetry operators. Such a set of matrices is called a *representation* of the group. Since the members of a group must be capable of being multiplied together in either order, the matrices in a representation must be square matrices and must have the same *dimension* (same number of rows and columns). A group must contain the identity and the inverse of every member of the group, so a representation of a group must include the identity matrix and the inverse of every matrix in the representation. A given group can have a number of different representations with various numbers of rows and columns in the matrices.

I.1 Representations of the C_{2v} Group

The C_{2v} group is the group to which the water molecule belongs. The operators in the group are $\widehat{E}$, $\widehat{C}_2$, $\widehat{\sigma}_{yz}$, and $\widehat{\sigma}_{xz}$, as labeled in Figure 21.11. The effect of the $\widehat{C}_2$ operation is to move a point from (x, y, z) to a point (x', y', z') such that:

$$\widehat{C}_2(x, y, z) = (x', y', z') = (-x, -y, z) \tag{I-1}$$

This equation can be written as three equations for x′, y′, and z′:

$$x' = -x + 0y + 0z \tag{I-2a}$$

$$y' = 0x - y + 0z \tag{I-2b}$$

$$z' = 0x + 0y + z \tag{I-2c}$$

These equations can be written in matrix form

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} x' \\ y' \\ z' \end{bmatrix} = \begin{bmatrix} -x \\ -y \\ z \end{bmatrix} \tag{I-3}$$

where the matrix multiplication is carried out as described in Appendix B and where the vectors (x, y, z) and (x', y', z') are considered to be 3 by 1 matrices, or *column vectors*.

The 3 by 3 matrix in Eq. (I-3) is a representative of $\widehat{C}_2$, denoted by $R(\widehat{C}_2)$. The representative matrices of the other three operations in the group are

$$R(\widehat{E}) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{I-4}$$

$$R(\widehat{\sigma}_{yz}) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{I-5}$$

$$R(\widehat{\sigma}_{xz}) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{I-6}$$

Each of these matrices, when applied to the Cartesian coordinates of an arbitrary point as in Eq. (I-3), gives the same result as operating on the point with the corresponding symmetry operator. They also have the same multiplication table as the symmetry operators and are a representation of the group C_{2v}.

Reducible and Irreducible Representations

The representation of the C_{2v} group that we just obtained is not the only representation of the C_{2v} group. This representation is called a *reducible representation*. This means that it can be divided somehow into representations consisting of matrices with fewer rows and columns (smaller dimension). This particular representation contains only diagonal matrices. Such matrices have elements that act on only one coordinate at a time. Because of this, we can make a set of 1 by 1 matrices by taking the upper left element of each of the 3 by 3 matrices, and these matrices will have the same multiplication table as the 3 by 3 matrices. The same thing is true of the set of center elements and the set of lower right elements. We say that the representation can be divided into three *irreducible representations*, which cannot be further subdivided. A representation consisting of 1 by 1 matrices is called a one-dimensional representation, a representation consisting of 2 by 2 matrices is called a two-dimensional representation, and so on. A one-dimensional representation is necessarily irreducible. A representation of higher dimension might or might not be irreducible.

The representation obtained by taking the upper left elements is

$$R(\widehat{E}) = [1] \tag{I-7}$$

$$R(\widehat{C}_2) = [-1] \tag{I-8}$$

$$R(\widehat{\sigma}_{yz}) = [-1] \tag{I-9}$$

$$R(\widehat{\sigma}_{xz}) = [1] \tag{I-10}$$

This set of 1 by 1 matrices consists of the only nonzero elements of the matrices that act on the x coordinate. For example, the $\widehat{C}_2$ operator turns x into $-x$, and $R(\widehat{C}_2)$ is the constant that multiplies x to turn it into $-x$. The other 1 by 1 matrices are similar.

We can show that these matrices obey the same multiplication table as the symmetry operations. For example,

$$R(\widehat{\sigma}_{yz})R(\widehat{C}_2) = [-1][-1] = [1] = R(\widehat{\sigma}_{xz}) \tag{I-11}$$

The other two one-dimensional representations also have the same multiplication table.

If a matrix has all zero elements except for those in square areas along the principal diagonal the matrix is said to be a *block-diagonal matrix*. An example of a block-diagonal 5 by 5 matrix is

$$\mathbf{F} = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & 2 & 3 & 0 & 0 \\ 0 & 4 & 3 & 0 & 0 \\ 0 & 0 & 0 & 5 & 6 \\ 0 & 0 & 0 & 7 & 8 \end{bmatrix} \tag{I-12}$$

This matrix contains a 1 by 1 block and two 2 by 2 blocks. If two matrices of the same size that are block-diagonal with blocks of the same sizes in the same positions are multiplied together, the product matrix is block-diagonal with blocks of the same sizes in the same positions.

If a representation of some group consists of a set of matrices that are all block-diagonal with blocks of the same sizes in the same positions, it is a reducible representation. A new set of matrices obtained by taking the corresponding block out of each matrix is also a representation of the group. Even if a representation consists of matrices that are not block-diagonal, it is a reducible representation if a similarity transformation produces matrices that are all block-diagonal in the same way. A *similarity transformation* on the matrix **B** means the carrying out of two matrix multiplications with some matrix and its inverse as follows to yield a new matrix **C**:

$$\mathbf{C} = \mathbf{A}^{-1}\mathbf{B}\mathbf{A} \tag{I-13}$$

The matrix **A** can be any square matrix of the same size as **B**. If the same similarity transformation is carried out on every matrix in a representation, the new set of matrices is also a representation. If the same similarity transformation when carried out on every matrix in a representation produces a set of matrices that are all block-diagonal with the same size blocks in the same order, then the original representation is reducible, and each set of corresponding blocks in the new set of matrices forms a new representation. If no such transformation can be found, then the original representation is irreducible.

I.2 Classes in a Group

A group can often be divided into classes. If **A** and **B** are both members of the same group the matrix **C** that results from the similarity transformation of Eq. (I-13) must be a member of the group. If the members **A** and $\mathbf{A}^{-1}$ are replaced in turn by every other member of the group and its inverse, keeping **B** fixed, it is found in many cases that only part of the members of the group will occur in the place of **C**. These members constitute a *class* within the group and if any one of them is put in place of **B** in Eq. (I-13) only members of the class will result in the place of **C**. Every operator of the C_{2v} group is in a class by itself.

Each member of an *abelian group* (a group in which all members commute with each other) is also in a class by itself. Since the operators commute with each other,

$$\mathbf{A}^{-1}\mathbf{B}\mathbf{A} = \mathbf{A}^{-1}\mathbf{A}\mathbf{B} = \mathbf{E}\mathbf{B} = \mathbf{B} \quad (\text{if } \mathbf{A},\ \mathbf{A}^{-1}, \text{ and } \mathbf{B} \text{ commute}) \tag{I-14}$$

The identity element is always in a class by itself, since the identity matrix commutes with every other matrix. If a group includes the inversion operator, this operator is also in a class by itself.

I.3 Character Tables

For some purposes it is not necessary to use the entire matrices in a representation to get useful information. The *trace* of a square matrix is defined to be the sum of the diagonal elements of the matrix. The set of traces of the matrices in a given representation are called the *characters* of the representation and the list of them is called a *character table*. We denote the three-dimensional representation of Eqs. (I-3)–(I-6) by the symbol Γ. Its character table is

C_{2v}	E	C_2	σ_{yz}	σ_{xz}
Γ	3	1	1	1

Each character is listed below the symbol for the symmetry operation. The character table for each of the three one-dimensional representations of the C_{2v} group is just the list of the elements of the one-by-one matrices, since there is only one term in each trace sum. These character tables are as follows:

C_{2v}	E	C_2	σ_{yz}	σ_{xz}	Function
A_1	1	1	1	1	z
B_1	1	-1	-1	1	x
B_2	1	-1	1	-1	y

The A and B symbols attached to these representations are obtained as follows:[14] One-dimensional representations are designated by A if they are symmetric to rotation by $2\pi/n$ radians about the principal n-fold rotation axis ($n = 2$ for a 180° rotation in this case) and are designated by B if they are antisymmetric to this rotation. The subscripts 1 and 2 designate whether (in this case) they are symmetric or antisymmetric to reflection in a vertical plane. A two-dimensional representation is designated by E (not to be confused with the identity operation), and a three-dimensional representation is designated by T. Subscripts g and u are sometimes added to specify the symmetry with respect to inversion (g = *gerade* = even; u = *ungerade* = odd). A representation with all characters equal to 1, like the A_1 representation in this case, is called the *totally symmetric representation*.

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[14] A. W. Adamson, *A Textbook of Physical Chemistry*, 3rd ed., Academic Press, Orlando, FL, 1986, p. 747ff.

I.4 Bases for Representations

The last entry in each row of the character table for the three one-dimensional representations specifies the coordinate that was acted on by the 1 by 1 matrix when we generated the representation. To generate each one of these representations we could have examined the effect of each of the symmetry operations on one of the Cartesian coordinates x, y, and z. The C_2 operation changes x to $-x$, and multiplication by -1 accomplishes the same thing, so that the 1 by 1 matrix representing the C_2 operation has -1 as its only element.

We say that we used z as the *basis* of the A_1 representation, x as the basis of the B_1 representation, and y as the basis of the B_2 representation. We could have examined the effect of the symmetry operators on any other functions of x, y, and z, including atomic orbitals or molecular orbitals, and could use these functions as the basis of a representation. Since the coordinate z is unchanged by any of the symmetry operations in the C_{2v} group, we would get the same representations of this group by using the functions z^2, xz, and yz as the bases as we do by using x, y, and z.

A theorem that we quote later implies that there must be four irreducible representations of the C_{2v} group. The fourth representation can be obtained by using xy as a basis function. This function gives the characters

	E	C_2	σ_{yz}	σ_{xz}	function
A_2	1	1	-1	-1	xy

and this is included in a complete character table for the C_{2v} group.[15]

The hydrogen-like atomic orbitals have definite symmetry properties, and are eigenfunctions of specific symmetry operators. When we use one of the real $2p$ orbitals on the oxygen atom as a basis for a one-dimensional representation of the C_{2v} group, we can obtain the characters by determining what the eigenvalue is when each symmetry operator in the group is applied to the function, since the eigenvalue is the single element of the 1 by 1 matrix. The result is the same character table as obtained with x, y, and z as the bases:

	E	C_2	σ_{yz}	σ_{xz}	Function
A_1	1	1	1	1	ψ_{2pz}
B_1	1	-1	-1	1	ψ_{2px}
B_2	1	-1	1	-1	ψ_{2py}

Character tables can be obtained for any group. Table A.26 of Appendix A lists character tables for a few common point groups. The following notation is used: If there are C_2 axes perpendicular to the principal rotation axis (this occurs in the D groups), a C_2 operation is labeled as a $C_2{}'$ axis if it passes through outer atoms of the molecule, and as a $C_2{}''$ axis if it passes between outer atoms. A vertical mirror plane is labeled as a σ_v plane if it passes through outer atoms and as a σ_d axis if it passes between outer atoms. The right column gives functions of x, y, and z that could be used as bases for the representations, as well as some rotations that match the representation. R_z stands for rotation about the z axis, etc.

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[15] A. W. Adamson, *op. cit.*, p. 748ff (note 1).

There are several theorems and facts that give useful information about the irreducible representations of groups. They can be used to understand and apply character tables.[16] We state a few of them without proof:

1. The totally symmetric representation (the one-dimensional representation with all characters equal to 1) occurs with all groups.
2. If there is more than one operation in a class, all of the operations in a class will have identical characters in any representation, and can be lumped together in the same column of a character table, as is done in Table A.26 of Appendix A.
3. The number of irreducible representations equals the number of classes. Therefore, in a complete character table containing the characters of all irreducible representations, the number of rows will equal the number of columns.
4. The sum of the square of the dimensions of the irreducible representations is equal to the order of the group (the number of operators in the group). If the dimension of irreducible representation number i is called l_i and if the order of the group is h, then

   $$\sum_i l_i^2 = h \tag{I-15}$$

   where the sum is over all irreducible representations of the group. If we denote the character of a given operation, O, in the representation number i by $\chi_i(O)$, then Eq. (I-15) can be written

   $$\sum_i [\chi_i(E)]^2 = h \tag{I-16}$$

   since the character of the identity operator equals the dimension of the representation.
5. The sum of the squares of the characters in any irreducible representation is equal to the order of the group.

   $$\sum_O [\chi(O)]^2 = h \tag{I-17}$$

   where the sum is over the members (operations) of the group.
6. Two irreducible representations of a group are orthogonal to each other. This means that if you take the product of the characters of a given operation in the two representations and then sum all such products, they will add to zero. If i and j denote two irreducible representations of a group,

   $$\sum_O \chi_i(O)\chi_j(O) = 0 \tag{I-18}$$

   where the sum is over all members of the group.
8. The number of times that an irreducible representation occurs in a reducible representation is given by

   $$\text{Number} = \frac{1}{h}\sum_O \chi_i(O)\chi_j(O) \tag{I-19}$$

   where h is the order of the group and where i stands for an irreducible representation and j stands for a reducible representation, and where the sum is over all members of the group.

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[16] G. L. Meissler and D. A. Tarr, *Inorganic Chemistry*, Prentice Hall, Englewood Cliffs, NJ, 1991, p. 104.

If the $3d_{xz}$, $3d_{yz}$, $3d_{xy}$, $3d_{x^2-y^2}$, and $3d_{z^2}$ orbitals are used as a basis for the C_{2v} group (in that order), we get the representation (with $R(\widehat{E})$ not displayed, since it is just the identity matrix):

$$R(\widehat{C}_2) = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{I-20}$$

$$R(\widehat{\sigma}_{xz}) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{I-21}$$

$$R(\widehat{\sigma}_{yz}) = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{I-22}$$

I.5 Applications of Group Theory to Molecular Orbitals

We can determine something about the molecular orbitals in a polyatomic molecule by the use of group theory. In Chapter 21 we first described the bonding in the water molecule in terms of hybrid orbitals on the oxygen atom in order to have only LCAOMOs containing two basis functions. In Hartree–Fock–Roothaan calculations, the LCAOMOs are linear combinations of the entire set of basis functions. In Section 21.8 we defined basis orbitals for the water molecule that were eigenfunctions of the symmetry operators belonging to the molecule. These basis functions have symmetry properties like those of the irreducible representations and produce a secular determinant that is in block-diagonal form, simplifying the calculation. If a basis orbital has the same symmetry properties as a representation labeled A_1, it is labeled with the subscript a_1, and so on. This label is called its *symmetry species* and identifies the irreducible representation to which it corresponds. The two basis orbitals of Eqs. (21.8-1) and (21.8-2) were

$$\psi_{a_1} = \psi_{1s\text{Ha}} + \psi_{1s\text{Hb}} \tag{I-23}$$

$$\psi_{b_2} = \psi_{1s\text{Ha}} - \psi_{1s\text{Hb}} \tag{I-24}$$

These linear combinations are called *symmetry-adapted basis functions*. Pitzer and Merrifield carried out a Hartree–Fock–Roothaan calculation on H_2O using a minimal basis set of Slater-type orbitals and obtained the orbitals displayed in Table 21.2. The a_1 orbitals are numbered from lower to higher energy, as are the b_1 and b_2 orbitals.

Only basis orbitals of the same symmetry species enter in any one molecular orbital. The a_1 basis function can combine with the $1s$, $2s$, and $2pz$ functions on the oxygen.

The b_2 basis function can combine with the $2py$ function on the oxygen, and the $2px$ function on the oxygen cannot combine with any of the other basis functions. Knowing the symmetry species of the basis orbitals and including only those that have the same symmetry species shortens the calculation, as did exclusion of the $2px$ and $2py$ orbitals from the sigma molecular orbitals that we formed for the lithium hydride molecule in Section 20.4.

A useful application of group theory is the prediction of whether an overlap integral will vanish. In various places in earlier chapters, we have occasionally asserted that an integral vanishes without actually calculating it by noting that the positive and negative contributions cancel because of the symmetry of the integrand function. Group theory provides a systematic means of doing this.[17] Consider an overlap integral of the type $\int \psi_1^* \psi_2 dq$ where ψ_1 and ψ_2 are two orbitals and where q stands for the coordinates of the electron. If the integrand changes sign under some symmetry operation belonging to the molecule, this means that positive and negative contributions will cancel. This generally means that the product of the two functions must have the symmetry species A_1 in order not to vanish automatically. We determine whether this is the case by forming the *direct product*, which is a representation obtained as follows: Write the characters for the irreducible representation for orbital ψ_1 and that for orbital ψ_2, one above the other with the symmetry operations in the same order. Multiply the two characters for each operator together, to obtain a representation of the group that can be reducible or irreducible. If the irreducible representation A_1 (the totally symmetric representation) is obtained, the integral will not vanish. If a reducible representation is obtained that contains the totally symmetric representation, the integral will not vanish. The number of times that a given irreducible representation is contained in a reducible representation is given by Eq. (I-19).

As an example, we show that the water molecule symmetry-adapted orbital $\psi_{b_2} = \psi_{1s\mathrm{Ha}} - \psi_{1s\mathrm{Hb}}$ has a vanishing overlap with the oxygen $2s$ orbital. The symmetry species of the oxygen $2s$ orbital is a_1, and that of the symmetry-adapted orbital is b_2. From the character table in Table A.26 of Appendix A,

C_{2v}	E	C_2	σ_{yz}	σ_{xz}
A_1	1	1	1	1
B_2	1	−1	1	−1
Direct product	1	−1	1	−1

The character of the direct product is that of B_2, so the integral vanishes. If we had not recognized the direct product as an irreducible representation, we could have used Eq. (I-19) to determine whether the irreducible representation A_1 is contained in the direct product:

$$n_{\mathrm{A}_1} = \frac{1}{4}(1 - 1 + 1 - 1) = 0$$

so that it is not contained in it and we know that the overlap integral must vanish.

An orbital with a given symmetry species belongs to a level with the degeneracy equal to the dimension of the irreducible representation. Using a character table, we can quickly determine the dimension of a reducible representation by looking at the trace of the matrix representing the identity E, which is equal to the dimension of the

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[17] A. W. Adamson, *op. cit.*, pp. 762ff (note 1).

representation (it is the sum of unity for each diagonal element of the matrix). For example, from the character table, we see that there is no irreducible representation with dimension greater than 1 for the C_{2v} group. There are no degenerate orbitals for the water molecule.

PROBLEMS

Appendix I

1 Show by matrix multiplication that each of the matrices is the inverse of the other:

$$\mathbf{A} = \begin{bmatrix} 2 & 1 & 0 \\ 1 & 2 & 1 \\ 0 & 1 & 2 \end{bmatrix} \quad \text{and} \quad \mathbf{A}^{-1} = \begin{bmatrix} 3/4 & -1/2 & 1/4 \\ -1/2 & 1 & -1/2 \\ 1/4 & -1/2 & 3/4 \end{bmatrix}$$

2 **a.** Verify that each of the matrices in Eqs. (I-4), (I-5), and (I-6) give the same results as the symmetry operators.

b. Using matrix multiplication, show that

$$R(\widehat{\sigma}_{yz})R(\widehat{C}_2) = R(\widehat{\sigma}_{xz})$$

3 **a.** Verify the entire multiplication table for the one-dimensional representation of Eqs. (I-7) to (I-10).

b. Generate the other two one-dimensional representations and show that they obey the same multiplication table.

4 Create another 5 × 5 matrix with blocks of the same sizes in the same positions as that of Eq. (I-12) and show by explicit matrix multiplication that the product of the two matrices has blocks of the same sizes in the same positions.

5 **a.** Show that each operator in the group C_{2v} is in a class by itself.

b. Show that the identity operation is always in a class by itself, no matter what group is being discussed.

6 Show that the character table for the C_{3v} group in Table A.26 of Appendix A conforms to the properties in the list of theorems.

7 **a.** Verify the representation of Eqs. (I-20) to (I-22) using the formulas for the real $3d$ orbitals from Table 17.3.

b. Obtain five one-dimensional representations from the matrices of Eqs. (I-20) to (I-22) plus the identity matrix.

c. Make a character table for these one-dimensional representations. Determine the number of times each irreducible representation occurs in this five-dimensional representation, using Eq. (I-19). Verify this result by inspection.

8 **a.** Show that the overlap integral of the oxygen $2s$ orbital and symmetry-adapted orbital in Eq. (21.8-1) does not vanish.

b. Show that the overlap integral of the two symmetry-adapted orbitals in Eqs. (21.8-1) and (21.8-2) vanishes.

9 **a.** Find the maximum degeneracy for orbitals of the ammonia (NH_3) molecule.

b. Find the maximum degeneracy for orbitals of the methane (CH_4) molecule.

10 Find the matrix product

$$\begin{bmatrix} 1 & 2 & 3 \\ 0 & 1 & 2 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} 4 & 5 & 6 \\ 4 & 5 & 0 \\ 4 & 0 & 0 \end{bmatrix}$$

11 Construct the multiplication table for the matrices in Eqs. (I-4)–(I-6) and show that it is identical to the multiplication table for the point group C_{2v}.

12 Carry out the similarity transformation as in Eq. (I-13), letting the matrix in Eq. (I-4) play the role of B and letting the matrix in Eq. (I-5) play the role of A. Identify the resulting matrix as a representative of one of the operations of the group C_{2v}.

13 Benzene belongs to the point group D_{6h}. Identify the eigenvalues of the following symmetry operations for each of the orbitals whose regions are depicted in Figure 21.9. If the orbital is not an eigenfunction, state that fact.

a. $\widehat{C}_6$ (axis perpendicular to the plane of the molecule)

b. $\widehat{C}_6^2$ (axis perpendicular to the plane of the molecule)

c. $\widehat{C}_6^3$ (axis perpendicular to the plane of the molecule)

d. $\widehat{\sigma}_h$ (reflection plane in the plane of the molecule)

14 Determine whether the oxygen $2s$ orbital and a hydrogen $1s$ orbital in the H_2O molecule in its equilibrium conformation will have zero overlap.

J

Symbols Used in This Book

Efforts have been made to avoid using the same letter for two or more different variables in the same section, but the use of the same letter for several quantities in different parts of the book is unavoidable. In addition to the quantities in this list, various letters are used for constants that occur in individual equations.

Symbol	Quantity
a	Constant parameter in various equations of state
a	Distance of closest ionic approach in Debye–Hückel theory
a_i	Activity of substance i
$\mathscr{A}$	Area
A	Helmholtz energy
A_n	nth pressure virial coefficient
A	Preexponential factor in Arrhenius expression for a rate constant
b	Constant parameter in various equations of state
b	Parameter in the extended Debye–Hückel theory
$\mathbf{B}$	Magnetic field (magnetic induction)
B_n	nth virial coefficient
c	Speed of light
c	Number of components
c_i	Concentration of substance i, also denoted by $[\mathscr{F}_i]$
c°	$1\ \mathrm{mol\,L^{-1}}$ (exactly)
C_{V}	Heat capacity at constant volume
$C_{\mathrm{V,m}}$	Molar heat capacity at constant volume
C_{P}	Heat capacity at constant pressure
$C_{\mathrm{P,m}}$	Molar heat capacity at constant pressure
d	Collision diameter
d	Reaction diameter
D_i	Diffusion coefficient of substance i
e	The base of natural logarithms, 2.71828182846 . . .
$\mathscr{e}$	Charge on a proton
E	General symbol for an energy
E_{c}	Center-of-mass energy
E_{r}	Relative energy
E	Cell voltage
E°	Cell voltage in the standard state
$\mathscr{E}$	Electric field
E_{AB}	Average bond energy of a bond between elements A and B

(continued)

Symbol	Quantity
E_a	Activation energy in the Arrhenius expression for a rate constant
F	Faraday constant
f	Number of independent intensive variables, or variance, given by the Gibbs phase rule
f	Usual symbol for a probability density, especially for molecular velocity components
$f_v(v)$	Probability density for molecular speeds
f	Friction coefficient
f	Electrostatic factor for diffusion-controlled reaction
f	Fraction of collisions leading to reaction
f	Tension force of a sample of rubber
$\mathbf{F}$	Force
$\mathscr{F}_i$	Abbreviation for the chemical formula of substance *i*
g	Probability density for molecular velocity in three dimensions
g	Acceleration due to gravity
G	Gibbs energy
$\Delta_f G^\circ(i)$	Gibbs energy change of formation of substance *i*
$G^{(\sigma)}$	Surface Gibbs energy
ΔG_mix	Gibbs energy change of mixing
G^E	Excess Gibbs energy
$\mathbf{H}$	Magnetic field strength
H	Enthalpy
$\Delta_f H^\circ(i)$	Enthalpy change of formation of substance *i*
$\Delta H_{\mathrm{int},i}$	Integral heat of solution of substance *i*
$\Delta H_{\mathrm{diff},i}$	Differential heat of solution of substance *i*
$\mathscr{H}$	Magnetic field
i	Degree of inhibition
$\mathbf{i}$	Unit vector in *x* direction
I	Ionic strength
I	Electric current
$\mathbf{j}$	Unit vector in *y* direction
$\mathbf{j}$	Electric current density
J	Rate of absorption of photons
J_i	Diffusion flux of substance *i*
J	Analogue to Gibbs energy
k_i	Henry's law constant for substance *i*
k	Force constant
k	Usual symbol for a rate constant
$\mathbf{k}$	Unit vector in the *z* direction
k_B	Boltzmann's constant
$k_\pm^{(m)}$	Proportionality constant for the vapor pressure of a volatile electrolyte
$\mathscr{K}$	Kinetic energy
K_d	Nernst distribution law constant
K_b	Boiling point elevation constant
K_f	Freezing point depression constant
K	Equilibrium constant
K_a	Acid ionization constant
K_m	Michaelis–Menten constant

Symbol	Quantity
L	Usual symbol for a length
L	Abbreviation for the liter (1 dm^3)
m	General symbol for a mass (w is also used)
m_i	Molality of substance i
$m_\pm$	Mean ionic molality
m°	1 mol kg^{-1} (exactly)
M	Molecular mass of a polymer
$\langle M \rangle_n$	Number-average molecular mass of a polymer
$\langle M \rangle_w$	Mass-average molecular mass of a polymer
$\langle M \rangle_v$	Viscosity-average molecular mass of a polymer
M_i	Molar mass of substance i
M	Symbol sometimes used for a sum of masses
n_i	The amount of substance i (measured in moles)
$n_i^{(\sigma)}$	Surface amount of substance i
N_{Av}	Avogadro’s constant
N_i	Number of molecules of substance i
$\mathcal{N}_i$	Number density of substance i
$\mathbf{p}$	Momentum vector
p	General symbol for a probability
p_i	Probability of state i
p	Number of phases
p	Fraction of functional groups reacted
$p\mathrm{H}$	$-\log_{10}[a(\mathrm{H}^+)]$
pK_{a}	$-\log_{10}(K_{\mathrm{a}})$
P	Pressure
P_i	Partial pressure of substance i
P_{c}	Critical pressure
P_{r}	Reduced pressure
P_{ext}	Externally imposed pressure
$P(\mathrm{transmitted})$	Pressure actually transmitted to or by the surroundings
P_1^*	Vapor pressure of pure substance i
P°	Standard pressure, equal to 1 bar
q	An amount of heat
$\mathbf{q}$	Heat flux
Q	Electric charge
Q	Activity quotient of a chemical reaction
r	Usual symbol for a radius or a scalar distance
$\mathbf{r}$	Position vector
r	Rate of a chemical reaction
r	Resistivity
R	Ideal gas constant
R	Electrical resistance
$\mathcal{R}$	Reynolds number
s	Number of substances
S	Entropy
$S_{m,i}^\circ$	Absolute molar entropy of substance i
S	Sedimentation coefficient
t	Time

(*continued*)

Symbol	Quantity
$t_{1/2}$	Half-life of a chemical reaction
t_C	Celsius temperature
T	Absolute temperature
T_c	Critical temperature
T_r	Reduced temperature
$u(x, y, z)$	Potential energy of one molecule
$u(r)$	Potential energy function for a pair of molecules as a function of internuclear distance
$\mathbf{u}$	Flow velocity
U	Thermodynamic energy (internal energy)
$\mathbf{v}$	Velocity vector
v	Speed (magnitude of a velocity)
v_rel	Relative speed
$\langle v\rangle$	Mean speed
v_p	Most probable speed
v_rms	Root-mean-square speed
V	Volume
V_m	Molar volume
V_mc	Critical molar volume
V_r	Reduced volume
V	Voltage
$\mathscr{V}$	Potential energy
w	An amount of work
w_net	Work other than compression work
w_rev	Reversible work
w	A general mass (m also used)
w_i	Mass of substance i
W_x	Mass fraction of polymer molecules with degree of polymerization x
x_i	Mole fraction of substance i
x	Degree of polymerization
X_x	Number fraction of polymer molecules with degree of polymerization x
Y	Letter used to stand for a general extensive thermodynamic variable Such as G, H, U, V, etc.
Y_m	Symbol used to stand for a general molar or mean molar quantity, Such as G_m, V_m, and so on
$\Delta_\mathrm{f} Y(i)$	Symbol used to stand for a general molar quantity of formation, such as $\Delta_\mathrm{f} G(i)$ or $\Delta_\mathrm{f} H(i)$
$\bar{Y}_i$	Symbol for a general partial molar quantity, such as $\overline{G}_i$, $\overline{V}_i$, and so on
$\bar{Y}_i^\circ$	Symbol used to stand for a general partial molar quantity, such as $\overline{G}_i$, $\overline{V}_i$, in the standard state
$Y_{\mathrm{m}i}^*$	Symbol used to stand for a general molar quantity, such as $G_{\mathrm{m}i}$, $V_{\mathrm{m}i}$, etc., in the pure state
ΔY_mix	Symbol used to stand for a general mixing quantity such as the change in Gibbs energy on mixing, ΔG_mix, etc.
$z_{i(j)}$	Rate of collisions of a molecule of substance i with molecules of substance j
z_i	Valence of ion i
Z	Compression factor of a gas

Symbol	Quantity
Z_{ij}	Total rate of collisions per unit volume of molecules of substance i with molecules of substance j
α	Coefficient of thermal expansion
α_L	Coefficient of linear thermal expansion
α, α'	Critical exponent for the heat capacity
α	Parameter in Debye–Hückel theory
α	Angle of rotation of polarized light
$[\alpha]$	Specific rotation
α	Transfer coefficient or symmetry factor
α	Degree of elongation of a sample of rubber
β	Critical exponent for the density
β	Parameter in Debye–Hückel theory
γ	Surface or interfacial tension
γ_i	Activity coefficient of substance i
$\gamma_\pm$	Mean ionic activity coefficient
Δ	Symbol for a difference or an increment
ε_0	Permittivity of the vacuum
ε	Permittivity of a medium
$\varepsilon_{\mathrm{rel}}$	Dielectric constant of a medium
ζ	Reaction coordinate
ζ	Configuration integral
η	Efficiency or coefficient of performance
η	Viscosity coefficient
η_{sp}	Specific viscosity
$[\eta]$	Intrinsic viscosity
η	Overpotential
θ	Thermodynamic temperature
θ	Angle coordinate in spherical polar coordinates
θ	Contact angle
θ	Fraction of a surface covered by adsorbed molecules
$\Theta(\theta)$	Angular factor in an atomic wave function
Θ_{D}	Debye temperature
Θ_{E}	Debye temperature
κ_{S}	Adiabatic compressibility
κ_{T}	Isothermal compressibility
κ	Parameter in Debye–Hückel theory, reciprocal of Debye length
κ	Thermal conductivity
λ	Mean free path
$\lambda_{i(j)}$	Mean free path between collisions of a molecule of substance i with molecules of substance j
λ	Wavelength
$\boldsymbol{\mu}$	Magnetic moment
$\boldsymbol{\mu}_0$	Permeability of a vacuum
Λ_i	Molar conductivity of substance
μ	Reduced mass
μ	Mean value of a distribution
μ_i	Chemical potential of component i
μ_i°	Chemical potential of component i in a standard state

(*continued*)

Symbol	Quantity
μ_i^*	Chemical potential of component *i* in a pure liquid or solid state
$\mu_{i(\text{chem})}$	Chemical part of the chemical potential of component *i*
ν_i	Stoichiometric coefficient of substance *i*
$\nu_\pm$	Mean ionic stoichiometric coefficient
ν	Rate of wall collisions
ν	Frequency
ξ	Reaction progress variable
π	3.14159265359 . . .
$\prod$	Symbol for a product of factors
Π	Osmotic pressure
ρ	Density
ρ_c	Charge density
σ	Standard deviation
σ	Electrical conductivity
$\sum$	Symbol for a sum
τ	A period of time, especially a relaxation time or a period of an oscillation
$\tau_{i(j)}$	Mean time between collisions of a molecule of substance *i* with molecules of substance *j*
φ	Electrical potential
φ	Steric factor
ϕ	Angular coordinate in spherical polar and cylindrical polar coordinates
ϕ	Osmotic coefficient
ω	Angular speed
Ψ	A general symbol for a time-dependent wave function or a multi-electron wave function
ψ	A general symbol for a time-dependent wave function
Ω	Thermodynamic probability – number of microstates
∇	Gradient operator
$\nabla\cdot$	Divergence operator
∇^2	Laplacian operator

K

Answers to Numerical Exercises and Odd-Numbered Numerical Problems

Chapter 1 Exercises

1.1

a. $R = 82.058\ \mathrm{cm^3\ atm\ K^{-1}\ mol^{-1}}$
b. $V = 97.86\ \mathrm{L}$
c. $P = 4.157 \times 10^5\ \mathrm{Pa} = 4.157\ \mathrm{bar}$
$= 4.103\ \mathrm{atm} = 3118\ \mathrm{torr}$

1.4

b. $\kappa_T = 1.000\ \mathrm{atm^{-1}}$
c. $\alpha = 3.4112 \times 10^{-3}\ \mathrm{K^{-1}}$

1.5

$V(100.0°\mathrm{C}) = 2.00154\ \mathrm{L}$

1.6

a. $V_m(1.000\ \mathrm{bar}) = 73.53\ \mathrm{cm^3\ mol^{-1}}$
b. $V_m(100.0\ \mathrm{bar}) = 72.63\ \mathrm{cm^3\ mol^{-1}}$

1.7

b. $P = 101250\ \mathrm{Pa} = 0.9993\ \mathrm{atm}$
$P(\text{ideal}) = 101322\ \mathrm{Pa} = 0.99998\ \mathrm{atm}$
c. $P = 2.429 \times 10^6\ \mathrm{Pa} = 23.97\ \mathrm{atm}$
$P(\text{ideal}) = 2.479 \times 10^6\ \mathrm{Pa} = 24.47\ \mathrm{atm}$

1.9

b. $T_{\text{Boyle}} = 505\ \mathrm{K}$
d. $V_m = 1.06 \times 10^{-4}\ \mathrm{m^3\ mol^{-1}}$
If $Z = 1$, $P = 211\ \mathrm{atm}$

1.13

$a = 1.56\ \mathrm{Pa\ K^{1/2}\ m^6\ mol^{-2}}$
$b = 2.68 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}$

Chapter 1 Problems

1.1

$c = 1.802617 \times 10^{12}$ furlongs fortnight^{-1}

1.3

a. $g = 32.3\ \mathrm{ft\ s^{-2}}$
b. $R = 22,591\ \mathrm{lb\ ft^2\ s^{-2}\ (°R)^{-1}\ mol^{-1}} = 22{,}591$ ft poundals $(°R)^{-1}\ \mathrm{mol^{-1}}$
c. $g = 32.3\ \mathrm{ft\ s^{-2}}$

1.5

a. 1 parsec $= 3.084 \times 10^{13}$ km
b. 1 parsec $= 3.259$ light-years
c. distance to sun $= 4.848 \times 10^{-6}$ parsec

1.7

roughly 50 piano tuners in Chicago

1.9

$V = 0.02514\ \mathrm{m^3} = 25.14\ \mathrm{L}$

1.11

$n(H_2O) = 120.2\ \mathrm{mol}\ H_2O$
$m(H_2O) = 2.165\ \mathrm{kg}\ H_2O$

1.15

$(\partial P/\partial \mathrm{V})_{\mathrm{T},n} = -4.526 \times 10^6\ \mathrm{Pa\ m^{-3}}$
$(\partial P/\partial T)_{\mathrm{V},n} = 371.2\ \mathrm{Pa\ K^{-1}}$
$(\partial P/\partial n)_{\mathrm{T,V}} = 1.014 \times 10^5\ \mathrm{Pa\ mol^{-1}}$

1.17

a. $\Delta V/V \approx 0.93 \times 10^{-3}$
b. $\Delta V/V \approx 0.05567$
c. $\Delta V/V \approx 0.00480$

1.19

$\Delta V = 0.52\ \mathrm{cm^3}$

1.23

$\Delta V/V = 0.006$

1.25

a. $V(10°\mathrm{C}) = 57.72\ \mathrm{cm^3}$
b. $V(30°\mathrm{C}) = 59.02\ \mathrm{cm^3}$

1.29

b. $\kappa_T = 4.120 \times 10^{-6}\,\text{Pa}^{-1}$
For an ideal gas,
$\kappa_T = 4.034 \times 10^{-6}\,\text{Pa}^{-1}$

1.31

b. $P = 1.97 \times 10^7\,\text{Pa} = 194\,\text{atm}$

1.33

b. $\alpha = 3.363 \times 10^{-3}\,\text{K}^{-1}$

1.37

Van der Waals: $Z = 1.1434$ (0.86% error)
Dieterici: $Z = 1.1255$ (0.71% error)
Redlich–Kwong: $Z = 1.1153$ (1.6% error)

1.39

a. $\kappa_T = 9.843 \times 10^{-6}\,\text{Pa}^{-1}$
b. $\kappa_T = 9.945 \times 10^{-6}\,\text{Pa}^{-1}$

1.41

a. $P = 28.8\,\text{bar}$
b. $P = 28.8\,\text{bar}$

1.43

a. $a = 0.4192\,\text{Pa}\,\text{m}^6\,\text{mol}^{-2}$
$b = 5.192 \times 10^{-5}\,\text{m}^3\,\text{mol}^{-1}$
b. $Z = 0.7305$

1.45

a. $N(\text{N}_2) = 1.9 \times 10^{22}$ molecules
b. $N(\text{N}_2$, in classroom, from Julius Caesar$) \approx 1 \times 10^6$

1.47

b. $V(25°\text{C}) = 1.00294\,\text{cm}^3$
d. 3.9601°C from the first set of parameters,
3.6066°C from the second set of parameters
e. $\alpha = 2.069 \times 10^{-4}$

1.49

a. TRUE
b. FALSE
c. FALSE
d. FALSE
e. TRUE
f. FALSE
g. TRUE
h. TRUE
i. FALSE
j. TRUE

Chapter 2 Exercises

2.1

a. $w_{\text{rev}} = -8934\,\text{J}$
b. $w_{\text{rev}} = -9065\,\text{J}$

2.2

a. $w = -507\,\text{J}$
b. $w = -859\,\text{J}$

2.4

a. $w_{\text{surr}} = 507\,\text{J}$
b. $\Delta P = -3.06\,\text{atm}$

2.5

$q = 1.602\,\text{Btu}$

2.6

a. $\Delta m = 2.801 \times 10^{-14}\,\text{kg}$

2.8

$w = -8106\,\text{J}$
$q = 8106\,\text{J}$

2.11

a. $\Delta U = 83\,\text{J}$
$w = -1824\,\text{J}$
$q = 1907\,\text{J}$
b. $\Delta T = -6.66\,\text{K}$

2.12

a. $w = -5690\,\text{J}$
$q = 6708\,\text{J}$
b. $q = 8151\,\text{J}$
$w = -7138\,\text{J}$
c. $\Delta U = 1013\,\text{J}$

2.13

$V = 7.98\,\text{L}$

2.14

$T_2 = 473.3\,\text{K}$
$\Delta U = 2184\,\text{J}$
$w = 2184\,\text{J}$

2.18

a. $P_2 = 1.231 \times 10^5\,\text{Pa} = 1.215\,\text{atm}$
b. $P = 1.231 \times 10^5\,\text{Pa}$

2.19

$w = -5066\,\text{J}$
$\Delta U = -5066\,\text{J}$
$T_2 = 418.8\,\text{K}$
$T_2(\text{rev}) = 315.0\,\text{K}$

$\Delta U(\text{rev}) = -11536\,\text{J}$
$w(\text{rev}) = -11536\,\text{J}$

2.21

a. $C_{\text{P},m}(\text{He}) = 20.786\,\text{J K Mol}^{-1}$
$C_{\text{P},m}(\text{Ne}) = 20.786\,\text{J K mol}^{-1}$
$C_{\text{P},m}(\text{Ar}) = 20.786\,\text{J K mol}^{-1}$
$5R/2 = 20.786\,\text{J K mol}^{-1}$
b. $C_{\text{P},m}(\text{N}_2) = 29.124\,\text{J K mol}^{-1}$
$C_{\text{P},m}(\text{O}_2) = 29.376\,\text{J K mol}^{-1}$
$C_{\text{P},m}(\text{CO}) = 29.142\,\text{J K mol}^{-1}$
$7R/2 = 29.101\,\text{J K mol}^{-1}$

2.22

$C_{\text{P},m}(298.15\,\text{K}) = 37.1\,\text{J K}^{-1}\,\text{mol}^{-1}$
$C_{\text{P},m}(500\,\text{K}) = 45.1\,\text{J K}^{-1}\,\text{mol}^{-1}$
$C_{\text{P},m}(1000\,\text{K}) = 52.1\,\text{J K}^{-1}\,\text{mol}^{-1}$
$5R/2 = 20.786\,\text{J K mol}^{-1}$

2.24

$C_{\text{P},m} = 25.10\,\text{J K}^{-1}\,\text{mol}^{-1}$
$3R = 24.944\,\text{J K}^{-1}\,\text{mol}^{-1}$. 0.6% difference

2.26

At 298.15 K, $C_{\text{P},m} = 29.37\,\text{J K}^{-1}\,\text{mol}^{-1}$
At 500 K, $C_{\text{P},m} = 31.42\,\text{J K}^{-1}\,\text{mol}^{-1}$
At 1000 K, $C_{\text{P},m} = 34.0\,\text{J K}^{-1}\,\text{mol}^{-1}$
At 2000 K, $C_{\text{P},m} = 38.3\,\text{J K}^{-1}\,\text{mol}^{-1}$

2.27

a. $\Delta U = 935\,\text{J}$
b. $\Delta H = 1559\,\text{J}$
$q = 3086\,\text{J}$
$w = -2151\,\text{J}$

2.28

$T_f = 5229\,\text{K}$

2.29

$T_f = 7263\,\text{K}$

2.30

$\Delta U^\circ = 54.530\,\text{kJ mol}^{-1}$

2.31

$\Delta T_{\text{cal}} = 3.771\,\text{K}$

2.32

$\Delta H \approx -199\,\text{kJ mol}^{-1}$
From $\Delta_f H$ values, $\Delta H^\circ = -174.264\,\text{kJ mol}^{-1}$

Chapter 2 Problems

2.1

$w_{\text{surr}} = 2079\,\text{J}$

2.3

$w = 4.79\,\text{J}$

2.7

b. $w = 1765\,\text{J}$
c. $w_{\text{surr}} = 507\,\text{J}$

2.9

$I = -8.3145 \times 10^4\,\text{Pa} = -0.8206\,\text{atm}$

2.11

$\Delta T = 0.117\,\text{K}$

2.13

a. $q = -w = 4543\,\text{J}$
b. $q = -w = 2975\,\text{J}$

2.15

$q = 120.9\,\text{kJ}$
$w = -8.771\,\text{kJ}$

2.17

$E = 9.0 \times 10^9\,\text{J mol}^{-1}$
$v = 4.2 \times 10^5\,\text{m s}^{-1}$

2.19

$q = 33.35\,\text{kJ}$
$w = 0.92\,\text{J}$
$\Delta U = 33.35\,\text{kJ}$

2.21

(1) $q = -w = 9221\,\text{J}, \Delta U = 0$
(2) $q = -w = 6916\,\text{J}$
(3) $q = -w = 3040\,\text{J}$

2.23

a. $\mu_{\text{J}} = -1.43 \times 10^4\,\text{K m}^{-3}\,\text{mol}$
b. $T_2 = 282\,\text{K}$

2.25

$P_2 = 0.947\,\text{atm}$

2.27

a. $T_2 = 25.7\,\text{K}$
b. $V_2 = 0.0705\,\text{m}^{-3}$

2.29

a. percent difference = -41.9%

b. $T_2 = 425.7\,\mathrm{K}$

c. $q = 0$

$\Delta U = w = -5103\,\mathrm{J}$

2.31

a. $T_2 = 282.8\,\mathrm{K}$

$q = 0$

$w = \Delta U = -1878\,\mathrm{J}$

b. $T_2 = 235.1\,\mathrm{K}$

$q = 0$

$w = \Delta U = -1722\,\mathrm{J}$

2.33

	298.15 K	500 K	1000 K	2000 K
Ar	0	0	0	0
H	−0.01	0		
He	0	0	0	0
O	5.41	2.27	0.62	0.19
C	0.25	0.087	0.024	0.80

2.35

a. $T_2 = 403.2\,\mathrm{K}$

b. $\Delta U = 2599\,\mathrm{J}$

$w = 2599\,\mathrm{J}$

c. $T_2 = 403.6\,\mathrm{K}$

2.37

a. $T_2 = 346.4\,\mathrm{K}$

b. $w = \Delta U = -4310\,\mathrm{J}$

c. $q = 0$

$\Delta U = w = -2770\,\mathrm{J}$

$T_2 = 383.4\,\mathrm{K}$

d. $\Delta U = 0$

$q = -w = 6860\,\mathrm{J}$

2.41

a. $w = 0$

$q = \Delta U = 2806\,\mathrm{J}$

b. $\Delta U = 2806\,\mathrm{J}$

$q = 4677\,\mathrm{J}$

$w = -1871\,\mathrm{J}$

2.43

a. $q = \Delta H = 2079\,\mathrm{J}$

$w = -831.45\,\mathrm{J}$

$\Delta U = 1248\,\mathrm{J}$

b. $q = \Delta U = 1247\,\mathrm{J}$

$w = 0$

$\Delta H = 2079\,\mathrm{J}$

2.45

$\Delta H = 5745\,\mathrm{J}$

2.47

$q = \Delta H = 24.80\,\mathrm{kJ}$

2.49

a. $\Delta H^\circ = 1236.79\,\mathrm{kJ\,mol^{-1}}$

$\Delta U^\circ = 1234.31\,\mathrm{kJ\,mol^{-1}}$

b. $\Delta H^\circ = -565.99\,\mathrm{kJ\,mol^{-1}}$

$\Delta U^\circ = -563.53\,\mathrm{kJ\,mol^{-1}}$

c. $\Delta H^\circ = -1366.84\,\mathrm{kJ\,mol^{-1}}$

$\Delta U^\circ = -1364.37\,\mathrm{kJ\,mol^{-1}}$

2.51

a. $\Delta H^\circ{}_{348\mathrm{K}} = -1233.38\,\mathrm{kJ\,mol^{-1}}$

b. $\Delta H^\circ{}_{348\mathrm{K}} = -566.66\,\mathrm{kJ\,mol^{-1}}$

c. $\Delta H^\circ{}_{348\mathrm{K}} = -1368.19\,\mathrm{kJ\,mol^{-1}}$

2.53

a. $\Delta H^\circ = -3119.71\,\mathrm{kJ\,mol^{-1}}$

b. $\Delta H^\circ = -2875.76\,\mathrm{kJ\,mol^{-1}}$

c. $\Delta H = -2855.68\,\mathrm{kJ\,mol^{-1}z}$

2.55

a. $\Delta_\mathrm{f} H^\circ(\mathrm{C_{12}H_{22}O_{11}}) = -2224.5\,\mathrm{kJ\,mol^{-1}}$

$\Delta U^\circ = -5640.9\,\mathrm{kJ\,mol^{-1}}$

b. $\Delta_\mathrm{f} H^\circ(\mathrm{C_{18}H_{36}O_2}) = -947.7\,\mathrm{kJ\,mol^{-1}}$

The enthalpy change per gram is = $-39.65\,\mathrm{kJ\,g^{-1}}$

The enthalpy change per gram of sucrose = $-16.48\,\mathrm{kJ\,g^{-1}}$

2.57

a. $\Delta H^\circ = -890.309\,\mathrm{kJ\,mol^{-1}}$

b. $\Delta U^\circ = -885.351\,\mathrm{kJ\,mol^{-1}}$

c. $\Delta U^\circ = -885.347\,\mathrm{kJ\,mol^{-1}}$

2.59

a. $\Delta U^\circ \approx -2796\,\mathrm{kJ\,mol^{-1}}$

$\Delta H^\circ \approx -2794\,\mathrm{kJ\,mol^{-1}}$

b. $\Delta H^\circ_{298\mathrm{K}} = -2855.68\,\mathrm{kJ\,mol^{-1}}$

$\Delta H^\circ_{373\mathrm{K}} = -2852.74\,\mathrm{kJ\,mol^{-1}}$

c. $\Delta U^\circ \approx -606\,\mathrm{kJ\,mol^{-1}}$

$\Delta H^\circ \approx -608\,\mathrm{kJ\,mol^{-1}}$

2.61

a. $\Delta H^\circ \approx 76\,\mathrm{kJ\,mol^{-1}}$
From enthalpy changes of formation,
$\Delta H^\circ = 71.488\,\mathrm{kJ\,mol^{-1}}$

b. $\Delta H^\circ \approx -542\,\mathrm{kJ\,mol^{-1}}$
From enthalpy changes of formation,
$\Delta H^\circ = -545.092\,\mathrm{kJ\,mol^{-1}}$

2.63

a. $\Delta H^\circ = 71.488\,\mathrm{kJ\,mol^{-1}}$
b. $\Delta U^\circ = 69.009\,\mathrm{kJ\,mol^{-1}}$
c. $E_B(\mathrm{P\text{-}Cl}) \approx 156\,\mathrm{kJ\,mol^{-1}}$

2.65

a. $\Delta H^\circ = -311.42\,\mathrm{kJ\,mol^{-1}}$
b. $\Delta U^\circ = -306.46\,\mathrm{kJ\,mol^{-1}}$
c. $\Delta U \approx -323\,\mathrm{kJ\,mol^{-1}}$
d. $\Delta H^\circ_{373} = -315.11\,\mathrm{kJ\,mol^{-1}}$

2.67

a. $v_s = 346\ \mathrm{m\,s^{-1}}$
b. $v_s = 1016\ \mathrm{m\,s^{-1}}$
$\gamma = 1.2117$

2.69

a. $w = \Delta U = q = 0$
$\Delta H = 180\,\mathrm{J}$
b. same as part a

2.71

a. TRUE
b. FALSE
c. FALSE
d. FALSE
e. TRUE
f. FALSE
g. TRUE
h. FALSE
i. FALSE

2.73

$T_2 = 217\,\mathrm{K}$
$t_C = -56°\mathrm{C}$

Chapter 3 Exercises

3.2

$\eta_c = 0.378$

3.3

a. $\eta_r = 15.4$
b. $\eta_{hp} = 16.4$
4.1×10^{-9} dollars $\mathrm{J^{-1}}$
c. 3.6×10^{-8} dollars $\mathrm{J^{-1}}$

3.5

$\Delta S = 40.15\,\mathrm{J\,K^{-1}}$
$\Delta S_{\mathrm{surr}} = -40.15\,\mathrm{J\,K^{-1}}$
$\Delta U = 0$
$q = -w = 11970\,\mathrm{J}$

3.6

$\Delta_{\mathrm{vap}} H = 43.93\,\mathrm{kJ}$
$F_g/\mathscr{A} = 9.7\,\mathrm{atm}$
$\Delta S = 124.9\,\mathrm{J\,K^{-1}}$

3.7

$\Delta S = 29.149\,\mathrm{J\,K^{-1}}$

3.8

a. $\Delta S = 12.26\,\mathrm{J\,K^{-1}}$
b. $\Delta S_{\mathrm{surr}} = -12.26\,\mathrm{J\,K^{-1}}$

3.9

$\Delta S_{\mathrm{surr}} = -9.85\,\mathrm{J\,K^{-1}}$

3.10

$\Delta S = 24.47\,\mathrm{J\,K^{-1}}$
$\Delta S_{\mathrm{surr}} = 0$
$\Delta S_{\mathrm{univ}} = 24.47\,\mathrm{J\,K^{-1}}$

3.11

$\Delta S = 12.97\,\mathrm{J\,K^{-1}}$
$\Delta S_{\mathrm{surr}} = -11.14\,\mathrm{J\,K^{-1}}$
$\Delta S_{\mathrm{univ}} = 1.83\,\mathrm{J\,K^{-1}}$

3.12

entropy production = $0.00274\,\mathrm{J\,K^{-1}\,s^{-1}}$

3.13

a. $\Delta S_{\mathrm{mix}} = 5.762\,\mathrm{J\,K^{-1}}$
b. $\Delta S_{\mathrm{mix}} = 4.322\,\mathrm{J\,K^{-1}}$

3.14

b. $N = 1296$
c. $N = 21$

3.15

$\Omega = 10^{6.61\times 10^{24}}$

3.19

b. $\Delta H = -565.990\,\mathrm{kJ\,mol^{-1}}$
c. $q_{\mathrm{surr}} > 0$ and $\Delta S_{\mathrm{surr}} > 0$

d. $\Delta S_{\text{surr}} = 1898.3\,\text{J K}^{-1}$
$\Delta S_{\text{univ}} = 1725.5\,\text{J K}^{-1}$

3.20
a. $\Delta S^\circ = -326.607\,\text{J K}^{-1}\,\text{mol}^{-1}$
b. $\Delta S^\circ = -94.678\,\text{J K}^{1}\,\text{mol}^{-1}$

3.21
$S_{\text{st}} = 14.90\,\text{J K}^{-1}\,\text{mol}^{-1}$

3.22
$\Delta_{\text{vap}}H_m = 16240\,\text{J mol}^{-1}$
Table A.7 value = $15646\,\text{J mol}^{-1}$

Chapter 3 Problems

3.1
a. $\eta = 0.211$
$V_2 = 2.52\,L$
$V_4 = 0.857\,L$
b. $w_1 = -1411\,\text{J}$
$w_2 = -312\,\text{J}$
$w_3 = 1113\,\text{J}$
$w_4 = 312\,\text{J}$

3.3
$h = 14.1\,\text{km}$

3.5
a. $\eta_c = 0.2114$
b. $\eta_c = 0.4107$
percentage improvement = 94.3%
c. $m = 1.996\,\text{kg}$

3.7
a. $q(\text{house}) = 8.4 \times 10^7\,\text{J}$
b. $q(\text{house}) = 4.68 \times 10^8\,\text{J}$
c. $q(\text{house}) = 4.00 \times 10^7\,\text{J}$

3.11
a. $\eta_c = 0.01649$
b. $dV/dt = 1.45 \times 10^3\,\text{m}^3\,\text{s}^{-1}$

3.13
a. $\Delta S_1 = 5.7632\,\text{J K}^{-1}$
$\Delta S_2 = 5.7587\,\text{J K}^{-1}$
$\Delta S_3 = -2.3919\,\text{J K}^{-1}$
$\Delta S_4 = -2.9612\,\text{J K}^{-1}$
$\Delta S_5 = -3.3712\,\text{J K}^{-1}$
$\Delta S_6 = -2.7985\,\text{J K}^{-1}$
b. All values are the same

3.15
$w = -1227\,\text{J}$
$q = 0$
$\Delta U = -1227\,\text{J}$
$T_f = 401.6\,\text{K}$
$\Delta S = 7.278\,\text{J K}^{-1}$
$\Delta S_{\text{rev}} = 0$
$q_{\text{rev}} = 0$
$\Delta U_{\text{rev}} = -3441\,\text{J}$
$w_{\text{rev}} = -3441\,\text{J}$

3.17
a. $\Delta S = 217.98\,\text{J K}^{-1}$
b. $\Delta S = 16.54\,\text{J K}^{-1}$

3.19
a. $\Delta S = -5.7632\,\text{J K}^{-1}$
$\Delta U = 0$
$q = -1718.3\,\text{J}$
$w = 1718.3\,\text{J}$
$\Delta S_{\text{univ}} = 0$
$\Delta S_{\text{surr}} = 5.7632\,\text{J K}^{-1}$
b. $q = 0$
$\Delta S = 0$
$\Delta S_{\text{surr}} = 0$
$\Delta S_{\text{univ}} = 0$
$T_2 = 473.3\,\text{K}$
$\Delta U = 2184.4\,\text{J}$
$w = 2184.4\,\text{J}$
c. $T_2 > 473.3\,\text{K}$
$\Delta U > 2184.4\,\text{K}$
$w > 2184.4\,\text{K}$
$q = 0$
$\Delta S > 0$
$\Delta S_{\text{surr}} = 0$
$\Delta S_{\text{univ}} > 0$
d. $\Delta S = -5.7632\,\text{J K}^{-1}$
$\Delta U = 0$
$w < 5066\,\text{J}$
$q > -5066\,\text{J}$
$\Delta S_{\text{univ}} > 0$
$\Delta S_{\text{surr}} > 5.7632\,\text{J K}^{-1}$

3.21
a. $\Delta S = 23.55\,\text{J K}^{-1}$
b. $\Delta S = 23.55\,\text{J K}^{-1}$
c. $\Delta S_{\text{surr}} = -23.55\,\text{J K}^{-1}$

d. $\Delta S = 23.55\,\mathrm{J\,K^{-1}}$
$\Delta S_{\mathrm{surr}} = -18.71\,\mathrm{J\,K^{-1}}$
$\Delta S_{\mathrm{univ}} = 4.84\,\mathrm{J\,K^{-1}}$

3.23

a. $T_2 = 271.4\,\mathrm{K}$
$q = 0$
$\Delta U = -5702\,\mathrm{J}$
$w = -5702\,\mathrm{J}$
$\Delta S = 0$
$\Delta S_{\mathrm{univ}} = 0$

b. $T_2 = 439.1\,\mathrm{K}$
$\Delta S = 0$
$w = -1520\,\mathrm{J}$
$q = -4183\,\mathrm{J}$
$\Delta U = -5703\,\mathrm{J}$
$\Delta S_{\mathrm{univ}} = 12.00\,\mathrm{J\,K^{-1}}$

3.25

$\Delta S = 18.71\,\mathrm{J\,K^{-1}}$

3.27

a. $S_{\mathrm{st}} = 14.898\,\mathrm{J\,K^{-1}}$

b. $S_{\mathrm{st}} = 11.526\,\mathrm{J\,K^{-1}}$

3.29

$S_{\mathrm{st}} = 3.7154 \times 10^{-21}\,\mathrm{J\,K^{-1}}$.

3.31

$\Delta S_{\mathrm{mix}} = 5.763\,\mathrm{J\,K^{-1}}$

3.33

$S^{\circ}_{\mathrm{m}}(\mathrm{CO_2}) = 30.00\,\mathrm{J\,K^{-1}\,mol^{-1}}$
$S^{\circ}_{\mathrm{m}}(\mathrm{H_2O}) = 40.00\,\mathrm{J\,K^{-1}\,mol^{-1}}$

3.35

a. $\Delta S^{\circ} = 100.97\,\mathrm{J\,K^{-1}\,mol^{-1}}$

b. $\Delta S^{\circ} = -169.4\,\mathrm{J\,K^{-1}\,mol^{-1}}$

c. $\Delta S^{\circ} = -232.72\,\mathrm{J\,K^{-1}\,mol^{-1}}$

d. $\Delta S^{\circ} = 1330.0\,\mathrm{J\,K^{-1}\,mol^{-1}}$

3.37

a. $S^{\circ}_{\mathrm{m,473K}} = 204.9\,\mathrm{J\,K^{-1}\,mol^{-1}}$

b. $S^{\circ}_{\mathrm{m,473K}} = 204.7\,\mathrm{J\,K^{-1}\,mol^{-1}}$

3.39

a. $\Delta_{\mathrm{f}} S^{\circ}(\mathrm{CO}) = 89.340\,\mathrm{J\,K^{-1}\,mol^{-1}}$
$\Delta_{\mathrm{f}} S^{\circ}(\mathrm{CO_2}) = 2.908\,\mathrm{J\,K^{-1}\,mol^{-1}}$
$\Delta_{\mathrm{f}} S^{\circ}(\mathrm{O_2}) = 0$

b. $\Delta S^{\circ} = -172.864\,\mathrm{J\,K^{-1}\,mol^{-1}}$

3.41

$S^{\circ}_{\mathrm{m}}(270\,\mathrm{K}) = 39.99\,\mathrm{J\,K^{-1}\,mol^{-1}}$

3.43

	$\Delta S/\mathrm{J\,k^{-1}\,mol^{-1}}$
ammonia	97.44
benzene	121.47
carbon monoxide	82.72
carbon tetrachloride	91.27
ethane	84.80
ethanol	115.12
methane	81.57
water	108.99

3.47

$\Delta S = -145.11\,\mathrm{J\,K^{-1}}$
$\Delta H = 44.004\,\mathrm{kJ^{-1}}$
$q_{\mathrm{surr}} = 44.004\,\mathrm{kJ}$

3.49

a. $q = -1.225 \times 10^{5}\,\mathrm{kJ}$

b. $h = 7.08\,\mathrm{km}$

c. $h = 6.03\,\mathrm{km}$

3.51

a. FALSE

b. FALSE

c. TRUE

d. FALSE

e. FALSE

f. TRUE

g. TRUE

h. FALSE

3.53

a. $\Delta S_{\mathrm{mix}} = 9.351\,\mathrm{J\,K^{-1}}$

b. five types of molecules
$n(\mathrm{C^{35}Cl_4}) = 0.316406\,\mathrm{mol}$
$n(\mathrm{C^{35}Cl_3^{37}Cl}) = 0.421876\,\mathrm{mol}$
$n(\mathrm{C^{35}Cl_2^{37}Cl_2}) = 0.210936\,\mathrm{mol}$
$n(\mathrm{C^{35}Cl^{37}Cl_3}) = 0.046875\,\mathrm{mol}$
$n(\mathrm{C^{37}Cl_4}) = 0.003906\,\mathrm{mol}$

c. $\Delta S_{\mathrm{mix}} = 10.157\,\mathrm{J\,K^{-1}}$

3.55

$S_{\mathrm{st}} = 20.66\,\mathrm{J\,K^{-1}}$

Chapter 4 Exercises

4.1

a. $(\partial V/\partial S)_{\mathrm{P},n}$ $8124\,\mathrm{K\,m^{-3}}$
b. $(\partial V/\partial S)_{\mathrm{P},n}$ $4062\,\mathrm{K\,m^{-3}}$
c. $(\partial V/\partial S)_{\mathrm{P},n}$ $16248\,\mathrm{K\,m^{-3}}$

4.2

a. $(\partial V/\partial S)_{\mathrm{P},n} = 0.00118\,\mathrm{K\,Pa^{-1}}$
b. Same as part a.

4.3

b. $(\partial S/\partial P)_{\mathrm{T},n} = -8.226 \times 10^{-5}\,\mathrm{J\,K^{-1}\,Pa^{-1}}$

4.4

$\Delta S = 19.37\,\mathrm{J\,K^{-1}}$
$\Delta S(\mathrm{ideal}) = 19.14\,\mathrm{J\,K^{-1}}$

4.5

$(\partial U/\partial V)_{\mathrm{T},n} = 309\,\mathrm{J\,m^{-3}} = 309\,\mathrm{Pa}$

4.6

a. $(\partial U/\partial V)_{\mathrm{T},n} = 1113\,\mathrm{atm}$

4.7

b. $(\partial H/\partial P)_{\mathrm{T},n} = -7.54 \times 10^{-5}\,\mathrm{J\,Pa^{-1}} = 7.441\,\mathrm{J\,atm^{-1}}$

4.8

a. $C_{\mathrm{V,m}} = 74.841\,\mathrm{J\,K^{-1}\,mol^{-1}}$
b. $C_{\mathrm{P,m}} - C_{\mathrm{V,m}} = 0$
d. $\gamma = 1.0106$
For argon gas, $\gamma = 1.667$

4.9

$C_{\mathrm{V}} = 0.4418\,\mathrm{J\,K^{-1}\,g^{-1}}$

4.11

a. $f = 504.2\,\mathrm{kPa}$
b. $f = 496900\,\mathrm{Pa}$
c. $f = 1.434 \times 10^{6}\,\mathrm{Pa}$

4.12

a. $G_{\mathrm{m}} - G^{\circ}_{\mathrm{m}} = 7.09 \times 10^{-2}\,\mathrm{J\,mol^{-1}}$
b. $G_{\mathrm{m}} - G^{\circ}_{\mathrm{m}} = 6.38\,\mathrm{J\,mol^{-1}}$

4.13

a. $\Delta G_{383.15\mathrm{K}} \approx -1090\,\mathrm{J\,mol^{-1}}$
b. $\Delta G_{383.15\mathrm{K}} \approx -1090\,\mathrm{J\,mol^{-1}}$

4.17

a. $\mu_i - \mu_i^{\circ} = 0.0326\,\mathrm{kJ\,mol^{-1}}$
b. $\mu_i - \mu_i^{\circ} = 5.741\,\mathrm{kJ\,mol^{-1}}$

Chapter 4 Problems

4.3

a. $\Delta H^{\circ} = -571.660\,\mathrm{kJ\,mol^{-1}}$
b. $w_{\mathrm{surr}} = 101.9\,\mathrm{kJ}$
c. $\Delta S^{\circ} = -326.607\,\mathrm{J\,K^{-1}\,mol^{-1}}$
$\Delta G^{\circ} = -474.282\,\mathrm{kJ\,mol^{-1}}$
d. $w_{\mathrm{net,surr,max}} = 474.282\,\mathrm{kJ}$
$w_{\mathrm{total,surr,max}} = 469.314\,\mathrm{kJ}$

4.7

b. $\Delta S = 11.376\,\mathrm{J\,K^{-1}}$

4.9

b. $\Delta S = 23.157\,\mathrm{J\,K^{-1}}$
$\Delta S_{\mathrm{ideal}} = 23.053\,\mathrm{J\,K^{-1}}$

4.13

$v_s = 1302\,\mathrm{m\,s^{-1}}$

4.15

c. $\lim_{P\to 0} \mu_{JT} = 4.3 \times 10^{-6}\,\mathrm{K\,Pa^{-1}}$

4.17

a. $H_{\mathrm{m}}(\mathrm{P_2}) - H_{\mathrm{m}}(\mathrm{P_1}) = 91.04\,\mathrm{J\,mol^{-1}}$
b. $H_{\mathrm{m}}(\mathrm{P_2}) - H_{\mathrm{m}}(\mathrm{P_1}) = 92.64\,\mathrm{J\,mol^{-1}}$
c. $\Delta_{\mathrm{fus}} H_{\mathrm{m}} = 6004\,\mathrm{J\,mol^{-1}}$

4.21

a. $w = -1716\,\mathrm{J}$
b. $\Delta S = 5.736\,\mathrm{J\,K^{-1}}$
c. $\Delta U = 0.0099\,\mathrm{J}$
d. $w = 0$
$\Delta U = 0.0099\,\mathrm{J}$
$q = 0.0099\,\mathrm{J}$
$\Delta S = 5.736\,\mathrm{J\,K^{-1}}$

4.23

b. $S_{\mathrm{m}} - S^{\circ}_{\mathrm{m}} = -7.53434\,\mathrm{J\,K^{-1}\,mol^{-1}}$

4.25

b. $\Delta U = 123.8\,\mathrm{J}$

4.27

b. $\Delta S = -0.0374\,\mathrm{J\,K^{-1}}$

4.29

a. $\Delta U = 0$
$\Delta H = 0$
$w = -3040\,\mathrm{J}$
$q = 3040\,\mathrm{J}$
$\Delta S = 23.05\,\mathrm{J\,K^{-1}}$
$\Delta S_{\mathrm{surr}} = -10.196\,\mathrm{J\,K^{-1}}$
$\Delta A = -6873\,\mathrm{J}$
$\Delta G = \Delta H - T\Delta S = -6873\,\mathrm{J}$

b. $\Delta U = 0$
$\Delta H = 0$
$w = -6872\,\mathrm{J}$
$q = 6872\,\mathrm{J}$
$\Delta S = 23.05\,\mathrm{J\,K^{-1}}$
$\Delta S_{\mathrm{surr}} = -23.05\,\mathrm{J\,K^{-1}}$
$\Delta A = -6873\,\mathrm{J}$
$\Delta G = -6873\,\mathrm{J}$

4.31

b. $\Delta A = 2723\,\mathrm{J}$ for part a
$\Delta A = 1718\,\mathrm{J}$ for part b

4.33

b. $\Delta A_{\mathrm{m}} = -2269\,\mathrm{J\,mol^{-1}}$
$A_{\mathrm{m}}(\mathrm{ideal}) = -2271\,\mathrm{J\,mol^{-1}}$

c. $\Delta A_{\mathrm{m}} = -\ 2269\,\mathrm{J\,mol^{-1}}$

4.35

b. $\Delta A_m = -2268\,\mathrm{J\,mol^{-1}}$

4.37

a. $\Delta H^\circ = -802.310\,\mathrm{kJ\,mol^{-1}}$
$\Delta S^\circ = -5.081\,\mathrm{J\,K^{-1}\,mol^{-1}}$
$\Delta H^\circ - T\Delta S^\circ = -800.795\,\mathrm{kJ\,mol^{-1}}$
$\Delta G^\circ = -800.785\,\mathrm{kJ\,mol^{-1}}$

b. $\Delta H^\circ(498.15\,\mathrm{K}) = -808.27\,\mathrm{kJ\,mol^{-1}}$
$\Delta S^\circ(498.15\,\mathrm{K}) = -20.378\,\mathrm{J\,K\,mol^{-1}}$
$\Delta G^\circ(498.15\,\mathrm{K}) = -818.421\,\mathrm{kJ\,mol^{-1}}$

c. $w_{\mathrm{surr}} = 205.0\,\mathrm{kJ}$

4.39

c. $\Delta G = 8562.1\,\mathrm{J}$

4.41

$\overline{V}_2 = 56.72 \pm 0.11\,\mathrm{cm^3\,mol^{-1}}$

4.43

a. $\mu(100.00\,\mathrm{bar}) - \mu(1.000\,\mathrm{bar}) = 178.4\,\mathrm{J\,mol^{-1}}$

b. $\mu(100.00\,\mathrm{bar}) - \mu(1.000\,\mathrm{bar}) = 11416\,\mathrm{J\,mol^{-1}}$

4.45

a. homogeneous, degree 2
b. not homogeneous
c. not homogeneous
d. not homogeneous
e. not homogeneous

4.47

a. $\Delta S_{\mathrm{mix}} = 9.351\,\mathrm{J\,K^{-1}}$
$\Delta G_{\mathrm{mix}} = -3273\,\mathrm{J}$

b. $\mu_1 - \mu_1^\circ = -4034\,\mathrm{J\,mol^{-1}}$
$\mu_2 - \mu_2^\circ = -837.2\,\mathrm{J\,mol^{-1}}$

c. $\Delta\mu_2 = 0.0333\,\mathrm{J\,mol^{-1}}$

4.49

a. FALSE
b. FALSE
c. FALSE
f. FALSE
h. TRUE

4.51

a. $C_{\mathrm{V}} = 74.854\,\mathrm{J\,K^{-1}\,mol^{-1}}$
b. $\kappa_{\mathrm{S}} = 4.54 \times 10^{-10}\,\mathrm{Pa^{-1}}$
c. $v_s = 1490\,\mathrm{m\,s^{-1}}$
d. $V = 17.99 \times 10^{-6}\,\mathrm{m^3}$
e. $\Delta T = 0.546\,\mathrm{K}$
f. $\Delta U = 0.409\,\mathrm{J}$

4.53

b. $G_m(T, P') - G_m^\circ(T) = 1543.4\,\mathrm{J\,mol^{-1}}$
$S_m(T, P') - S_m^\circ(T) = -5.986\,\mathrm{J\,K^{-1}\,mol^{-1}}$
$H_m(T, P') - H_m^\circ(T) = -91.6\,\mathrm{J\,mol^{-1}}$
$A_m(T, P') - A_m^\circ(T) = 1574\,\mathrm{J\,mol^{-1}}$
$U_m(T, P') - U_m^\circ(T) = -61\,\mathrm{J\,mol^{-1}}$

4.57

$\Delta V = -13.30\,\mathrm{cm^3}$
$\Delta S = -23.15\,\mathrm{J\,K^{-1}}$

Chapter 5 Exercises

5.2

a. $c = 3$
b. $c = 4$
c. $c = 2$

d. $c = 2$
e. $c = 2$
f. $c = 1$
g. $c = 2$

5.4
$P_2 - P_1 = 1.350 \times 10^6\,\mathrm{Pa} = 13.32\,\mathrm{atm}$

5.5
$P_2 - P_1 = 13.32\,\mathrm{atm}$

5.6
$V_\mathrm{m}(\mathrm{liquid}) = 1.80 \times 10^{-5}\,\mathrm{m^3\,mol^{-1}}$
$V_\mathrm{m}(\mathrm{gas}) = 3.06 \times 10^{-2}\,\mathrm{m^3\,mol^{-1}}$

5.8
$P_2 = 2.226\,\mathrm{atm} = 1692\,\mathrm{torr} = 2.255\,\mathrm{bar}$

5.9
$P_2 = 0.666\,\mathrm{atm} = 506\,\mathrm{torr} = 67.5\,\mathrm{kPa}$

5.10
$P_2' = 328000\,\mathrm{Pa} = 3.24\,\mathrm{atm} = 2460\,\mathrm{torr}$

5.12
$T_c = 5074\,\mathrm{K}$

5.13
a. $\gamma = 0.142\,\mathrm{J\,m^{-2}}$
b. ratio $= 8.5 \times 10^{-9}$

5.14
$h = 0.00050\,\mathrm{m} = 0.50\,\mathrm{mm}$

5.15
$h = -0.0131\,\mathrm{m} = -13.1\,\mathrm{mm}$

5.16
$P_2 = 23.753\,\mathrm{torr}$

Chapter 5 Problems

5.1
$G_\mathrm{m}^{(\mathrm{l})} - G_\mathrm{m}^{(\mathrm{s})} = 0$
$A_\mathrm{m}^{(\mathrm{l})} - A_\mathrm{m}^{(\mathrm{s})} = -0.167\,\mathrm{J\,mol^{-1}}$
$H_\mathrm{m}^{(\mathrm{l})} - H_\mathrm{m}^{(\mathrm{s})} = 6006\,\mathrm{J\,mol^{-1}}$
$U_\mathrm{m}^{(\mathrm{l})} - U_\mathrm{m}^{(\mathrm{s})} = 6006\,\mathrm{J\,mol^{-1}}$
$S_\mathrm{m}^{(\mathrm{l})} - S_\mathrm{m}^{(\mathrm{s})} = 21.99\,\mathrm{J\,K^{-1}\,mol^{-1}}$

5.3
$G_\mathrm{m}^{(\mathrm{g})} - G_\mathrm{m}^{(\mathrm{l})} = 0$
$A_\mathrm{m}^{(\mathrm{g})} - A_\mathrm{m}^{(\mathrm{l})} = -2.479\,\mathrm{kJ\,mol^{-1}}$
$H_\mathrm{m}^{(\mathrm{g})} - H_\mathrm{m}^{(\mathrm{l})} = 44.010\,\mathrm{kJ\,mol^{-1}}$
$U_\mathrm{m}^{(\mathrm{g})} - U_\mathrm{m}^{(\mathrm{l})} = 41.531\,\mathrm{kJ\,mol^{-1}}$
$S_\mathrm{m}^{(\mathrm{g})} - S_\mathrm{m}^{(\mathrm{l})} = 147.6\,\mathrm{J\,K^{-1}\,mol^{-1}}$

5.5
a. $f = 3$
b. $f = 2$
c. $f = 3$
d. $f = 2$
e. $f = 0$

5.7
a. $c = 2,\ f = 3$
b. $c = 1,\ f = 1$
c. $c = 2,\ f = 2$

5.9
$P - P^\circ = 1.506 \times 10^9\,\mathrm{Pa}$

5.13
a. $T_2 = 239.5\,\mathrm{K}$, $t_\mathrm{C} = -33.6^\circ\mathrm{C}$
b. $\Delta_\mathrm{vap} H_m = 24400\,\mathrm{J\,mol^{-1}}$

5.15
a. $\Delta_\mathrm{sub} H_m = 25900\,\mathrm{J\,mol^{-1}}$
b. $T = 194.6\,\mathrm{K}$

5.17
a. $P = 1.95\,\mathrm{atm}$
$P(\mathrm{gauge}) = 0.95\,\mathrm{atm} = 13.9\,\mathrm{psig}$
b. $T_\mathrm{f} = 273.145\,\mathrm{K}$
$t_\mathrm{Cf} = -0.00488^\circ\mathrm{C}$

5.19
$T = 367.9\,\mathrm{K}$
$t_\mathrm{C} = 94.7^\circ\mathrm{C}$

5.21
a. $\Delta_\mathrm{vap} H_m = 42.7\,\mathrm{kJ\,mol^{-1}}$
b. $P_2 = 182.6\,\mathrm{torr}$

5.23
$\Delta_\mathrm{sub} H_m = 26.1\,\mathrm{kJ\,mol^{-1}}$

5.25
$\Delta H_\mathrm{vap} = 259.4\,\mathrm{kJ\,mol^{-1}}$

5.27

$P_2 = 92.44$ torr (modified equation)
$P_2 = 93.91$ torr (original equation)
$P_2 = 92.51$ torr (experiment)

5.29

$P_2 = 148.8$ torr

5.31

a. $\Delta G = 0$
$\Delta S = 104.6\,\mathrm{J\,K^{-1}}$
$q = 25110\,\mathrm{J}$
$w = 1995\,\mathrm{J}$
b. $\Delta G = -4595\,\mathrm{J}$
$\Delta S = 19.14\,\mathrm{J\,K^{-1}}$
$q = -w = 4595\,\mathrm{J}$

5.35

a. $\Delta\mathrm{slope} = -21.99\,\mathrm{J\,K^{-1}\,mol^{-1}}$
b. $\Delta\mathrm{slope} = 0.163\,\mathrm{J\,bar^{-1}\,mol^{-1}}$
c. $\Delta\mathrm{slope} = -109.0\,\mathrm{J\,K^{-1}\,mol^{-1}}$
d. $\Delta\mathrm{slope} = 3060\,\mathrm{J\,bar^{-1}\,mol^{-1}}$

5.39

$h = 0.309\,\mathrm{m} = 30.9\,\mathrm{cm}$

5.41

$h = 0.0421\,\mathrm{m}$

5.43

$F = 0.00357\,\mathrm{N}$

5.45

a. $P(l) = 2.16 \times 10^5\,\mathrm{Pa}$
b. $P_{\mathrm{vap}} = 23.776$ torr

5.49

$\Gamma_2 = 5.7 \times 10^{-6}\,\mathrm{mol\,m^{-2}}$
area $= 2.91 \times 10^{-19}\,\mathrm{m^2\,molecule^{-1}}$

5.53

a. FALSE
b. TRUE
c. FALSE
d. TRUE
e. FALSE
f. FALSE
g. FALSE
h. TRUE
i. TRUE
j. FALSE
k. TRUE

Chapter 6 Exercises

6.7

$x(\text{benzene}) \approx 0.86$
$T(\text{boil}) \approx 357\,\mathrm{K}$

6.9

$k_1 = 985$ torr

6.13

$P = 1.47 \times 10^6\,\mathrm{Pa} = P = 14.5\,\mathrm{atm}$

6.14

$a_i^{(\mathrm{I})} = 0.9513$
$\gamma_i^{(\mathrm{I})} = 1.312$

6.15

$a_i^{(\mathrm{I})} = 0.9232$
$\gamma_i^{(\mathrm{I})} = 1.026$

6.17

$I = 0.600\,\mathrm{mol\,kg^{-1}}$

6.21

$\gamma_\pm = 0.902$
$\%\,difference = 0.3\%$

6.28

$x(\mathrm{Au}) \approx 0.88$

6.31

b. $\dfrac{x_2^2}{2} = 5 \times 10^{-5}$

$\dfrac{x_2^3}{3} = 3.33 \times 10^{-7}$

c.

$-x_2$	%difference
−0.100	5.36%
−0.0100	0.50%
−0.00100	0.05%
−0.000100	0.005%

6.33

$\Delta T = 0.188\,\mathrm{K}$

6.34

$t_\mathrm{b} = 100.014°\mathrm{C}$

6.35

a. $P_1 = 0.99947\,\mathrm{atm} = 101272\,\mathrm{Pa}$

6.36

b. $\Pi = 6.88 \times 10^4\,\mathrm{Pa} = 0.679\,\mathrm{atm}$
c. $h = 7.01\,\mathrm{m}$

Chapter 6 Problems

6.5
$\Delta S_{\text{mix}} = 22.00\,\text{J K}^{-1}$
$\Delta G_{\text{mix}} = -6560\,\text{J}$
$\Delta H_{\text{mix}} = 0$
$\Delta U_{\text{mix}} = 0$

6.11
$\Delta S = 9.464\,\text{J K}^{-1}$

6.13
$M_2 = 127.9\,\text{g mol}^{-1}$

6.15
a. $K_{\text{d}}^{(\text{c})} = 0.012$
b. $V_{\text{thio}} = 4.5\,\text{mL}$

6.17
$k_2^{(\text{u})} = 2380\,\text{torr}$

6.19
$x = 1.40 \times 10^{-4}$

6.21
$a_1 = 0.99955$

6.23
$\gamma_2^{(\text{m})} = 0.9275$
$\gamma_2^{(\text{c})} = 1.036$

6.25
$\gamma = 1.0044$

6.27
a. $k_2 = 0.689\,\text{atm}$
b. $P_2 = 0.754\,\text{atm}$
c. At $x_2 = 0.0500$: $\gamma_2^{(\text{II})} = 1.00, a_2^{(\text{II})} = 0.05$
$\gamma_2^{(\text{I})} = 0.914, a_2^{(\text{I})} = 0.0457$
At $x_2 = 0.600$: $\gamma_2^{(\text{II})} = 1.052, a_2^{(\text{II})} = 0.631$
$\gamma_2^{(\text{I})} = 0.962, a_2^{(\text{I})} = 0.577$
At $x_2 = 0.950$: $\gamma_2^{(\text{II})} = 1.094, a_2^{(\text{II})} = 1.039$
$\gamma_2^{(\text{I})} = 1, a_2^{(\text{I})} = 0.950$

6.29
a. $\Delta H_{\text{diff}}^{\circ}(\text{KOH}) = -57.61\,\text{kJ mol}^{-1}$
b. $\mu^{\circ(m)}(\text{KOH,aq}) - G_{\text{m}}^{*}(\text{KOH,s}) = -61.43\,\text{kJ mol}^{-1}$

6.35
a. $\alpha = 3.89\,\text{kg}^{1/2}\,\text{mol}^{-1/2}$
$\beta = 4.53 \times 10^{9}\,\text{kg}^{1/2}\,\text{mol}^{-1/2}\,\text{m}^{-1}$
b. For methanol, $\gamma_{\pm} = 0.710$
For water, $\gamma_{\pm} = 0.899$
percent difference $= -21\%$

6.39
a. $a_1^{(\text{I})} = 0.669$
$\gamma_1^{(\text{I})} = 0.944$
$a_2^{(\text{I})} = 0.1892$
$\gamma_2^{(\text{I})} = 0.650$
b. $\Delta G_{\text{mix}} = -1973\,\text{J}$
$G^{E} = -427\,\text{J}$
c. $a_2^{(\text{II})} = 0.382$
$\gamma_2^{(\text{II})} = 1.31$

6.41
a. $a_c = 0.381, \gamma_c = 0.771$
$a_a = 0.394, \gamma_a = 0.779$
b. $\Delta G_{\text{mix}} = -1777\,\text{J}$

6.43
a. $\Delta H_{\text{mix}} = 38.97\,\text{J}$
$\Delta G_{\text{mix}} = -552\,\text{J}$
b. $\Delta H = 46.0\,\text{J}$
$\Delta G = -399\,\text{J}$

6.45
a. $\gamma_2 = 2.978, \gamma_1 = 1.312$
b. $\Delta G_{\text{mix}} = -452.5\,\text{J}$

6.47
a. $a_{\text{A}} = 0.669, \gamma_{\text{A}} = 0.944$
$a_{\text{C}} = 0.1982, \gamma_{\text{C}} = 0.650$
b. $\Delta G_{\text{mix}} = -1938\,\text{J}$
c. $a_{\text{C}} = 0.382, \gamma_{\text{C}} = 1.31$

6.49
$\Delta H_{\text{diff}} = -20.28\,\text{kJ mol}^{-1}$

6.63
$x(60°\text{C}) = 0.637$

6.65
$\Delta T = 0.0748\,\text{K}$

6.67
a. $\Delta T_{\text{b}} = 0.0788\,\text{K}$
b. $\Delta T_{\text{b}} = 0.0786\,\text{K}$ (0.3% difference)
c. $\Delta T_{\text{b}} = 0.0789\,\text{K}$ (0.1% difference)

6.69
$M_2 = 16.9\,\text{kg mol}^{-1}$

6.71
$T_f = 254.2\,\text{K}$

6.73
a. $\Pi = 3.63 \times 10^5\,\text{Pa} = 3.58\,\text{atm}$
$h = 36.3\,\text{m}$
b. $\Pi = 3.75 \times 10^5\,\text{Pa} = 3.70\,\text{atm}$
$h = 37.5\,\text{m}$

6.75
$T' = 250.8\,\text{K} = -22.3°\text{C}$

6.77
$\Pi = 1458\,\text{Pa} = 0.0144\,\text{atm}$
$\Delta T_f = 1.13 \times 10^{-6}\,\text{K}$

6.79
a. FALSE
b. FALSE
c. FALSE
d. TRUE
e. TRUE
f. TRUE
g. TRUE
h. TRUE
i. TRUE
j. TRUE

6.81
a. $K_f = 3.14\,\text{K kg mol}^{-1}$
b. $T_f = 259.9\,\text{K}$
c. $T_f = 273.15\,\text{K} - 0.300\,\text{K} = 272.85\,\text{K}$
e. 2.94 parts of ethylene glycol to 1 part of water by volume

Chapter 7 Exercises

7.1
a. $\Delta G° = 20.661\,\text{kJ mol}^{-1}$
b. $\Delta H° = 71.488\,\text{kJ mol}^{-1}$
$\Delta S° = 170.473\,\text{J K}^{-1}\,\text{mol}^{-1}$
c. $\Delta G° = 20.661\,\text{kJ mol}^{-1}$
d. $\Delta G° = 20.665\,\text{kJ mol}^{-1}$

7.3
$$\left(\frac{\partial G}{\partial \xi}\right)_{\text{T,P}} = 7527\,\text{J mol}^{-1}$$

7.4
a. $P(\text{C}_3\text{H}_8) = 7.4 \times 10^{-58}\,\text{Pa}$
$P(\text{O}_2) = 3.7 \times 10^{-57}\,\text{Pa}$
b. volume per molecule $= 5.5 \times 10^{36}\,\text{m}^3$

7.5
$\Delta G^{\circ(\text{II})} = -558.518\,\text{kJ mol}^{-1}$

7.6
$V = 1.06 \times 10^{47}\,\text{m}^3$

7.7
$m(\text{H}^+) = m(\text{OH}^-) = 1.004 \times 10^{-7}\,\text{mol kg}^{-1}$

7.8
pH = 11.13

7.9
pH = 2.38

7.10
pH = 1.63

7.11
pH = 5.13

7.12
$\gamma_\pm = (\gamma_+^3 \gamma_-^2)^{1/5}$
$m_\pm = (m_+^3\, m_-^2)^{1/5} = m(3^3 2^2)^{1/5} = 2.55085\,\text{m}$

7.14
a. pH = 3.91
b. pH = 3.91

7.18
$K(1000\,\text{K}) = 0.098$

7.19
b. $K = 14.8$
$\Delta G° = -8.37\,\text{kJ mol}^{-1}$

7.20
$\alpha = -0.4826$ (unacceptable)

7.21
$\Delta\text{pH} = 6.47$

7.22
$(\partial G/\partial \xi)_{\text{T,P}} = -37.3\,\text{kJ mol}^{-1}$

7.23
$c(\text{ATP}) = 0.00993\,\text{mol L}^{-1}$

7.24
b. $\Delta G^{\circ'} = -9.9\,\text{kJ mol}^{-1}$
$K = 54$

Chapter 8 Problems

7.1
$K = 7.51$

7.5
a. $K = 6.90 \times 10^{24}$
b. $P(O_2) = 3.3 \times 10^{-9}$ bar
$P(SO_2) = 6.6 \times 10^{-9}$ bar
$P(SO_3) = 1.000$ bar

7.7
a. $\Delta H^\circ = 0.66\,\mathrm{kJ\,mol^{-1}}$
$\Delta S^\circ = 11.85\,\mathrm{J\,K^{-1}\,mol^{-1}}$
b. $\Delta G^\circ = -2.92\,\mathrm{kJ\,mol^{-1}}$, $K = 3.248$
c. $P(HD)/P^\circ = 0.474$ bar,
$P(H_2)/P^\circ = P(D_2)/P^\circ = 0.263$ bar

7.9
a. $\Delta G^\circ = -141.782\,\mathrm{kJ\,mol^{-1}}$
b. $\Delta G^\circ = -300.125\,\mathrm{kJ\,mol^{-1}}$
c. $\Delta G^\circ = -70.692\,\mathrm{kJ\,mol^{-1}}$

7.11
a. $\Delta G^\circ = -1138.86\,\mathrm{kJ\,mol^{-1}}$
$\Delta H^\circ - T\Delta S^\circ = -1138.7\,\mathrm{kJ\,mol^{-1}}$
b. $\Delta G^\circ = 130.90\,\mathrm{kJ\,mol^{-1}}$
$\Delta H^\circ - T\Delta S^\circ = 130.87\,\mathrm{kJ\,mol^{-1}}$

7.13
a. $K = 3.30 \times 10^{199}$
b. $K = 1.17 \times 10^{-23}$

7.15
$P(NO_2) = 0.318$ bar
$P(N_2O_4) = 0.682$ bar

7.17
a. $K = 5.43 \times 10^{5}$
b. $P(N_2) = 0.01555$ atm,
$P(H_2) = 0.04665$ atm,
$P(NH_3) = 0.9378$ atm

7.19
a. $\Delta G^\circ = -162.715\,\mathrm{kJ\,mol^{-1}}$
$K = 3.2 \times 10^{28}$
b. $\Delta G^\circ = 28.644\,\mathrm{kJ\ \ mol^{-1}}$

7.21
$P = 0.111$ bar $= 11100$ Pa

7.23
a. $\Delta H^\circ = -223.94\,\mathrm{kJ\,mol^{-1}}$
$\Delta S^\circ = -216.537\,\mathrm{J\,K^{-1}\,mol^{-1}}$
$\Delta G^\circ = -159.316\,\mathrm{kJ\,mol^{-1}}$
b. $\Delta H^\circ = -753.99\,\mathrm{kJ\,mol^{-1}}$
$\Delta S^\circ = -156.63\,\mathrm{J\,K^{-1}\,mol^{-1}}$
$\Delta G^\circ = -707.79\,\mathrm{kJ\,mol^{-1}}$

7.25
a. $K = 1.77 \times 10^{-10}$
b. $m(Ag^+) = 1.34 \times 10^{-5}\,\mathrm{mol\,kg^{-1}}$

7.27
a. pH $= 1.11$ ($\gamma \approx 1$)
pH $= 1.18$
b. pH $= 2.597$ (γ assumed to equal 1)
pH $= 2.60$

7.29
pH $= 2.95$ (γ assumed to equal 1)
pH $= 2.96$

7.31
$m(HCO_3^-)/m^\circ = 1.25 \times 10^{-3}$
$m(H_2CO_3)/m^\circ = 2.86 \times 10^{-7}$

7.33
pH $= 3.75$

7.35
a. pH $= 5.22$
b. $K_b = 2.5 \times 10^{-5}$
c. pH $= 11.18$

7.37
a. pH $= 6.72$

7.39
a. $\gamma_\pm = (\gamma_+^2\gamma_-)^{1/3}$
$m_\pm = (m_+^2 m_-)^{1/3} = 4^{1/3}\,\mathrm{m}$
b. $\gamma_\pm = (\gamma_+\gamma_-^3)^{1/4}$
$m_\pm = (m_+ m_-^3)^{1/4} = 9^{1/4}\,\mathrm{m}$
c. $\gamma_\pm = (\gamma_+\gamma_-)^{1/2}$
$m_\pm = (m_+ m_-)^{1/2} = \mathrm{m}$
d. $\gamma_\pm = (\gamma_+^2\gamma_-)^{1/3}$
$m_\pm = (m_+ m_-^2)^{1/3} = 4^{1/3}\,\mathrm{m}$

7.41
a. pH $= 4.98$
b. pH $= 4.84$

7.43
a. 0.0863 mol of NaOH
b. 0.0890 mol of NaOH

7.45
a. $K = 1.80 \times 10^{-5}$
b. $\mathrm{pOH} = 4.92$
$m(\mathrm{OH}^-)m^\circ = 10^{-4.92} = 1.20 \times 10^{-5}$
c. $\mathrm{pOH} = 4.80$

7.47
a. $K(323.15\,\mathrm{K}) = 5.746 \times 10^{-14}$
b. $m(\mathrm{H}^+) = 2.397 \times 10^{-7}\,\mathrm{mol\,kg^{-1}}, \mathrm{pH} = 6.62$
c. $m(\mathrm{H}^+)/m^\circ = 3.03 \times 10^{-7}$
$\mathrm{pH} = 6.62$

7.51
a. $K_{400\mathrm{K}} = 43.6$
b. $x_{\mathrm{N_2}} = 0.121, x_{\mathrm{H_2}} = 0.363, x_{\mathrm{NH_3}} = 0.516$

7.53
a. $K = 9.59 \times 10^{-6}$
b. $K(373\,\mathrm{K}) = 2.70 \times 10^{-4}$
c. $P(\mathrm{H_2}) = P(\mathrm{CO_2}) = 0.492\,\mathrm{bar}$
$P(\mathrm{H_2O}) = P(\mathrm{CO}) = 0.00808\,\mathrm{bar}$

7.55
a. $\Delta H^\circ = 151.255\,\mathrm{kJ\,mol^{-1}}$
$\Delta G^\circ = 121.175\,\mathrm{kJ\,mol^{-1}}$
$K_{298.15\mathrm{K}} = 5.90 \times 10^{-22}$
b. $K_{1000\mathrm{K}} = 2.34 \times 10^{-3}$
c. $T = 1499\,\mathrm{K}$
d. $K_{1000\mathrm{K}} = 3.11 \times 10^{-3}$

7.57
a. $K_{750\mathrm{K}} = 9.05 \times 10^{3}$
b. $K_{750\mathrm{K}} = 9.7 \times 10^{3}$

7.59
a. $K(750\,\mathrm{K}) = 7.64 \times 10^{-12}$
b. $K(750\,\mathrm{K}) = 7.65 \times 10^{-12}$
c. $K(750\,\mathrm{K}) = 7.64 \times 10^{-12}$

7.61
$\Delta G^\circ = 1.3\,\mathrm{kJ\,mol^{-1}}$
$\Delta H^\circ = 36.5\,\mathrm{kJ\,mol^{-1}}$
$\Delta S^\circ = 122\,\mathrm{J\,K^{-1}\,mol^{-1}}$

7.63
$c(\mathrm{GlyP})/c^\circ = c(\mathrm{ADP})/c^\circ = 0.00998$
$c(\mathrm{Gly})/c^\circ = 0.00202$
$c(\mathrm{ATP})/c^\circ = 0.000017$

7.65
$\Delta\mathrm{pH} = 5.13$

7.67
a. FALSE
b. TRUE
c. TRUE
d. TRUE
e. FALSE
f. FALSE
g. FALSE

Chapter 8 Exercises

8.3
b. $E = 1.091\,\mathrm{V}$

8.6

b. number = 4950

8.7
$E = 1.1076\,\mathrm{V}$

8.8
$E = -0.0464\,\mathrm{V}$

8.9
$E^\circ(348.15\,\mathrm{K}) = 0.1899\,\mathrm{V}$

8.10
$\mathrm{pH} = 1.100$

8.12
$E^{(\mathrm{II})} - E^{(\mathrm{I})} = 0.325\,\mathrm{V}$

8.13
$K = 7.6 \times 10^{36}$

8.14
a. $K_{\mathrm{sp}} = 6.55 \times 10^{-15}$
b. volume for 1.00 mol = $45.6\,\mathrm{m^3}$
area = $0.0283\,\mathrm{m^2} = 283\,\mathrm{cm^2}$

Chapter 8 Problems

8.1
$|\nabla c| = 4 \times 10^{7}\,\mathrm{mol\,L^{-1}\,m^{-1}}$

8.3
a. $\Delta\varphi = 0.051\,\mathrm{V}$
b. $|\mathscr{E}| = 1.03 \times 10^{7}\,\mathrm{V\,m^{-1}}$

8.5
$E = 0.2333\,\mathrm{V}$

8.7
$E = 2.019\,\text{V}$

8.9
c. $E = -0.4195\,\text{V}$

8.13
c. $E^\circ = -0.5673\,\text{V}$
d. $E = 0.2994\,\text{V}$

8.15
$E = 0.083\,\text{V}$ ($\gamma_\pm$ assuming $= 1$)
$E = 0.092\,\text{V}$

8.17
a. $E^\circ = 2.041\,\text{V}$
b. $\Delta H^\circ = -571.66\,\text{kJ mol}^{-1}$
c. $E^\circ(255\,\text{K}) = 2.173\,\text{V}$

8.19
$\gamma_\pm = 0.822$

8.21
$\text{pH} = 12.88$
$E = 1.0424\,\text{V}$

8.23
a. $K_{\text{sp}} = 2.58 \times 10^{-5}$
b. $m(\text{Cl}^-)/m^\circ = 0.0598$
c. $m(\text{Pb}^{2+})/m^\circ = 0.00852$

8.25
a. $K_{\text{sp}} = 1.46 \times 10^{-51}$
b. $m(\text{S}^{2-}) = 7.15 \times 10^{-18}\,\text{mol kg}^{-1}$
c. $m(\text{S}^{2-}) = 1.12 \times 10^{-17}\,\text{mol kg}^{-1}$

8.27
$-0.7538\,\text{V} < E^\circ < -0.6444\,\text{V}$

8.29
a. $K = 1.68 \times 10^{8}$
b. $m(\text{Pb}^{2+})/m^\circ = 1.30 \times 10^{-4}$
c. $m(\text{Pb}^{2+})/m^\circ = 4.18 \times 10^{-4}$
d. $m(\text{SO}_4^{2-})/m^\circ = 2.00 \times 10^{-6}$

8.31
a. $K_{\text{sp}} = 1.42 \times 10^{-18}$
b. $K_{\text{sp}} = 1.8 \times 10^{-52}$

8.33
a. $K = 3.23 \times 10^{8}$
b. $m(\text{Ce}^{4+}) = m(\text{Cl}^-) = 0.004121\,\text{mol kg}^{-1}$
$m(\text{Ce}^{3+}) = 0.0209\,\text{mol kg}^{-1}$

8.35
$K = 3.57 \times 10^{2}$

8.37
b. $E^\circ = 1.229\,\text{V}$
c. $E^\circ = 1.229\,\text{V}$
d. $E = 1.229\,\text{V} + 0.062\,\text{V} = 1.291\,\text{V}$

8.39
a. $\Delta G^\circ = -817.903\,\text{kJ mol}^{-1}$
$E^\circ = 1.060\,\text{V}$
b. $w_{\text{max}} = 2.013 \times 10^{6}\,\text{kJ}$
c. $w_{\text{max}} = 559.2\,\text{kWh}$
d. $w_{\text{max}} = 1416\,\text{kWh}$

Chapter 9 Exercises

9.1
$\langle w \rangle = 78.4$

9.2
$\langle w^2 \rangle = 6276$
$w_{\text{rms}} = 79.2$

9.5
b. $v = 1040\,\text{m s}^{-1}$
c. $K = 7.25 \times 10^{-20}\,\text{J}$

9.8
a. $\sigma_{k_x} = 2.91 \times 10^{-21}\,\text{J}$
b. fraction $= \sqrt{2}$

9.9
probability $\approx 8 \times 10^{-5}$

9.10
a. probability $= 0.683$
b. $v'_x = 583\,\text{m s}^{-1}$
c. $v'_x = 1068\,\text{m s}^{-1}$

9.11
ratio $= 1.798 \times 10^{-6}$

9.13
$v_p = 1112\,\text{m s}^{-1}$

9.15
$v_p = 1112\,\text{m s}^{-1}$
$\langle v \rangle = 1256\,\text{m s}^{-1}$
$v_{\text{rms}} = 1363\,\text{m s}^{-1}$

9.16

$\langle v\rangle/v_p = 1.1284$

$v_{\mathrm{rms}}/v_p = 1.2247$

9.17

a. ratio = 0.103218
b. ratio = 0.103218
c. ratio = 0.103218
d. ratio = 0.109915
e. ratio = 0.109915
f. ratio = 0.109915

9.18

$N = 2.15 \times 10^{27}$

9.19

a. $N \approx 2 \times 10^{30}$ (other estimates vary)
b. amount of CO per second = $1.2 \times 10^3\ \mathrm{mol\,s^{-1}}$

9.20

$P = 0.55\ \mathrm{atm}$

9.23

a. $P = 1.018 \times 10^5\ \mathrm{Pa}$
b. $P(\mathrm{ideal}) = 1.0160 \times 10^5\ \mathrm{Pa}$
percent difference = 0.2%

9.24

a. $L = 3.44 \times 10^{-9}\ \mathrm{m}$
b. $\lambda = 1.94 \times 10^{-7}\ \mathrm{m}$

9.25

a. $\lambda_{1(2)} = 3.56 \times 10^{-7}\ \mathrm{m}$
$\lambda_{2(1)} = 8.33 \times 10^{-8}\ \mathrm{m}$
$\lambda_{1(1)} = 8.30 \times 10^{-8}\ \mathrm{m}$
$\lambda_{2(2)} = 3.56 \times 10^{-7}\ \mathrm{m}$
b. $z_{1(2)} = 1.34 \times 10^9\ \mathrm{s^{-1}}$
$z_{2(1)} = 5.34 \times 10^9\ \mathrm{s^{-1}}$
$z_{1(1)} = 5.72 \times 10^9\ \mathrm{s^{-1}}$
$z_{2(2)} = 1.25 \times 10^9\ \mathrm{s^{-1}}$
c. $Z_{12} = 2.63 \times 10^{34}\ \mathrm{s^{-1}\,m^{-3}}$
$Z_{11} = 5.63 \times 10^{34}\ \mathrm{s^{-1}\,m^{-3}}$
$Z_{22} = 3.08 \times 10^{33}\ \mathrm{s^{-1}\,m^{-3}}$
d. total collision rate = $2.10 \times 10^{33}\ \mathrm{s^{-1}}$

9.26

number ≈ 9.2

Chapter 9 Problems

9.1

a. $p(33000) = 0.09023$
$p(34000) = 0.11278$
$p(35000) = 0.13534$
$p(36000) = 0.18045$
$p(37000) = 0.14286$
$p(38000) = 0.15038$
$p(39000) = 0.09023$
$p(40000) = 0.06015$
$p(55000) = 0.01504$
$p(95000) = 0.02256$
b. median = \$36000
c. mean = \$37940
d. rms = \$39032
e. mode = \$36000

9.3

a. number = 1.000×10^{24}
b. number = $10^{1.445 \times 10^{25}}$

9.5

$z_{\max} = 5.1\ \mathrm{m}$

9.7

a. probability = 0.0003698
b. probability = 0.0003771
c. probability = 0.0007541

9.9

$\langle h\rangle = 0$

$h_{\mathrm{rms}} = 1/\sqrt{2}$

9.11

$\langle x\rangle = 7.00$

$\sigma_x = 2.449$

9.13

$\langle \cos(x)\rangle = 0.60653$

$(\cos(x))_{\mathrm{rms}} = 0.75344$

9.15

fraction ≈ $10^{-2.11\times10^{11}}$

9.17

fraction = 0.317

9.19

a. $v_{\text{esc}} = 2414\,\text{m s}^{-1}$
b. fraction $= 1.9 \times 10^{-4}$
$\Delta U = 3.335\,\text{kJ}$

9.21

a. fraction $= 0.801$
b. fraction $= 0.801$

9.23

a. $T = 8.0 \times 10^{7}\,\text{K}$
b. $\langle v \rangle = 1.30 \times 10^{6}\,\text{m s}^{-1}$
c. $T = 8.0 \times 10^{7}\,\text{K}$

9.27

a. $v_s = 352.0\,\text{m s}^{-1}$
air: $v_s = 346\,\text{m s}^{-1}$
b. $v_s = 352.0\,\text{m s}^{-1}$
c. $v_s = 931.1\,\text{m s}^{-1}$
d. ratio $= 0.741$
e. fraction $= 0.5757$

9.29

c. $\sigma_v = 187.4\,\text{m s}^{-1}$

9.31

$\langle v \rangle = 5.72 \times 10^{-10}\,\text{m s}^{-1}$

9.37

a. $F = 2.0 \times 10^{5}\,\text{N}$ (estimates will vary)
b. $m = 4.4 \times 10^{4}$ pounds (estimates will vary)

9.39

$m(\text{atmosphere}) = 5.27 \times 10^{18}\ \text{kg}$
ratio $= 8.80 \times 10^{-7}$

9.41

mass lost $= 3.24 \times 10^{-5}\,\text{kg} = 32.4\,\text{mg}$

9.43

a. $\mathcal{N}_{O_2} = 6.5 \times 10^{11}\,\text{m}^{-3}$
$\mathcal{N}_{N_2} = 2.6 \times 10^{12}\,\text{m}^{-3}$
b. total number per second $= 3.8 \times 10^{10}\,\text{s}^{-1}$

9.45

$dn/dt = 4.31 \times 10^{14}\,\text{mol s}^{-1}$

9.47

a. $P = 20.8\,\text{Pa} = 0.000205\,\text{atm}$
b. $t = 5.84 \times 10^{-6}\,\text{s}$

9.49

$t = 4.39$ hours

9.51

b. At 273 K, $r = 3.16 \times 10^{-10}\,\text{m}$
At 373 K, $r = 3.12 \times 10^{-10}\,\text{m}$
At 473 K, $r = 3.08 \times 10^{-10}\,\text{m}$

9.53

a. side of cube $= 2.28 \times 10^{-9}\,\text{m}$
b. $u_{\text{LJ}}(r) = -7.20 \times 10^{-26}\,\text{J}$
c. $u_{\text{LJ}}(\text{min}) = -1.66 \times 10^{-21}\,\text{J}$
ratio $= 4.35 \times 10^{-5}$

9.55

$P_{\text{total}} = 0.0692\,\text{atm}$
percent $N_2 = 85.3\%$
percent $O_2 = 14.7\%$
percent error $= 3.0\%$

9.57

$P - P_0 = -0.014\,\text{atm}$

9.61

$P = 14.18\,\text{Pa} = 1.40 \times 10^{-4}\,\text{atm}$

9.63

For helium	$4\varepsilon\sigma^6 = 1.59 \times 10^{-79}\,\text{J m}^6$
For neon	$4\varepsilon\sigma^6 = 8.36 \times 10^{-79}\,\text{J m}^6$
For nitrogen	$4\varepsilon\sigma^6 = 1.35 \times 10^{-77}\,\text{J m}^6$
For oxygen	$4\varepsilon\sigma^6 = 1.2 \times 10^{-77}\,\text{J m}^6$
For argon	$4\varepsilon\sigma^6 = 1.02 \times 10^{-77}\,\text{J m}^6$
For CO_2	$4\varepsilon\sigma^6 = 8.66 \times 10^{-77}\,\text{J m}^6$

9.65

At 70 K, $B_2 = -3.2 \times 10^{-4}\,\text{m}^3\,\text{mol}^{-1}$
At 140 K, $B_2 = -9.65 \times 10^{-5}\,\text{m mol}^{-1}$
At 300 K, $B_2 = -1.55 \times 10^{-5}\,\text{m mol}^{-1}$
$B_2 = 0$ at 403.5 K

9.69

a. $z_{1(2)} = 5.87 \times 10^{9}\,\text{s}^{-1}$
b. $z_{2(1)} = 2.94 \times 10^{9}\,\text{s}^{-1}$
c. number of collisions per second $= 3.54 \times 10^{33}\,\text{s}^{-1}$

9.71

a. $\lambda = 1.46 \times 10^{-4}\,\text{m}$
b. $z = 2.60 \times 10^{6}\,\text{s}^{-1}$

9.73

a. $Z_{12} = 3.66 \times 10^{34}\,\text{m}^{-3}\,\text{s}^{-1}$

9.75 $\lambda \approx 6 \times 10^{18}\,\text{m} \approx 3 \times 10^{15}$ miles

9.77
a. $\rho = 3130\,\mathrm{kg\,m^{-3}}$
b. No. of nearest neighbors ≈ 11.7

9.79
a. $v_{\mathrm{mp}} = 2.24 \times 10^{-4}\,\mathrm{m\,s^{-1}}$
$\langle v \rangle = 2.53 \times 10^{-4}\,\mathrm{m\,s^{-1}}$
$v_{\mathrm{rms}} = 2.74 \times 10^{-4}\,\mathrm{m\,s^{-1}}$
b. ratio $\approx 10^{-1.7\times10^{8}}$($\approx$0 to 64 digits)
c. $z_{2(2)} = 2.8 \times 10^{-5}\,\mathrm{s^{-1}}$
d. $Z_{22} = 1.4 \times 10^{4}\,\mathrm{m^{-3}\,s^{-1}}$
e. $z_{2(1)} = 1.8 \times 10^{17}\,\mathrm{s^{-1}}$
f. number of collisions $= 1.8 \times 10^{17}\,\mathrm{s^{-1}}$

9.81
a. rate $= 1.43 \times 10^{17}\,\mathrm{s^{-1}}$
b. rate $= 1.81 \times 10^{17}\,\mathrm{s^{-1}}$
c. rate of mass growth $= 1.12 \times 10^{-9}\,\mathrm{kg\,s^{-1}}$

9.81
a. $\langle v \rangle = 142.2\,\mathrm{m\,s^{-1}}$
b. $\langle v \rangle = 141.6\,\mathrm{m\,s^{-1}}$
c. $\lambda = 3.14 \times 10^{-8}\,\mathrm{m}$
d. $z = 5.5 \times 10^{9}\,\mathrm{s^{-1}}$

9.83
a. FALSE
b. TRUE
c. TRUE
d. TRUE
e. TRUE
f. TRUE
g. TRUE
h. FALSE
i. FALSE
j. FALSE
k. FALSE
l. TRUE

Chapter 10 Exercises

10.1
$|q| = 533\,\mathrm{J}$

10.6
speed $= 0.039\,\mathrm{m\,s^{-1}} = 3.9\,\mathrm{cm\,s^{-1}}$

10.7
$\mathscr{R} = 1.2 \times 10^{-3}$

10.8
$\mathscr{R} = 2.11 \times 10^{5}$
$(P_2 - P_1)_{\mathrm{max}} = 48.2\,\mathrm{Pa}$

10.9
a. $v = 374\,\mathrm{m\,s^{-1}}$
$\mathscr{R} = 1.86 \times 10^{6}$ (not laminar)
b. $v = 5.77\,\mathrm{m\,s^{-1}}$
$\mathscr{R} = 244$ (laminar)
c. $r_{\mathrm{max}} = 0.0547\,\mathrm{m}$

10.10
$D_{\mathrm{Ar}} = 1.41 \times 10^{-5}\,\mathrm{m^2\,s^{-1}}$

10.11
At 77.7 K, $d = 4.61 \times 10^{-10}\,\mathrm{m} = 461\,\mathrm{pm}$
At 273.2 K, $d = 346\,\mathrm{pm}$
At 353.2 K, $d = 333\,\mathrm{pm}$

10.12
$d = 269\,\mathrm{pm}$

10.13
$d = 4.18 \times 10^{-10}\,\mathrm{m}$

10.14
$\eta/\mathscr{N}mD = 5/6$
$c_{\mathrm{V}}\eta/\kappa\mathrm{m} = 2/5$
$Dc_{\mathrm{V}}\mathscr{N}/\kappa = 12/25$

10.15
a. $V_{\mathrm{m}} = 75\,\mathrm{L\,mol^{-1}}$
b. $V_{\mathrm{m}} = 51\,\mathrm{L\,mol^{-1}}$

10.16
$E_{a,\eta} = 69750\,\mathrm{J\,mol^{-1}}$

10.17
a. distance $= 2.03 \times 10^{-6}\,\mathrm{m} = 2.03 \times 10^{-4}\,\mathrm{cm}$
b. $z_{\mathrm{rms}} = 2.16 \times 10^{-4}\,\mathrm{m} = 0.0216\,\mathrm{cm}$

10.21
$r_{\mathrm{eff}}\,(\mathrm{Li^+}) = 2.38 \times 10^{-11}\,\mathrm{m} = 238\,\mathrm{pm}$

10.22
a. $\Lambda = 390.72\,\mathrm{cm^2\ ohm^{-1}\ mol^{-1}}$

Chapter 10 Problems

10.3
$|q| = 114\,\mathrm{J}$

10.5
c. $b_2 = 1.00 \times 10^{7}\,\mathrm{s}$

10.7

a. rate $= 5.6 \times 10^{-11}$ mol s^{-1}
b. $z_{\text{rms}} = 2.2$ mm

$$t = \frac{(0.100\,\text{m})^2}{2(1.4 \times 10^{-9}\,\text{m}^2\,\text{s}^{-1})} = 3.6 \times 10^6\,\text{s} = 990\,\text{hours}$$

10.9

$t = 2.5 \times 10^{-6}$ s

10.11

a. $u(0.002\,\text{m}) = 0.0382\,\text{m s}^{-1}$
b. $P_2 - P_1 = 3.65$ Pa
c. $dV/dt = 1.79 \times 10^{-6}\,\text{m}^3\,\text{s}^{-1}$
d. $\mathscr{R} = 114$

10.13

$v = 633\,\text{m s}^{-1}$
flow is apparently not laminar

10.15

$t(H_2SO_4) = 2970$ s

10.17

t(ethanol) $= 86.0$ s

10.19

a. $P_2 - P_1 = 350\,\text{N m}^{-2} = 350$ Pa
b. $\mathscr{R} = 2.3 \times 10^4$

10.23

a. $D = 1.01 \times 10^{-5}\,\text{m}^2\,\text{s}^{-1}$
b. $D = 2.65 \times 10^{-5}\,\text{m}^2\,\text{s}^{-1}$

10.27

a. $\eta = 2.70 \times 10^{-5}\,\text{kg m}^{-1}\,\text{s}^{-1}$
b. $\eta = 2.10 \times 10^{-5}\,\text{kg m}^{-1}\,\text{s}^{-1}$
c. $\eta = 2.70 \times 10^{-5}\,\text{kg m}^{-1}\,\text{s}^{-1}$

10.29

$D_{12} = 3.60 \times 10^{-5}\,\text{m}^2\,\text{s}^{-1}$

10.31

At 100°C, $d = 4.18 \times 10^{-10}\,\text{m} = 418$ pm
At 200°C, $d = 3.88 \times 10^{-10}\,\text{m} = 388$ pm

10.33

a. $D(\text{He})/D(\text{Ar}) = 8.74$
b. $\hbar(\text{He})/\hbar(\text{Ar}) = 0.876$
c. $\eta(1.00\,\text{atm})/\hbar(0.100\,\text{atm}) = 1$
d. $\kappa(\text{Ar})/\kappa(\text{Xe}) = 3.22$

10.35

$E_{a\eta} = 10.2\,\text{kJ mol}^{-1}$
$\eta_0 = 9.94 \times 10^{-4}\,\text{kg m}^{-1}\,\text{s}^{-1}$

10.37

$M_2 = 17.4\,\text{kg mol}^{-1} = 17400\,\text{g mol}^{-1}$

10.39

$r = 2.5 \times 10^{-10}$ m

10.43

a. $v_{\text{max}} = 0.0081\,\text{m s}^{-1} = 0.018\,\text{mi h}^{-1}$
b. $F = 0.00017$ N

10.45

$v = 2.9 \times 10^4\,\text{m s}^{-1}$ (unusable)
$\mathscr{R} = 2.9 \times 10^9$

10.47

a. $r = 2.7 \times 10^{-9}$ m
b. $D_2 = 9.1 \times 10^{-11}\,\text{m}^2\,\text{s}^{-1}$
c. $z_{\text{rms}} = 7.4 \times 10^{-5}\,\text{m} = 0.074$ mm
d. $v_{\text{sed}} = 3.5 \times 10^{-6}\,\text{m s}^{-1}$

10.49

a. $\dfrac{dV}{dt} = 0.628\,\text{mL s}^{-1}$
b. $P_2 - P_1 = 100$ Pa
c. $u_z(0) = 0.100\,\text{m s}^{-1}$
d. $\mathscr{R} = 99.5$, laminar

10.51

a. $|F| = 8.37 \times 10^{19}$ N
b. $m = 8.54 \times 10^{18}\,\text{kg} = 1.88 \times 10^{19}$ lb

10.53

$t_+ = 0.491$
$t_- = 0.509$

10.55

$R = 13340$ ohm

10.57

a. $t(\text{Na}^+) = 0.437$
$t(\text{Cl}^-) = 0.444$
$t(\text{Ac}^-) = 0.119$
b. $\sigma = 0.01720\,\text{ohm}^{-1}\,\text{m}^{-1}$
c. $R = 5820$ ohm

10.59

a. $z_{\text{rms}} = 5.02 \times 10^{-4}$ m
b. $r_{\text{eff}} = 7.7 \times 10^{-9}$ m
c. $M = 345\,\text{kg mol}^{-1} = 345{,}000\,\text{g mol}^{-1}$

d. $S = 8.87 \times 10^{-13}\,\mathrm{s} = 8.87$ svedberg
e. $t = 206\,\mathrm{s}$

10.63
a. TRUE
b. FALSE
c. TRUE
d. FALSE
e. FALSE
f. TRUE
g. FALSE
h. TRUE

10.65
torque = 0.0079 N m

Chapter 11 Exercises

11.2
b. $t_{1/2} = 135\,\mathrm{s}$
$\tau = 195\,\mathrm{s}$

11.3
$t = 2.4 \times 10^{9}$ yr

11.5
a. $[NO_3] = 0.026\,\mathrm{mol\,L^{-1}}$
b. $[NO_3] = 0.034\,\mathrm{mol\,L^{-1}}$
c. $k_f(\text{press}) = 9.15 \times 10^{-5}\,\mathrm{atm^{-1}\,s^{-1}}$
d. $P(NO_3) = 0.558\,\mathrm{atm}$

11.6
a. $t_{1/2} = 380$ minutes
b. $t_{1/2} = 75.8$ minutes

11.7
$t = 15t_{1/2}$

11.8
d. $t = 21t_{1/2}$

11.9
a. $t = 66.7\,\mathrm{s}$
b. $t_{1/2} = 33.3\,\mathrm{s}$

11.12
b. $t_{1/2} = 0.77\,\mathrm{s}$
c. $t_{1/2} = 0.015\,\mathrm{s}$

11.19
$[A] = 0.0986\,\mathrm{mol\,L^{-1}}$
$[B] = 0.0514\,\mathrm{mol\,L^{-1}}$

Chapter 11 Problems

11.1
a. $\text{rate} = -\dfrac{d[NO]}{dt} = 1.42 \times 10^{-4}\,\mathrm{mol\,L^{-1}\,s^{-1}}$
b. $\dfrac{d[NO]}{dt} = -1.42 \times 10^{-4}\,\mathrm{mol\,L^{-1}\,s^{-1}}$

$\dfrac{d[NOCl]}{dt} = 1.42 \times 10^{-4}\,\mathrm{mol\,L^{-1}\,s^{-1}}$

$\dfrac{d[Cl_2]}{dt} = -7.1 \times 10^{-5}\,\mathrm{mol\,L^{-1}\,s^{-1}}$

11.3
a. $k_f = 0.00276\,\mathrm{s^{-1}}$
$t_{1/2} = 251\,\mathrm{s}$
b. $k_f = 0.0361\,\mathrm{L\,mol^{-1}\,s^{-1}}$
$t_{1/2} = 278\,\mathrm{s}$

11.5
At 10.00 s, $P = 0.3437$ bar
At 100.0 s, $P = 2.30 \times 10^{-5}$ bar

11.7
a. $t_{1/2} = 3.2 \times 10^{4}\,\mathrm{s}$
b. $t = 1.05 \times 10^{5}\,\mathrm{s}$

11.9
first order, $k = 6.25 \times 10^{-4}\,\mathrm{s^{-1}}$

11.11
a. $[A] = 0.0443\,\mathrm{mol\,L^{-1}}$
b. $[A] = 0.0357\,\mathrm{mol\,L^{-1}}$

11.13
$k = 0.008284\,\mathrm{L^{1/2}\,mol^{-1/2}\,s^{-1}}$

11.15
a. $[HI] = 0.0930\,\mathrm{mol\,L^{-1}}$
b. $t_{1/2} = 1.15 \times 10^{6}\,\mathrm{s}$

11.17
a. $t_{1/2} = 1.19 \times 10^{5}\,\mathrm{s}$
b. $t = 3.6 \times 10^{5}\,\mathrm{s}$
c. $t = 2.3 \times 10^{6}\,\mathrm{s}$

11.19
The order with respect to A is 1/2
The order with respect to B is 1
The order with respect to C is 2
$k = 3.79\,\mathrm{L^{5/2}\,mol^{-5/2}\,min^{-1}}$

11.25
first order, $k_f = 1.23 \times 10^{-4}\,\mathrm{s}^{-1}$
$V(0) - V(\infty) = 14.01\,\mathrm{mL}$

11.27
a. pseudo first order, $k_f = 4.24 \times 10^{-4}\,\mathrm{s}^{-1}$
b. $P = 22.62 - 11.975 = 10.64$

11.29
$[\mathrm{A}] = 0.110\,\mathrm{mol\,L}^{-1}$
$[\mathrm{B}] = 0.890\,\mathrm{mol\,L}^{-1}$

11.41
a. $m(\mathrm{OH}^-) = M(\mathrm{NH}_4^+) = 4.10 \times 10^{-4}\,\mathrm{mol\,kg}^{-1}$
b. $k_f = 7.0 \times 10^{6}\,\mathrm{s}^{-1}$
c. $\tau = 6 \times 10^{-9}\,\mathrm{s}$

Chapter 12 Exercises

12.3
$f = 1.11 \times 10^{-11}$

12.5
For $z_2z_3 = 2, \quad f = 0.174$
For $z_2z_3 = 1, \quad f = 0.450$
For $z_2z_3 = 0, \quad f = 1$
For $z_2z_3 = -1, \quad f = 1.88$
For $z_2z_3 = -2, \quad f = 3.03$

12.6
a. $E_a = 51.2\,\mathrm{kJ\,mol}^{-1}$
b. $E_a = 78.0\,\mathrm{kJ\,mol}^{-1}$

12.7
$\varphi = 7.0 \times 10^{-3}$

12.19
$\nu_{\mathrm{min}} = 4.86 \times 10^{14}\,\mathrm{s}^{-1}$
$\lambda_{\mathrm{max}} = 6.17 \times 10^{-7}\,\mathrm{m} = 617\,\mathrm{nm}$

Chapter 12 Problems

12.1
$k = 1.2 \times 10^{-10}\,\mathrm{L\,mol}^{-1}\,\mathrm{s}^{-1}$

12.3
$d_{23} = 5.6 \times 10^{-10}\,\mathrm{m} = 560\,\mathrm{pm}$

12.5
a. $k = 1.1 \times 10^{6}\,\mathrm{m}^3\,\mathrm{mol}^{-1}\,\mathrm{s}^{-1}$
$= 1.1 \times 10^{9}\,\mathrm{L\,mol}^{-1}\,\mathrm{s}^{-1}$
b. fraction $= 1.3 \times 10^{-17}$

12.7
a. $E_a = 200.6\,\mathrm{kJ\,mol}^{-1}$
$A = 4.008 \times 10^{14}\,\mathrm{s}^{-1}$
b. $k = 1.371 \times 10^{-3}\,\mathrm{s}^{-1}$
c. $t = 1174\,\mathrm{s}$

12.9
$E_a = 170{,}000\,\mathrm{J\,mol}^{-1} = 170\,\mathrm{kJ\,mol}^{-1}$
$A = 5.98 \times 10^{9}\,\mathrm{L\,mol}^{-1}\,\mathrm{s}^{-1}$

12.11
a. $E_a = 194\,\mathrm{kJ\,mol}^{-1}$
$A = 2.38 \times 10^{12}\,\mathrm{L\,mol}^{-1}\,\mathrm{s}^{-1}$
b. $k(773\,\mathrm{K}) = 0.185\,\mathrm{L\,mol}^{-1}\,\mathrm{s}^{-1}$
c. $t_{1/2} = 686\,\mathrm{s}$

12.13
a. $E_a = 9.22 \times 10^{4}\,\mathrm{J\,mol}^{-1} = 92.2\,\mathrm{kJ\,mol}^{-1}$
$A = 4.55 \times 10^{12}\,\mathrm{s}^{-1}$
b. $k(288.15\,\mathrm{K}) = 8.77 \times 10^{-5}\,\mathrm{s}^{-1}$
c. $t_{1/2} = 7.90 \times 10^{3}\,\mathrm{s}$

12.15
a. $E_a = 213\,\mathrm{kJ\,mol}^{-1}$
$A = 3.46 \times 10^{9}\,\mathrm{L}^{-1}\,\mathrm{mol\,s}^{-1}$
b. $\varphi = 0.0077$

12.39
a. $E_a = 230\,\mathrm{kJ\,mol}^{-1}$
$A = 3.81 \times 10^{14}\,\mathrm{s}^{-1}$
b. $k(823\,\mathrm{K}) = 0.940\,\mathrm{s}^{-1}$
c. At $t = 10.00\,\mathrm{s}$, $\mathrm{P(C_2H_5Br)} = 8.3 \times 10^{-3}\,\mathrm{atm}$
At $100.0\,\mathrm{s}$, $\mathrm{P(C_2H_5Br)} = 1.5 \times 10^{-41}\,\mathrm{atm}$

12.41
b. $E_a = -6.0\,\mathrm{kJ\,mol}^{-1}$
$A = 2.3 \times 10^{33}\,\mathrm{cm}^6\,\mathrm{s}^{-1}$

12.43
a. TRUE
b. FALSE
c. FALSE
d. TRUE
e. TRUE
f. TRUE
g. FALSE
h. FALSE
i. FALSE
j. TRUE

Chapter 13 Exercises

13.12
$K_\mathrm{m} = 16.3\ \mu\mathrm{mol\,L^{-1}}$

13.24
$k_2(300\,\mathrm{K}) = 2.72 \times 10^5\ \mathrm{L\,mol^{-1}\,s^{-1}}$
$k_2(800\,\mathrm{K}) = 1.50 \times 10^7\ \mathrm{L\,mol^{-1}\,s^{-1}}$

Chapter 13 Problems

13.13
a. $K_\mathrm{m} = 5.92\ \mathrm{m\,mol\,L^{-1}}$
b. $\dfrac{d[\mathrm{P}]}{dt} = 0.148\ \mathrm{m\,mol\,L^{-1}\,s^{-1}}$

13.15
$K_\mathrm{m} = 0.000561\ \mathrm{mol\,L^{-1}}$

13.17
a. $\dfrac{d[\mathrm{P}]}{dt} = 7.98 \times 10^{-5}\ \mathrm{mol\,L^{-1}\,s^{-1}}$
b. $\left(\dfrac{d[\mathrm{P}]}{dt}\right)_\mathrm{max} = 2.11 \times 10^{-4}\ \mathrm{mol\,L^{-1}\,s^{-1}}$

13.19
c. initial rate $= 0.141\ \mu\mathrm{mol\,L^{-1}\,s^{-1}}$
d. slope $= 76.4\ \mathrm{s}$
intercept $= 4.55\ \mu\mathrm{mol^{-1}\,s}$

13.27
$\langle \mathrm{M}\rangle_n = 20000$ amu
$\langle \mathrm{M}\rangle_w = 25000$ amu

13.29
a. For $p = 0.950, t = 3.8 \times 10^4$ min
For $p = 0.990, t = 2.0 \times 10^5$ min
b. $p = 0.987$
c. $\langle \mathrm{M}\rangle_n = 1.0 \times 10^4$ amu
d. $\langle \mathrm{X}\rangle_n = 76$

13.31
$a(\mathrm{Cl^-}) = 153$

13.35
charge transfer resistance $= 5 \times 10^{12}$ ohm

13.37
$v = 657\ \mathrm{m\,s^{-1}}$

13.39
$\Delta\alpha \approx 0.456$ deg

13.41
a. FALSE
b. TRUE
c. FALSE
d. TRUE
e. TRUE

Chapter 14 Exercises

14.3
$k = 574.75\ \mathrm{N\,m^{-1}}$

14.11
$\lambda = 0.780\ \mathrm{m}$

14.13
$T = 4450\ \mathrm{K}$

14.16
b. $\lambda = 4.86407 \times 10^{-7}\ \mathrm{m}$
$\nu = 6.16798 \times 10^{14}\ \mathrm{s^{-1}}$
c. $R_\mathrm{H}(\mathrm{air}) = 1.09699 \times 10^7\ \mathrm{m^{-1}}$

Chapter 14 Problems

14.1
a. $k = 1923\ \mathrm{N\,m^{-1}}$
b. $\nu = 6.395 \times 10^{13}\ \mathrm{s^{-1}}$
c. $\nu = 6.458 \times 10^{13}\ \mathrm{s^{-1}}$

14.3
a. $\nu = 8.840 \times 10^{13}\ \mathrm{s^{-1}}$
b. $\nu = 1.501 \times 10^{13}\ \mathrm{s^{-1}}$

14.5
$\nu = 9.532 \times 10^{13}\ \mathrm{s^{-1}}$

14.7
a. $k = 965.5\ \mathrm{N\,m^{-1}}$
b. $k = 516.4\ \mathrm{N\,m^{-1}}$
c. $k = 411.5\ \mathrm{N\,m^{-1}}$
d. $k = 249.1\ \mathrm{N\,m^{-1}}$

14.9
$\nu_b = 528\ \mathrm{Hz}$
$\nu_c = 792\ \mathrm{Hz}$
$\nu_d = 1056\ \mathrm{Hz}$

14.11

a. $L = \dfrac{0.786\,\mathrm{m}}{2} = 0.393\,\mathrm{m}$

b. $L = 0.197\,\mathrm{m}$

14.15

a. $T = 580.1\,\mathrm{N}$

b. $c = 440\,\mathrm{m\,s^{-1}}$

14.17

a. $\nu = 5.087 \times 10^{14}\,\mathrm{s^{-1}}$

b. $\lambda = 3.626 \times 10^{-7}\,\mathrm{m}$

14.19

$\lambda_{\mathrm{max}} = 0.00106\,\mathrm{m}$

14.21

a. $\nu(\text{threshold}) = 1.52 \times 10^{15}\,\mathrm{s^{-1}}$
$\lambda(\text{threshold}) = 1.97 \times 10^{-7}\,\mathrm{m}$

b. $\mathscr{K}(\text{max}) = 1.95 \times 10^{-19}\,\mathrm{J}$

14.23

a. For $n = 4, v = 5.47 \times 10^5\,\mathrm{m\,s^{-1}}$
For $n = 400, v = 5.47 \times 10^3\,\mathrm{m\,s^{-1}}$

b. For $n = 4, \dfrac{v}{c} = 1.82 \times 10^{-3}$
For $n = 400, \dfrac{v}{c} = 1.82 \times 10^{-5}$

14.25

$r = 52.9\,\mathrm{m}$

14.27

For $n_2 = 2, \lambda = 1.2157 \times 10^{-7}\,\mathrm{m}$
For $n_2 = 3, \lambda = 1.0257 \times 10^{-7}\,\mathrm{m}$
For $n_2 = 4, \lambda = 9.7254 \times 10^{-8}\,\mathrm{m}$
For $n_2 = 5, \lambda = 9.4975 \times 10^{-8}\,\mathrm{m}$
For $n_2 = 6, \lambda = 9.3781 \times 10^{-8}\,\mathrm{m}$
For $n_2 = 7, \lambda = 9.3075 \times 10^{-8}\,\mathrm{m}$

14.29

number of orbits = 140

14.31

a. $\mu = 4.5547 \times 10^{-31}\,\mathrm{kg}$

b. $a(\text{positronium}) = 1.0584 \times 10^{-10}\,\mathrm{m}$

c. $E_1(\text{positronium}) = -6.80\,\mathrm{eV}$

14.33

a. $a_0 = 1.201 \times 10^{29}\,\mathrm{m}$

b. $E_1 = -4.234 \times 10^{-97}\,\mathrm{J} = -2.643 \times 10^{-78}\,\mathrm{eV}$
$E_2 = -1.058 \times 10^{-97}\,\mathrm{J} = -6.604 \times 10^{-79}\,\mathrm{eV}$
$E_3 = -4.704 \times 10^{-98}\,\mathrm{J} = -2.936 \times 10^{-79}\,\mathrm{eV}$

14.35

a. TRUE
b. FALSE
c. FALSE
d. TRUE
e. TRUE

Chapter 15 Exercises

15.1

$v = 3.38 \times 10^6\,\mathrm{m\,s^{-1}}$

15.6

a. $\nu = 4.546 \times 10^{14}\,\mathrm{s^{-1}}$
$\lambda = 6.594 \times 10^{-7}\,\mathrm{m}$

15.7

a. For the $n = 2$ state, $\nu = 3.637 \times 10^{14}\,\mathrm{s^{-1}}$
For the $n = 3$ state, $\nu = 8.183 \times 10^{14}\,\mathrm{s^{-1}}$

b. $\Delta\nu = 4.546 \times 10^{14}\,\mathrm{s^{-1}}$

15.8

a.

state	E divided by $\dfrac{h^2}{8ma^2}$	degeneracy
1,1,1	3	1
1,1,2; 1,2,1; 1,1,2	6	3
1,2,2; 2,1,2; 2,2,1	9	3
1,1,3; 1,3,1; 3,1,1	11	3
2,2,2	12	1

b.

state	E divided by $\dfrac{h^2}{8ma^2}$	degeneracy
1,1,1	$2\frac{1}{16}$	1
1,1,2	$2\frac{1}{4}$	1
1,1,3	$2\frac{9}{16}$	1
1,2,1; 2,1,1	$5\frac{1}{16}$	2
1,2,2; 2,1,2	$5\frac{1}{4}$	2
1,2,3; 2,1,3	$5\frac{9}{16}$	2

2,2,1	$8\frac{1}{16}$	1
2,2,2	$8\frac{1}{4}$	1
2,2,3	$8\frac{9}{16}$	1
2,3,1; 3,2,1	$13\frac{1}{16}$	2
2,3,2; 3,2,2	$13\frac{1}{4}$	2
3,3; 3,2,3	$13\frac{9}{16}$	2
3,3,1	$18\frac{1}{16}$	1
3,3,2	$18\frac{1}{4}$	1
3,3,3	$18\frac{9}{16}$	1

Chapter 15 Problems

15.1

$v_{\mathrm{rms}} = 432.8\ \mathrm{m\,s^{-1}}$
$\lambda = 2.307 \times 10^{-11}\ \mathrm{m}$

15.3

$v_{\mathrm{p}} = 2224\ \mathrm{m\,s^{-1}}$
$\lambda = 1.78 \times 10^{-10}\ \mathrm{m}$

15.9

a. $E_1 = 1.247 \times 10^{-19}\ \mathrm{J}$
$E_2 = 4.989 \times 10^{-19}\ \mathrm{J}$
$E_3 = 1.1226 \times 10^{-18}\ \mathrm{J}$
b. $\nu = 9.41 \times 10^{14}\ \mathrm{s^{-1}}$
$\lambda = 319\ \mathrm{nm}$

15.13

number of nodes $= 3.4 \times 10^{35}$
$\lambda = 5.4 \times 10^{-35}\ \mathrm{m}$

15.15

a. $E_{111} = 1.81 \times 10^{-19}\ \mathrm{J}$
$E_{211} = 3.62 \times 10^{-19}\ \mathrm{J}$
b. $g_{111} = 1$, $g_{211} = 3$
c. $\nu = 2.73 \times 10^{14}\ \mathrm{s^{-1}}$
$\lambda = 1.10 \times 10^{-6}\ \mathrm{m}$

15.17

$\lambda = 1.34 \times 10^{-7}\ \mathrm{m}$

15.19

b. $\psi_2(x_t) = 0.39238a^{1/4}$
c. $\psi_2(x_t)^2 = 3.2347 \times 10^{10}\ \mathrm{m^{-1}} = 3.2347\ \text{Å}^{-1}$

15.23

b. Relative maxima at $x = 0$ and $x = \pm\sqrt{\frac{5}{2a}}$
Relative minima at $x = \pm\sqrt{\frac{1}{2a}}$
c. Relative maxima at $x = 0$ and $x/x_t = \pm\sqrt{1/2}$
Relative minima at $x/x_t = \sqrt{1/10}$
d. At $x = \pm\sqrt{\frac{5}{2a}}$, $\psi_2^2 = 0.37049\sqrt{a}$
At $x = 0$, $\psi_2^2 = 0.28209\sqrt{a}$

15.25

b.

v_1, v_2 values	$E/h\nu$	degeneracy
0,0	1	1
1,0; 0,1	2	2
1,1; 0,2; 2,0	3	3
1,2; 2,1; 0,3; 3,0	4	4
2,2; 1,3; 3,1; 0,4; 4,0	5	5
2,3; 3,2; 4,1; 1,4; 0,5; 5,0	6	6
3,3; 2,4; 4,2; 5,1; 1,5; 0,6; 6,0	7	7
3,4; 4,3; 2,5; 5,2; 1,6; 6,1; 0,7; 7,0	8	8
4,4; 3,5; 5,3; 2,6; 6,2; 1,7; 7,1; 0,8; 8,0	9	9
4,5; 5,4; 3,6; 6,3; 2,7; 7,2; 1,8; 8,1; 0,9; 9,0	10	10
5,5; 4,6; 6,4; 3,7; 7,3; 2,8; 8,2; 1,9; 9,1; 0,10; 10,0	11	11

15.27

a. $\mu = 1.653 \times 10^{-27}\ \mathrm{kg}$
$\mu/m_{\mathrm{H}} = 0.9877$
b. $k = 411.8\ \mathrm{N\,m^{-1}}$

15.31

$\lambda = 1.6629 \times 10^{-9}\ \mathrm{m}$

15.33

a. FALSE
b. FALSE
c. TRUE
d. TRUE
e. TRUE
f. FALSE
g. FALSE

h. FALSE
i. TRUE
j. FALSE
k. TRUE
l. TRUE
m. TRUE
n. FALSE

Chapter 16 Exercises

16.6
$\langle x\rangle = \frac{a}{2}$

16.7
ratio = 0.36788

16.8.
Probability ≈ 0

16.10
b. $\langle E\rangle = \frac{3}{2}h\nu$
$\sigma_E^2 = 0$

16.11
$p_0 = 1/2$ and $p_1 = 1/2$ for both examples

16.14
$\Delta t \geq 5 \times 10^{-14}$ s

Chapter 16 Problems

16.23
$\langle \mathscr{V}\rangle = \frac{3}{4}h\nu = \frac{1}{2}E_1$

16.27
a. For $n = 1$, $\langle p_x^2\rangle = \frac{h^2}{4a^2}$
For $n = 2$, $\langle p_x^2\rangle = \frac{h^2}{a^2}$
For $n = 3$, $\langle p_x^2\rangle = \frac{9h^2}{4a^2}$
b. $\langle p_x^2\rangle = \frac{h^2 n^2}{4a^2}$
c. $\lim_{n\to\infty} \langle p_x^2\rangle \to \infty$

16.29
a. $z_t = \sqrt{\frac{3}{a}}$
c. Probability = 0.12666

16.33
a. $\Delta p_x \geq 5.27 \times 10^{-26}\ \mathrm{kg\,m\,s^{-1}}$
$\Delta v_x \geq 5.79 \times 10^4\ \mathrm{m\,s^{-1}}$
b. least upper bound = $1.38 \times 10^6\ \mathrm{m\,s^{-1}}$
greatest lower bound = $1.27 \times 10^6\ \mathrm{m\,s^{-1}}$

16.35
a. $\sigma_x\sigma_p = 5.989 \times 10^{-35}$ J s
c. $\sigma_x\sigma_{px} = 1.7614 \times 10^{-34}$ J s
d. $\sigma_x\sigma_{px} = 2.7706 \times 10^{-34}$ J s

16.39
d. $\langle E\rangle = 2.50\,E_1 = \frac{5h^2}{16ma^2}$
$\sigma_{\mathrm{E}} = 1.50\,E_1 = \frac{3h^2}{16ma^2}$
e. Same as part d
f. Same as part d

16.45
a. $\langle p_x\rangle = \frac{1}{3}\hbar a$
$\sigma_{p_x} = \sqrt{\frac{8}{9}}\hbar a$
b. $\hbar$a and $-\hbar$a

16.47
a. TRUE
b. FALSE
c. TRUE
d. TRUE
e. TRUE
f. FALSE
g. TRUE
h. TRUE
i. TRUE
j. TRUE

Chapter 17 Exercises

17.4
eigenvalue = 0

17.8
percentage error = 0.054%

17.13
$\langle \frac{1}{r} \rangle = 1.89 \times 10^{10}\,\mathrm{m}^{-1}$
$\langle \mathscr{V} \rangle = 4.36 \times 10^{-18}\,\mathrm{J}$

17.15
$v_{\mathrm{rms}} = 2.012 \times 10^{8}\,\mathrm{m\,s}^{-1}$
67% of the speed of light

Chapter 17 Problems

17.1

Distance from the nucleus to the center of mass $= 5.44 \times 10^{-14}\,\mathrm{m}$
Distance from the electron to center of mass $= 9.995 \times 10^{-11}\,\mathrm{m}$

17.3
$x = 449.5\,\mathrm{km}$

17.9
$\langle \theta \rangle = \frac{\pi}{2} = 1.5708$ radians $= 90.00°$
$\sigma_\theta = 0.68367$ radians $= 39.171°$

17.11
a. $\langle \phi \rangle = \pi = 180°$
$\sigma_\phi = 1.94676 = 111.541°$
b. $\langle \phi \rangle = \pi = 180°$
$\sigma_\phi = 1.6703 = 95.701°$

17.13
$\langle r \rangle_{2s} = \frac{6a}{Z}$
$\langle r \rangle_{2p} = \frac{5a}{Z}$

17.15
For $b = a$: probability $= 0.3233 = 32.33\%$
For $b = 2a$: probability $= 0.7619 = 76.19\%$
For $b = 3a$: probability $= 0.9380 = 93.80\%$

17.17
$1s$: $r_{\mathrm{max}} = a = 5.2947 \times 10^{-11}\,\mathrm{m}$
$2s$: $r_{\mathrm{max}} = 5.23606a = 2.7724 \times 10^{-10}\,\mathrm{m}$
$2p$: $r_{\mathrm{max}} = 4a = 2.1179 \times 10^{-10}\,\mathrm{m}$

17.21
$\lambda = 91.176\,\mathrm{nm}$

17.23
$\langle p_x \rangle = 0$
$\langle p_x^2 \rangle = 1.32228 \times 10^{-48}\,\mathrm{kg}^2\,\mathrm{m}^2\,\mathrm{s}^{-2}$

17.25
For $Z = 2$, $\langle \mathscr{K} \rangle = 8.7148 \times 10^{-18}\,\mathrm{J}$
For $Z = 3$, $\langle \mathscr{K} \rangle = 1.9608 \times 10^{-17}\,\mathrm{J}$
For $Z = 4$, $\langle \mathscr{K} \rangle = 3.4859 \times 10^{-17}\,\mathrm{J}$

17.33
For $l = 1$: ratio $= 1.4142\ldots$
For $l = 2$: ratio $= 1.2247\ldots$
For $l = 3$: ratio $= 1.1547\ldots$
For $l = 4$: ratio $= 1.1180\ldots$

17.35
For $Z = 1$, $\langle r \rangle = \frac{3a}{2} = 7.942 \times 10^{-11}\,\mathrm{m}$
For $Z = 2$, $\langle r \rangle = \frac{3a}{4} = 3.971 \times 10^{-11}\,\mathrm{m}$
For $Z = 3$, $\langle r \rangle = \frac{3a}{6} = 2.647 \times 10^{-11}\,\mathrm{m}$

17.37
$r_{\mathrm{max}} = 4a = 2.1179 \times 10^{-10}\,\mathrm{m}$

17.39
a. $\nu = 2.466 \times 10^{15}\,\mathrm{s}^{-1}$
b. $\frac{d\phi_{\mathrm{node}}}{dt} = 1.5495 \times 10^{16}$ radians s^{-1}
$= 2.466 \times 10^{15}$ revolutions s^{-1}
c. $\omega = 2.580 \times 10^{15}$ radians s^{-1}
d. $v = 5.464 \times 10^{5}\,\mathrm{m\,s}^{-1}$

17.41
The smallest angle $= 9.7356°$
The largest angle $= 170.264°$

17.43
a. $\lambda = 3.368 \times 10^{-10}\,\mathrm{m}$
b. ratio to the circumference $= 1.012$

17.45
$\langle L_z \rangle = 0$
$\sigma_{\mathrm{L}_z} = \hbar$

17.47
$\langle L_x \rangle = 0$
$\langle L_x^2 \rangle = 0$
$\langle L_y^2 \rangle = \hbar^2$

17.49
a. 5
b. 4
c. 0
d. 0

17.51
a. TRUE
b. FALSE
c. FALSE
d. TRUE
e. TRUE
f. FALSE
g. FALSE

Chapter 18 Problems

18.1
a. $\mathscr{V}_{ee} = 2.307 \times 10^{-18}$ J
$\mathscr{V}_{en} = -1.846 \times 10^{-17}$ J
b. $\mathscr{V}_{ee} = 4.614 \times 10^{-18}$ J
$\mathscr{V}_{en} = -1.846 \times 10^{-17}$ J

18.5
a. $\langle \mathscr{K} \rangle = 1.7430 \times 10^{-17}$ J
b. $\langle \mathscr{V} \rangle = -3.4859 \times 10^{-17}$ J
c. $\langle E \rangle = -1.7430 \times 10^{-17}$ J

18.9
The terms are ^3F, ^1F, ^3D, ^1D, ^3P, and ^1P

18.11
$S_y = \pm 1.633\hbar$ and $S_z = 0$
$S_z = 0$ and $S_y = 0$

18.19
The terms are $^4\mathrm{P}$, $^2\mathrm{P}$, and $^2\mathrm{P}$

18.21
The terms are $^2\mathrm{P}_{1/2}$ and $^2\mathrm{P}_{3/2}$

18.25
a. The terms are $^1\mathrm{D}$, $^3\mathrm{P}$, and $^1\mathrm{S}$. The $^3\mathrm{P}$ term is the lowest in energy
b. The terms are $^1\mathrm{D}$, $^3\mathrm{P}$, and $^1\mathrm{S}$. The $^3\mathrm{P}$ term is the lowest in energy

18.27
a. $^1\mathrm{S}$
b. $^3\mathrm{S}$ and $^1\mathrm{S}$
c. $^5\mathrm{S}$, $^3\mathrm{S}$, $^3\mathrm{S}$, $^3\mathrm{S}$, $^1\mathrm{S}$, and $^1\mathrm{S}$

18.29
a. 15
b. 28
c. 2

18.31
a. 5
b. 4
c. 0
d. 0

Chapter 19 Exercises

19.3
$E_1^{(0)} = 1.506 \times 10^{-20}$ J
$E_1^{(1)} = 3.268 \times 10^{-21}$ J

19.5
a. Be: $^1\mathrm{S}_0$
b. B: $^2\mathrm{P}_{1/2}$
c. C: $^3\mathrm{P}_0$
d. O: $^3\mathrm{P}_2$
e. F: $^2\mathrm{P}_{3/2}$

Chapter 19 Problems

19.3
$W_{\min} = 0.19758\dfrac{h^2}{ma^2}$, too high by about 58%

19.5
$$W_{\min} = \frac{1}{2}h\nu - 1.086 \times 10^{-54}\ \mathrm{J}$$
$$= 3.0945 \times 10^{-20}\ \mathrm{J} - 2.33 \times 10^{-55}\ \mathrm{J}$$

19.7
$W_{\min} = \dfrac{h^2}{6ma^2}$, 33.3% too high

19.9
$$W_{\min} = (0.66065)\left(\frac{c\hbar^4}{m^2}\right)^{1/3}$$

19.11
$W_{\min} = -1.3624 \times 10^{-18}$ J

19.15
b. $W_{\min} = 1.67029h\nu$

19.19

a. $E^{(1)} = 8.011 \times 10^{-20}$ J
$E^{(0)} = 6.025 \times 10^{-20}$ J

b. $E^{(1)} = 8.011 \times 10^{-22}$ J
$E^{(0)} = 6.025 \times 10^{-20}$ J

19.21

$E = E^{(0)+}E^{(1)} = 4.37 \times 10^{-20}\,\mathrm{J} + 1.73 \times 10^{-24}\,\mathrm{J}$

19.25

The terms are ^{3}D and ^{1}D

19.27

For $Z = 1.776$, $\langle r\rangle_{2s} = 179$ pm
For $Z = 2.686$, $\langle r\rangle_{2s} = 118$ pm

19.29

a. Fe: $[\mathrm{Ar}](4s)^2(3d)^6$
b. Rn: $[\mathrm{Xe}](6s)^2(4f)^{14}(5d)^{10}(6p)^6$
c. Tc: $[\mathrm{Kr}](5s)^2(4d)^5$
d. Rb: $[\mathrm{Kr}](5s)^1$

19.31

a. ^4S
b. ^3P
c. ^7S
d. ^5D

19.33

a. $^7D_5$
b. $^1S_0$
c. $^4S_{3/2}$
d. $^2S_{1/2}$

19.37

H, He, Li, Be, N, and Ne

19.39

a. Fe^{3+}: $[\mathrm{Ar}](3d)^5$
V : $[\mathrm{Ar}](4s)^2(3d)^3$

b. Fe^{3+}: ^6S
V : ^4F

19.41

a. $E_1^{(0)} + \mathrm{E}_1^{(1)} = \dfrac{h^2}{8ma^2} + \dfrac{ba}{2}$

b. $W = \dfrac{h^2}{8ma^2} + \dfrac{ba}{2}$

c. $W = \dfrac{7h^2}{4\pi^2 ma^2} + \dfrac{5ba}{8}$

d. $W = \dfrac{\hbar^2}{2ma^2}\left(\dfrac{n(2n+2)(2n+3)}{2(2n-1)}\right) + ba\left(\dfrac{2n+1}{2n+4}\right)$

e. By the formula of part a, $W = 5.225 \times 10^{-20}$ J
By the formula of part c, $W = 7.546 \times 10^{-20}$ J

f. For $n = 1$, $W = 5.304 \times 10^{-20}$ J

19.43

b. $E^{(0)} = 6.025 \times 10^{-20}$ J
$E^{(1)} = 4.24 \times 10^{-21}$ J

19.47

a. FALSE
b. FALSE
c. FALSE
d. TRUE
e. FALSE
f. TRUE
g. FALSE
h. TRUE
i. FALSE
j. FALSE
k. TRUE

Chapter 20 Exercises

20.1

a. $\widehat{i}(1,2,3) = (-1,-2,-3)$
b. $\widehat{\sigma}_h(4,-2,-2) = (4,-2,2)$
c. $\widehat{\sigma}_{vyz}(7,-6,3) = (-7,-6,3)$

20.2

a. $\widehat{C}_{4x}(1,2,3) = (1,-3,2)$
b. $\widehat{C}_{3y}(1,1,0) = (-0.500, 1, -0.866)$

20.16

b. $\Psi_{4\sigma} = -1.34\Psi_{2\mathrm{sp}(1)\mathrm{Li}} + 1.24\Psi_{1\mathrm{sH}}$

20.19

a. $\mu = 1.807 \times 10^{-29}$ Cm $= 5.418$ Debye

20.20

a. $|X_\mathrm{O} - X_\mathrm{C}| = 1.1$ (Table value = 1.0)
b. $|X_\mathrm{Cl} - X_\mathrm{C}| = 0.6$ (Table value = 0.5)

20.21

a. polar covalent
b. polar covalent
c. polar covalent
d. primarily ionic
f. pure covalent

Chapter 20 Problems

20.1
$\widehat{C}_{2z}$

20.3
$\psi_{2py}(r, \theta, \phi)$

20.11
a. $2px$
b. $2py$

20.15
a. $^1\Sigma$
b. $^1\Sigma$ and $^3\Sigma$

20.17
$^3\Sigma_u^+$ and $^3\Pi_u$

20.19

	bond order	unpaired electrons
a.	3/2	1
b.	5/2	1
c.	5/2	1

20.33
41.3% ionic
$c_I = 0.643$
$c_C = 0.766$

20.35
a. $|X_C - X_N| = 0.63$ (Table value = 0.5)
b. $|X_C - X_F| = 1.58$ (Table value = 1.5)

20.37
a. $|X_H - X_N| = 1.35$ (Table value = 0.9)
b. $|X_H - X_F| = 1.68$ (Table value = 1.9)

20.41
a. FALSE
b. FALSE
c. TRUE
d. TRUE
e. FALSE
f. FALSE
g. FALSE
h. TRUE
i. FALSE

Chapter 21 Exercises

21.1

E	1
i	−1
σ_h	−1
$C_{\infty z}$	1
σ_v	1
C_2	−1

21.13
60% of a bond length

21.14

	$\widehat{E}$	$\widehat{C}_2$	$\widehat{\sigma}_x$	$\widehat{\sigma}_y$
O1s	1	1	1	1
O2s	1	1	1	1
O2px	1	−1	1	−1
O2py	1	−1	−1	1
O2pz	1	1	1	1
a_1	1	1	1	1
b_2	1	−1	−1	1

21.16
$x' = 1$
$y' = 0.23205$
$z' = -3.59308$

21.17
a. $E, C_3, C_3^2,$ and $3\sigma_v$
b. $E, C_3, C_3^2, 3\sigma_v, 3C_2, \sigma_h, S_3$

21.19
a. $XeOF_4$
b. PH_3, SO_3^{2-}, XeO_3
c. BH_3

21.20
a. C_{2v}
b. C_{2h}
c. C_{2v}

Chapter 21 Problems

21.31
$W = \alpha + 2\beta, \alpha - \beta,$ and $\alpha - \beta$

21.33
For benzene, $\beta = -5.5 \times 10^{-19}\,\text{J} = -3.4\,\text{eV}$
For 1,3-butadiene, $\beta = -7.4 \times 10^{-19}\,\text{J} = -4.6\,\text{eV}$

21.37
$\frac{1}{\lambda} = 2.23 \times 10^6\,\mathrm{m}^{-1} = 2.23 \times 10^4\,\mathrm{cm}^{-1}$

21.39
$\lambda = 7.89 \times 10^{-8}\,\mathrm{m} = 0.789\,\mathrm{nm}$

21.41
$C_2, S_2, \sigma_\mathrm{h}, i$

21.43
$E, 2C_6, 2C_3, C_2, C_2^{'}, 3C_2^{''}, i, 2S_3, 2S_6, \sigma_\mathrm{h}, 3\sigma_d, 3\sigma_v$

21.45
$2\sigma_v, C_2, S_4$

21.49
$\widehat{\sigma}_\mathrm{h}$

21.51
$\widehat{E}, \widehat{C}_2$ and two $\widehat{\sigma}_v'$, s. C_{2_v}

21.53
C_3, three C_2''s, $3\sigma_v'$'s, and σ_h. D_{3h}

21.57
a. D_2h
b. C_2v
c. D_2h

21.59
S_2

21.61
$HClO_4$

21.85
$Q_\mathrm{Cl} = -2.90 \times 10^{-20}\,\mathrm{C} = -0.181e$
$Q_\mathrm{H} = 9.7 \times 10^{-21}\,\mathrm{C} = 0.060e$

21.89
a. TRUE
b. FALSE
c. FALSE
d. TRUE
e. TRUE

Chapter 22 Exercises

22.1
$\Delta E = 7.55 \times 10^{-41}\,\mathrm{J} = 4.71 \times 10^{-22}\,\mathrm{eV}$

22.2
$\nu = 3.640 \times 10^{11}\,\mathrm{s}^{-1} = 1.820 \times 10^{11}\,\mathrm{Hz}$
$\lambda = 8.236 \times 10^{-4}\,\mathrm{m} = 0.8236\,\mathrm{mm}$

22.6
J must be even

22.8
a. $\sigma = 3$
b. $\sigma = 2$
c. $\sigma = 12$

22.9
ratio $= 3.3 \times 10^{-173}$

22.10
a. $J_\mathrm{mp} = 2$
b. $J_\mathrm{mp} = 46$

22.11
ratio $= 0.539$

Chapter 22 Problems

22.1
$\Delta E = 9.835 \times 10^{-41}\,\mathrm{J} = 6.14 \times 10^{-22}\,\mathrm{eV}$

22.3
$n_x = 3.087 \times 10^9$

22.5
a. $n = 9.07 \times 10^9$
b. $\Delta E = 4.57 \times 10^{-31}\,\mathrm{J}$
$\frac{\Delta E}{E} = 7.36 \times 10^{-11}$
c. ratio $= 3.43 \times 10^{-13}$

22.7
a. $\mu = 8.36312 \times 10^{-28}\,\mathrm{kg}$
b. $k = 574.8\,\mathrm{J\,m}^{-2}$

22.9
$J = 10, g_\mathrm{J} = 21$

22.11
$\nu(\mathrm{HD}) = 1.14278 \times 10^{14}\,\mathrm{s}^{-1}$

22.13
a. $\lambda = 4.6737 \times 10^{-6}\,\mathrm{m} = 4.6737\,\mu\mathrm{m}$
$\nu = 6.4144 \times 10^{13}\,\mathrm{Hz}$
b. $\lambda = 4.6743 \times 10^{-4}\,\mathrm{cm} = 4.6743\,\mu\mathrm{m}$
c. $\lambda = 4.6169 \times 10^{-4}\,\mathrm{cm} = 4.6169\,\mu\mathrm{m}$

22.15

$\frac{D_e}{hc} \approx 42320\,\text{cm}^{-1}$

22.17

a. $\lambda = 0.29332\,\text{cm}$
$\nu = 1.02205 \times 10^{11}\,\text{s}^{-1}$

b. $\lambda = 0.14666\,\text{cm}$
$\nu = 2.0441 \times 10^{11}\,\text{s}^{-1}$

22.19

J must be odd
All values of J occur with $^{16}O^{17}O$

22.21

$I = 7.1664 \times 10^{-46}\,\text{kg m}^2$

22.23

a. $\sigma = 2$
b. $\sigma = 1$
c. $\sigma = 24$

22.25

a. oblate symmetric top
b. asymmetric top
c. spherical top

22.27

a. asymmetric top, $\sigma = 2$
b. linear, $\sigma = 1$
c. asymmetric top, $\sigma = 1$
d. asymmetric top, $\sigma = 2$
e. prolate symmetric top, $\sigma = 6$
f. prolate symmetric top, $\sigma = 3$

22.29

a. 6
b. 4
c. 12
d. 12
e. 18
f. 18

22.31

a. 30
b. 18
c. 18
d. 12
e. 7
f. 12

22.35

17 normal vibrational modes

22.37

a. $I_A = I_B = 2.96 \times 10^{-45}\,\text{kg m}^2$
$I_C = 4.92 \times 10^{-45}\,\text{kg m}^2$

b. $E_{1,1} = 3.01 \times 10^{-24}\,\text{J}$

c. population ratio = 2.9978

22.39

a. 30
b. 7 (linear)
c. 12
d. 18
e. 72
f. 7 (linear)

22.41

$I_A = I_B = I_C = 5.78 \times 10^{-45}\,\text{kg m}^2$
$E_1 = 1.92 \times 10^{-24}\,\text{J}$
$g_1 = 9$

22.45

a. ratio $= 5.128 \times 10^{-10}$
b. ratio $= 3.675 \times 10^{-8}$
c. ratio $= 6.18 \times 10^{-7}$

22.47

a. ratio $= 1.449 \times 10^{-6}$
b. ratio $= 1.542 \times 10^{-6}$
c. ratio $= 3.01 \times 10^{-5}$
d. ratio $= 9.42 \times 10^{-5}$

22.49

For *ortho*-hydrogen, $J_{mp} = 1$
For *para*-hydrogen, $J_{mp} = 0$

22.51

a. $E_{1,1,1} = 2.891 \times 10^{-23}$ J, degeneracy = 1
$E_{2,1,1} = 5.782 \times 10^{-23}$ J, degeneracy = 3
$E_{2,2,1} = 8.673 \times 10^{-23}$ J, degeneracy = 3

b. $\nu = 4.36 \times 10^{10}\,\text{s}^{-1}$
$\lambda = 6.871 \times 10^{-3}\,\text{m} = 6.87\,\text{mm}$

22.53

a. For HF, $k = 965\,\text{N m}^{-1}$
For HI, $k = 314\,\text{N m}^{-1}$

22.55

a. FALSE
b. TRUE
c. FALSE
d. FALSE
e. TRUE
f. FALSE
g. TRUE
h. FALSE
i. TRUE
j. TRUE
k. FALSE

Chapter 23 Exercises

23.1

a. $E_{\text{photon}} = 1.99 \times 10^{-23}\,\text{J}$
$E_{\text{einstein}} = 12.0\,\text{J}\,\text{mol}^{-1}$
b. $E_{\text{photon}} = 6.62 \times 10^{-20}\,\text{J}$
$E_{\text{einstein}} = 3.99 \times 10^{4}\,\text{J}\,\text{mol}^{-1}$
c. $E_{\text{photon}} = 9.93 \times 10^{-19}\,\text{J}$
$E_{\text{einstein}} = 5.98 \times 10^{5}\,\text{J}\,\text{mol}^{-1}$
d. $E_{\text{photon}} = 1.99 \times 10^{-15}\,\text{J}$
$E_{\text{einstein}} = 1.20 \times 10^{9}\,\text{J}\,\text{mol}^{-1}$

23.2

$N_2/N_1 = 3.2 \times 10^{-173}$

23.3

For $2 \rightarrow 1, \lambda = 121.568\,\text{nm}$
For $3 \rightarrow 2, \lambda = 656.467\,\text{nm}$
For $4 \rightarrow 3, \lambda = 1875.62\,\text{nm}$

23.4

For $H^{35}Cl$, $21.17\,\text{cm}^{-1}$
For $H^{37}Cl$, $21.13\,\text{cm}^{-1}$

23.5

a. $J_{\text{mp}} = 3$
b. $J_{\text{mp}} = 35$

23.7

$\lambda = 154.3\,\text{nm}$

23.8

no

23.9

$E_{\text{photon}} = 6.62 \times 10^{-19}\,\text{J}$
$E_{\text{einstein}} = 399\,\text{kJ}\,\text{mol}^{-1}$

23.10

b. For 11-*cis*-retinal, $\lambda = 7.02 \times 10^{-7}\,\text{m}$
For rhodopsin, $\lambda = 8.31 \times 10^{-7}\,\text{m}$

23.11

ν_1 Raman active $\quad$ ν_2 Raman active
ν_3 Raman active $\quad$ ν_4 Raman active
ν_5 Raman active $\quad$ ν_6 Raman active
ν_7 IR active $\quad$ ν_8 Raman active
ν_9 IR active $\quad$ ν_{10} IR active
ν_{11} IR active $\quad$ ν_{12} IR active

Chapter 23 Problems

23.1

$a = 9.34 \times 10^{3}\,\text{L}\,\text{mol}^{-1}\,\text{cm}^{-1}$

23.3

$c = 1.50 \times 10^{-4}\,\text{mol}\,\text{L}^{-1}$

23.5

$a = 39.2\,\text{L}\,\text{mol}^{-1}\,\text{cm}^{-1}$

23.7

a. $\lambda = 1.099 \times 10^{-6}\,\text{m}$

23.9

a. $\lambda = 1.3122 \times 10^{-4}\,\text{cm} = 1312.2\,\text{nm}$
b. $\lambda = 9.7201 \times 10^{-5}\,\text{cm} = 972.01\,\text{nm}$
c. $\lambda = 8.6787 \times 10^{-5}\,\text{cm} = 867.87\,\text{nm}$
d. $\lambda = 8.2014 \times 10^{-5}\,\text{cm} = 820.14\,\text{nm}$

23.11

a. $\nu = 1.8267 \times 10^{15}\,\text{s}^{-1}$
$\lambda = 1.6412 \times 10^{-7}\,\text{m} = 164.12\,\text{nm}$
b. $\nu = 9.8642 \times 10^{15}\,\text{s}^{-1}$
$\lambda = 3.0392 \times 10^{-8}\,\text{m} = 303.92\,\text{nm}$
c. $\nu = 2.9593 \times 10^{14}\,\text{s}^{-1}$
$\lambda = 1.0131 \times 10^{-6}\,\text{m} = 1.0131\,\mu\text{m}$

23.13

a. allowed
b. allowed
c. forbidden
d. forbidden

23.15

a. forbidden
b. forbidden

23.19

b. For $J = 0, \lambda = 0.2601\,\text{cm}$
For $J = 1, \lambda = 0.1301\,\text{cm}$
For $J = 2, \lambda = 0.08671\,\text{cm}$
For $J = 3, \lambda = 0.06504\,\text{cm}$

23.21

a. $\lambda_{\text{BC}} = 1.2082 \times 10^{-4}\,\text{cm} = 1.208\,\mu\text{m}$
b. splitting $= 41.912\,\text{cm}^{-1}$
c. $\lambda_{\text{P}} = 1.214 \times 10^{-4}\,\text{cm} = 1.214\,\mu\text{m}$
$\lambda_{\text{R}} = 1.202 \times 10^{-4}\,\text{cm} = 1.202\,\mu\text{m}$

23.23

$1/\lambda = 22.027\,\text{cm}^{-1}, 44.054\,\text{cm}^{-1}, 66.081\,\text{cm}^{-1}$, and so on. $J_{\text{mp}} = 2$

23.25

(a) CH_3Cl and (c) NH_3

23.27

For the fundamental band,
$$\frac{1}{\lambda_{\text{BC}}} = 2558.54\,\text{cm}^{-1}$$
For the first overtone band,
$$\frac{1}{\lambda_{\text{BC}}} = 5026.64\,\text{cm}^{-1}$$
For the second overtone band,
$$\frac{1}{\lambda_{\text{BC}}} = 7404.30\,\text{cm}^{-1}$$
For the $v = 1$ to $v = 2$ transition,
$$\frac{1}{\lambda_{\text{BC}}} = 2468.10\,\text{cm}^{-1}$$

23.29

For $J_{\text{mp}} = 2, T = 191\,\text{K}$
For $J_{\text{mp}} = 3, T = 373\,\text{K}$

23.31

c. For $J = 0, \dfrac{1}{\lambda_{\text{R}}} = 4263.6\,\text{cm}^{-1}$
For $J = 1, \dfrac{1}{\lambda_{\text{R}}} = 4267.3\,\text{cm}^{-1}$
For $J = 2, \dfrac{1}{\lambda_{\text{R}}} = 4271.0\,\text{cm}^{-1}$

23.33

For $v'' = 0$ and $v' = 0$
band origin: $\dfrac{1}{\lambda} = 77422\,\text{cm}^{-1}$
Lines at $77440\,\text{cm}^{-1}, 77456\,\text{cm}^{-1}, 77440\,\text{cm}^{-1}$ and $77377\,\text{cm}^{-1}$
For $v'' = 0$ and $v' = 1$,
band origin: $\dfrac{1}{\lambda} = 80106\,\text{cm}^{-1}$
Lines at $80124\,\text{cm}^{-1}$ $80140\,\text{cm}^{-1}, 80084\,\text{cm}^{-1}$ and $80061\,\text{cm}^{-1}$
For $v'' = 1$ and $v' = 0$,
band origin: $\dfrac{1}{\lambda} = 74431\,\text{cm}^{-1}$
Lines at $74449\,\text{cm}^{-1}, 74465\,\text{cm}^{-1}, 74409\,\text{cm}^{-1}$ and $74386\,\text{cm}^{-1}$

23.35

$712.1\,\text{cm}^{-1}$: bend
$2089.0\,\text{cm}^{-1}$: symmetric stretch
$3312.0\,\text{cm}^{-1}$: asymmetric stretch
$1412.0\,\text{cm}^{-1}$: first overtone of the bend
$2116.7\,\text{cm}^{-1}$: second overtone of the bend
$2800.3\,\text{cm}^{-1}$: is a combination band: bend and symmetric stretch
$4004.5\,\text{cm}^{-1}$: combination band: bend and asymmetric stretch
$5394\,\text{cm}^{-1}$: combination band: symmetric stretch and asymmetric stretch
$6521.7\,\text{cm}^{-1}$: first overtone of the asymmetric stretch

23.37

overtones near $1178\,\text{cm}^{-1}, 2570\,\text{cm}^{-1}$, and $4447\,\text{cm}^{-1}$
bend–symmetric stretch combination band near $1874\,\text{cm}^{-1}$
bend–asymmetric stretch combination band near $2228\,\text{cm}^{-1}$
symmetric stretch–asymmetric stretch combination band near $3508\,\text{cm}^{-1}$

23.41

a. $\nu = 7.97 \times 10^{14}\,\text{s}^{-1}$
$\lambda = 3.76 \times 10^{-7}\,\text{m} = 376\,\text{nm}$
b. $\nu = 7.24 \times 10^{14}\,\text{s} - 1$
$\lambda = 4.14 \times 10^{-7}\,\text{m} = 414\,\text{nm}$

23.43

Biphenyl, 9,10-diphenylanthracene, and *trans*-1,3-pentadiene

23.45

$r_{\text{e}} = 7.57 \times 10^{-11}\,\text{m} = 75.7\,\text{pm} = 0.757\,\text{Å}$

23.47
BF_3 and CO_2

23.49
all but CCl_4

23.53
a. No
b. No
c. Yes
d. Yes

23.55
a. $41.912\,\mathrm{cm}^{-1}$, $83.824\,\mathrm{cm}^{-1}$, $125.736\,\mathrm{cm}^{-1}$, and $167.648\,\mathrm{cm}^{-1}$
b. band center will be at $4138.3\,\mathrm{cm}^{-1}$, splitting $= 41.912\,\mathrm{cm}^{-1}$
c. slightly lower than $8276.6\,\mathrm{cm}^{-1}$
d. $125.736\,\mathrm{cm}^{-1}$, $209.56\,\mathrm{cm}^{-1}$, $293.38\,\mathrm{cm}^{-1}$, and $377.21\,\mathrm{cm}^{-1}$

23.57
a. Raman
b. emission/absorption
c. neither
d. Raman
e. Raman

23.59
a. N_2: no microwave spectrum. CO: $3.862\,\mathrm{cm}^{-1}$ $7.724\,\mathrm{cm}^{-1}$, $11.586\,\mathrm{cm}^{-1}$, and $15.448\,\mathrm{cm}^{-1}$
b. N_2: no infrared spectrum. CO: band center at $2169.8\,\mathrm{cm}^{-1}$ with splittings $7.724\,\mathrm{cm}^{-1}$
c. CO: $11.586\,\mathrm{cm}^{-1}$, $19.31\,\mathrm{cm}^{-1}$, $27.03\,\mathrm{cm}^{-1}$, and $84.76\,\mathrm{cm}^{-1}$. N_2: $11.99\,\mathrm{cm}^{-1}$, $19.98\,\mathrm{cm}^{-1}$, $27.97\,\mathrm{cm}^{-1}$, and $35.96\,\mathrm{cm}^{-1}$
d. N_2 : Q branch at $2358.6\ \mathrm{cm}^{-1}$, S branch at $2370.6\ \mathrm{cm}^{-1}$, $2378.6\ \mathrm{cm}^{-1}$, etc.
O branch at $2346.6\ \mathrm{cm}^{-1}$, $2338.6\ \mathrm{cm}^{-1}$, etc.
CO: Q branch at $2169.8\ \mathrm{cm}^{-1}$, S branch at $2181.4\ \mathrm{cm}^{-1}$, $2189.1\ \mathrm{cm}^{-1}$, etc.
O branch at $2258.2\ \mathrm{cm}^{-1}$, $2150.5\ \mathrm{cm}^{-1}$, etc.

23.61
a. $\frac{1}{\lambda_{BC}} = 2143.2\,\mathrm{cm}^{-1}$
b. $\frac{1}{\lambda} = 4259.9\,\mathrm{cm}^{-1}$
c. $\frac{1}{\lambda} = 3.844\,\mathrm{cm}^{-1}$
d. $\frac{1}{\lambda} = 7.688\,\mathrm{cm}^{-1}$

23.63
IR: yes; Raman: no

23.67
a. FALSE
b. FALSE
c. FALSE
d. TRUE
e. FALSE
f. FALSE
g. FALSE
h. FALSE
i. FALSE
k. FALSE
l. FALSE
m. FALSE
n. TRUE

Chapter 24 Exercises

24.1
b. south; $B = 3.00 \times 10^{-6}\,\mathrm{T} = 0.0300$ gauss

24.2
a. $F = 0$
b. $\mathbf{F} = \mathbf{k}(1.394 \times 10^{-22}\,\mathrm{N})$

24.3
$\mu = 2.39 \times 10^{-5}\,\mathrm{A\,m}^2$

24.4
$\nu = 1.40 \times 10^{10}\,\mathrm{s}^{-1}$
$\lambda = 2.14 \times 10^{-2}\,\mathrm{m}$

24.5
population ratio $= 0.999996575$

24.6
two lines of equal intensity

24.7
There will be a peak of area 1 with $\delta \approx 10$ ppm. There will be a peak of area 2 with a value of δ around $\delta \approx 4$. There will be a peak of area 3 around $\delta \approx 2$

Chapter 24 Problems

24.1
$I = 500\,\mathrm{A}$
$I = 3.12 \times 10^{22}$ electrons s^{-1}

24.3
$I = 7.96\,\mathrm{A}$

24.5
a. $v = 3.05 \times 10^{8}\,\mathrm{m\,s^{-1}}$
b. $\mathscr{K} = 3.3 \times 10^{-12}\,\mathrm{J}$

24.7
a. $\Delta E_{\mathrm{mag}} = 1.413 \times 10^{-30}\,\mathrm{J}$
b. $\nu = 2.132 \times 10^{3}\,\mathrm{s}^{-1}$
$\lambda = 1.406 \times 10^{5}\,\mathrm{m}$

24.9.
six lines with equal intensities

24.11
a. three lines with intensities in the ratios 1 : 2 : 1
b. five lines with intensities in the ratios 1 : 2 : 3 : 2 : 1

24.13
three lines with equal intensities

24.15
three lines with intensities in the ratios 1 : 2 : 1

24.19
ratio = 0.99853

24.21
$B_z = 12.0786\,\mathrm{T}$

24.25
two lines

24.27
a. 1,1,1-trichloroethane

24.29
$\Delta\delta = 0.0175$ ppm

24.33
a. single line
b. single line

24.41
a. Seven lines with equal intensities
b. A single line
c. Five lines with equal intensities
d. A single line without splitting

24.43
a. FALSE
b. FALSE
c. TRUE
d. TRUE
e. FALSE

Chapter 25 Exercises

25.4
$\langle \varepsilon_{\mathrm{vib}} \rangle = (0.99997)h\nu \approx h\nu$

25.5
$\langle \varepsilon_{\mathrm{vib}} \rangle = (1.0000)h\nu$

25.6
sum = 0.99218

25.7
a. fermion
b. boson
c. fermion
d. boson
e. fermion

25.8
percent error = 0.0000003%

25.10
For $N = 10$, 13.76% error and 0.05516% error
For $N = 60$, 1.537% error and 0.00074% error
For $N = 200$, 0.413% error and 0.0000483% error
For $N = 1 \times 10^{9}$, no difference to 9 significant digits

25.13
a. $z_{\mathrm{tr}} = 1.937 \times 10^{29}$
b. $z_{\mathrm{tr}} = 3.639 \times 10^{31}$

25.14
difference $= 1.705 \times 10^{-11}$

25.15
$T = -5.95 \times 10^{4}\,\mathrm{K}$

25.18
$z_{\mathrm{rot}} = 424.6$

25.20
$z_{\mathrm{vib}} = 1.095$

Chapter 25 Problems

25.1

a. 10 states

b. $p_0 = \frac{4}{10} = 0.4$

$p_1 = \frac{3}{10} = 0.3$

$p_2 = \frac{2}{10} = 0.2$

$p_3 = \frac{1}{10} = 0.1$

c. $p_0 = \frac{1}{3} = 0.3333$

$p_1 = \frac{1}{3} = 0.3333$

$p_2 = \frac{1}{3} = 0.3333$

$p_3 = 0$

25.3

a. There are 5 system states

b. Each $p_v = 0.200$

c. $p_0 = 0.250$

$p_1 = 0.250$

$p_2 = 0$

$p_3 = 0.250$

$p_4 = 0.250$

25.5

$s = 1.1114$

25.7

a. 2.02%

b. 0.00200%

25.9

$\mathscr{V} = -0.00034\,\mathrm{J}$

$\mathscr{K} = 3718\,\mathrm{J}$

25.11

$x = 1, y = 1$

$f = 0.1353$ at the constrained maximum

25.13

$x = y = 0.65327$

$f = 0.39665$ at the constrained maximum

25.15

a. $z = 8.7701 \times 10^{31}$

b. probability $= 2.54 \times 10^{-33}$

25.17

a. ratio $= 2.836 \times 10^{-5}$ at 298.15 K

b. ratio $= 1.943 \times 10^{-3}$ at 500 K

c. ratio $= 0.04408$ at 1000 K

d. ratio $= 0.5356$ at 5000 K

e. ratio $\rightarrow 1$

25.19

a. ratio $= 2.9446$ at 298.15 K

b. ratio $= 2.9834$ at 1000 K

c. ratio $\rightarrow 3$

25.21

a. $z_{\mathrm{rot}} = 180.0$

b. $J_{\mathrm{mp}} \approx 9$

c. probability $= 0.06402$

25.23

For $V = 0.02500\,\mathrm{m}^3, z = 6.107 \times 10^{30}$

For $V = 1.00\,\mathrm{m}^3, z = 2.443 \times 10^{32}$

25.25

$z = 9.92 \times 10^{30}$

25.27

For helium, $z = 1.911 \times 10^{29}$

For krypton, $z = 1.815 \times 10^{31}$

25.29

At 300.0 K, $z = 2.71 \times 10^{33}$

At 500.0 K, $z = 1.04 \times 10^{34}$

25.31

$z_{\mathrm{rot}} = 1.880$

25.33

$z_{\mathrm{rot}} = 424.8$

25.35

fraction $= 0.36788$

25.37

$z_{\mathrm{rot}} = 36.42$

25.41

b. $\Omega = 60$

c. $\Omega = 24$

25.45

a. FALSE

b. FALSE
c. FALSE
d. TRUE
e. TRUE
f. TRUE
g. TRUE
h. TRUE
i. FALSE
j. TRUE

25.47

a. $z_{\mathrm{rot}} = 2.85554$
b. $z_{\mathrm{rot}} = 3.02824$
c. $z_{\mathrm{rot}} = 3.02828$

25.49

a. ratio $= 4.83 \times 10^{-7}$
b. ratio $= 5.14 \times 10^{-7}$
c. ratio $= 3.01 \times 10^{-5}$
d. ratio $= 3.14 \times 10^{-5}$

25.51

a. ratio $= 2.12 \times 10^{-9}$ at 298.15 K
ratio $= 6.74 \times 10^{-6}$ at 500 K
ratio $= 2.60 \times 10^{-3}$ at 1000 K
ratio $= 0.304$ at 5000 K
ratio $\rightarrow 1$ in the limit as $T \rightarrow \infty$
b. ratio $= 2.451$ at 298.15 K
ratio $= 2.824$ at 1000 K
ratio $\rightarrow 3$ in the limit as $T \rightarrow \infty$
c. $J_{\mathrm{mp}} = 3$

Chapter 26 Exercises

26.1

$S_{\mathrm{st}} = 4.9087 \times 10^{-23}\ \mathrm{J\,K^{-1}}$

26.2

a. $d\ln(x)/dx = 1$
b. $d\ln(x)/dx = 1.00 \times 10^{-5}$
c. $d\ln(x)/dx = 1.00 \times 10^{-100000}$

26.7

a. $U_{\mathrm{vib}} = 12979\ \mathrm{J\,mol^{-1}}$
b. $z_{\mathrm{vib}} = 2.1713$
$U_{\mathrm{vib}} = 3005\ \mathrm{J\,mol^{-1}}$
c. $z_{\mathrm{vib}} = 1.595$
$U_{\mathrm{vib}} = 4288\ \mathrm{J\,mol^{-1}}$

26.8

$C_{\mathrm{V,et}} = 0.63927\ \mathrm{J\,K^{-1}}$

26.10

$K \approx 3.56$

26.11

$K_c = 1.4 \times 10^{-39}\ \mathrm{mol\,m^{-3}}$

26.12

a. $k = 0.399\ \mathrm{m^3\,mol^{-1}\,s^{-1}} = 399\ \mathrm{L\,mol^{-1}\,s^{-1}}$
b. $K = 1.12 \times 10^7$
$K(\text{thermodynamic}) = 0.754 \times 10^7$

26.14

$A \approx 2.4 \times 10^8\ \mathrm{m^3\,mol^{-1}\,s^{-1}}$
$= 2.4 \times 10^{11}\ \mathrm{L\,mol^{-1}\,s^{-1}}$

Chapter 26 Problems

26.1

a. no difference
b. difference of a factor of 2
c. no difference
d. no difference
e. differ by $5.7631\ \mathrm{J\,K^{-1}\,mol^{-1}}$

26.5

$S^{\mathrm{o}}_{\mathrm{m,tr}} = 149.6\ \mathrm{J\,K^{-1}mol^{-1}}$
$S^{\mathrm{o}}_{\mathrm{m,rot}} = 54.84\ \mathrm{J\,K^{-1}mol^{-1}}$
$S^{\mathrm{o}}_{\mathrm{m,vib}} = 0.142\ \mathrm{J\,K^{-1}mol^{-1}}$
$S_{\mathrm{m}} = 196.3\ \mathrm{J\,K^{-1}mol^{-1}}$

26.7

$C_{\mathrm{P},m} = 37.048\ \mathrm{J\,K^{-1}\,mol^{-1}}$

26.9

$S^{\mathrm{o}}_{\mathrm{m}} = 126.16\ \mathrm{J\,K^{-1}\,mol^{-1}}$

26.11

$U^{\mathrm{o}}_{\mathrm{m}} = 3718.5\ \mathrm{J\,mol^{-1}}$
$H^{\mathrm{o}}_{\mathrm{m}} = 6197.4\ \mathrm{J\,mol^{-1}}$
$S^{\mathrm{o}}_{\mathrm{m}} = 164.09\ \mathrm{J\,K^{-1}\,mol^{-1}}$
$A^{\mathrm{o}}_{\mathrm{m}} = 45.204\ \mathrm{J\,mol^{-1}}$
$G^{\mathrm{o}}_{\mathrm{m}} = 45.725\ \mathrm{J\,mol^{-1}}$
$G^{V}_{\mathrm{m}} = 12.475\ \mathrm{J\,K^{-1}\,mol^{-1}}$

26.13

difference $= 5.763\ \mathrm{J\,K^{-1}}$

26.15

$U^{\mathrm{o}}_{\mathrm{m}} = (298.15\,\mathrm{K}) = 3718.5\,\mathrm{J\,mol^{-1}}$
$S^{\mathrm{o}}_{\mathrm{m}} = 169.69\,\mathrm{J\,K^{-1}\,mol^{-1}}$
$G^{\mathrm{o}}_{\mathrm{m}} = -44.40\,\mathrm{k\,J\,mol^{-1}}$

26.17

At298.15 K, $H^{\mathrm{o}}_{\mathrm{m}} = 6.1974\,\mathrm{kJ\,mol^{-1}}$
At500.0 K, $H^{\mathrm{o}}_{\mathrm{m}} = 10.393\,\mathrm{kJ\,mol^{-1}}$

26.19

$K = 27.0$

26.21

$K = 0.462$

26.23

a. $K \approx 6$
b. $K \approx 2$

26.25

a. $K \approx 2$
b. $K \approx 1$

26.29

$K = 3.393$

26.31

$\Delta S^{\ddagger\mathrm{o}} \approx -100\,\mathrm{J\,K^{-1}\,mol^{-1}}$

26.33

$k = 5.23 \times 10^{6}\,\mathrm{m^3\,mol^{-1}\,s^{-1}}$
$= 5.23 \times 10^{9}\,\mathrm{L\,mol^{-1}\,s^{-1}}$
$E_a = 7.13\,\mathrm{kJ\,mol^{-1}}$
$\mathrm{N_{A\nu}}\Delta\varepsilon_0^{\ddagger} = 5.00\,\mathrm{kJ\ mol^{-1}}$

26.35

a. $S_{\mathrm{st}} = 4.9099 \times 10^{-23}\,\mathrm{J\,K^{-1}}$
b. $\Omega = 56$
c. $\Omega = 20$
d. For part b, $S_{\mathrm{st}} = 5.55764 \times 10^{-23}\,\mathrm{J\,K^{-1}}$
For part c, $S_{\mathrm{st}} = 4.13609 \times 10^{-23}\,\mathrm{J\,K^{-1}}$
e. $S_{\mathrm{st}} = 8.1745 \times 10^{-23}\,\mathrm{J\,K^{-1}}$
f. $S_{\mathrm{st}} = 8.6937 \times 10^{-23}\,\mathrm{J\,K^{-1}}$
g. For $\langle\varepsilon\rangle = 5h\nu, T = 1633\,\mathrm{K}$
For $\langle\varepsilon\rangle = 4h\nu, T = 1385\,\mathrm{K}$
For $\langle\varepsilon\rangle = 3h\nu, T = 1133\,\mathrm{K}$

26.37

a. $A_{\mathrm{m},36} - A_{\mathrm{m},40} = 391.6\,\mathrm{J\,K^{-1}\,mol^{-1}}$
b. $U_{\mathrm{m},36} - U_{\mathrm{m},40} = 0$
c. $S_{\mathrm{m},36} - S_{\mathrm{m},40} = -1.3136\,\mathrm{J\,K^{-1}\,mol^{-1}}$
d. $\Delta S_{\mathrm{mix}} = 0.2168\,\mathrm{J\,K^{-1}}$

26.39

a. $E_a = 272\,\mathrm{kJ\,mol^{-1}}$
b. ratio = 243

Chapter 27 Exercises

27.4

a. At 298.15 K, $z_{\mathrm{vib}} = 1.2627$
At 1000.0 K, $z_{\mathrm{vib}} = 2.6753$
b. At 298.15 K, $\dfrac{k_{\mathrm{B}}T}{hc\tilde{\nu}_e} = 0.63699$
At 1000.0 K, $\dfrac{k_{\mathrm{B}}T}{hc\tilde{\nu}_e} = 2.1365$

27.7

b. At 1000.0 K, $U_{\mathrm{vib}} = 6519.9\,\mathrm{J\,mol^{-1}}$
c. At 298.15 K, $U_{\mathrm{vib}} = 0.0000314\,\mathrm{J\,mol^{-1}}$
At 1000.0 K, $U_{\mathrm{vib}} = 93.775\,\mathrm{J\,mol^{-1}}$

27.8

$S_{\mathrm{vib,cl}} = 18.0895\,\mathrm{J\,K^{-1}}$

27.10

$B_2 = 6.13 \times 10^{-5}\,\mathrm{m^3\,mol^{-1}}$

27.11

b. $B_2 = -2.1 \times 10^{-5}\,\mathrm{m^3\,mol^{-1}}$

Chapter 27 Problems

27.1

$\mathcal{Z} = 10^{4.48\times10^{24}}$

27.5

a. $\mathcal{Z} \approx e^{9.70\times10^{24}} \approx 10^{4.21\times10^{24}}$
b. $\ln(\text{probability}) = -1.06 \times 10^{25}$

27.9

a. $U = 3718.5\,\mathrm{J}$
b. $z = 2.4429 \times 10^{32}$
$\mathcal{Z} = 10^{5.4455\times10^{24}}$
c. probability $\approx 10^{-5.838\times10^{24}}$

27.11

a. $G^{\circ}_{\mathrm{m}}(298.15\,\mathrm{K}) - H^{\circ}_{\mathrm{m}}(0\,\mathrm{K}) = -37.430\,\mathrm{kJ\,mol^{-1}}$
$A^{\circ}_{\mathrm{m}}(298.15\,\mathrm{K}) - H^{\circ}_{\mathrm{m}}(0\,\mathrm{K}) = -39.909\,\mathrm{kJ\,mol^{-1}}$
b. $\mathcal{Z} = 10^{4.2105\times10^{24}}$

27.17

$C_{V,m(\mathrm{vib})} = 0.632\,\mathrm{J\,K^{-1}\,mol^{-1}}$
For 5% agreement, $T = 3960\,\mathrm{K}$
For 1% agreement, $T = 8985\,\mathrm{K}$

27.19

a. $S_{\mathrm{m}} = -1302\,\mathrm{J\,K^{-1}\,mol^{-1}}$
b. $S_{\mathrm{m}} = 154.847\,\mathrm{J\,K^{-1}\,mol^{-1}}$

27.21

$B_2 = 1.29 \times 10^{-5}\,\mathrm{m^3\,mol^{-1}}$

27.23

a. FALSE
b. FALSE
c. FALSE
d. TRUE
e. FALSE
f. FALSE
g. FALSE
h. TRUE

Chapter 28 Exercises

28.1

cubic, P: 1
cubic, I: 2
cubic, F: 4
tetragonal, P: 1
tetragonal, I: 2
orthorhombic, P: 1
orthorhombic, C: 2
orthorhombic, I: 2
orthorhombic, F: 4
monoclinic, P: 1
monoclinic, C: 2
triclinic: 1
hexagonal: 1

28.2

coordination number = 8
packing fraction = 0.680175

28.4

$C_{V,m}(298.15\,\mathrm{K}) = 5.983\,\mathrm{J\,K^{-1}\,mol^{-1}}$
$C_{V,m}(500.0\,\mathrm{K}) = 14.386\,\mathrm{J\,K^{-1}\,mol^{-1}}$
$C_{V,m}(1320.0\,\mathrm{K}) = 22.965\,\mathrm{J\,K^{-1}\,mol^{-1}}$

28.5

$c = 2700\,\mathrm{m\,s^{-1}}$

28.11

$\Delta S^{\ddagger\circ} \approx -13\,\mathrm{J\,K^{-1}\,mol^{-1}}$

28.12

$E_{a\eta} = 11.9\,\mathrm{kJ\,mol^{-1}}$

28.16

b. $q = -0.00083\,\mathrm{J}$
$w = 0.00083\,\mathrm{J}$

Chapter 28 Problems

28.1

$a = 4.077 \times 10^{-10}\,\mathrm{m} = 407.7\,\mathrm{pm}$
$d = 2.883 \times 10^{-10}\,\mathrm{m}$

28.5

unit cell volume = $1.96 \times 10^{-23}\,\mathrm{cm^3}$

28.7

$a = 4.123 \times 10^{-10}\,\mathrm{m}$

28.9

a. $a = 5.402 \times 10^{-10}\,\mathrm{m}$
b. $\rho = 1.683 \times 10^{3}\,\mathrm{kg\,m^{-3}}$

28.11

a. $d_{110} = 2.023 \times 10^{-10}\,\mathrm{m}$
b. $\theta = 0.3916$ radian $= 22.439^\circ$

28.13

b. $k = 11\,\mathrm{N\,m^{-1}}$

28.17

a. $\nu = 2.75 \times 10^{12}\,\mathrm{s^{-1}}$
c. 1678 K gives 95% of $3R$
3799 K gives 99% of $3R$

28.23

a. $\varepsilon_{\mathrm{F}} = 8.814 \times 10^{-19}\,\mathrm{J} = 5.50\,\mathrm{eV}$
b. At 15.00 K, $C_{m,\mathrm{el}} = 9.63 \times 10^{-3}\,\mathrm{J\,K^{-1}\,mol^{-1}}$
At 298.15 K, $C_{m,\mathrm{el}} = 0.192\,\mathrm{J\,K^{-1}\,mol^{-1}}$

28.25

a. ratio = 2.25×10^{-19}
b. ratio = 4.51×10^{-19}

28.27

$r = 1.6 \times 10^{-8}$ ohm m (Your value will likely differ)

The correct value is 1.72×10^{-8} ohm m

28.31
number ≈ 4.4

28.33
$P = 6.46 \times 10^3$ atm

28.35
$E_a = 15800\,\mathrm{J\,mol^{-1}} = 15.8\,\mathrm{kJ\,mol^{-1}}$

28.39
a. $r_{\mathrm{rms}} = 1.11 \times 10^{-8}$ m
ratio $= 0.0316$
b. $r_{\mathrm{rms}} = 1.11 \times 10^{-7}$ m
ratio $= 0.00316$

28.41
$\langle M \rangle_n = 21000$ amu
$\langle M \rangle_w = 23570$ amu

28.43
$\langle M \rangle_v = 23300$ amu

28.45
a. FALSE
b. TRUE
c. TRUE
d. TRUE
e. FALSE
f. TRUE
g. TRUE
h. FALSE
i. FALSE
j. TRUE
k. FALSE
l. FALSE

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