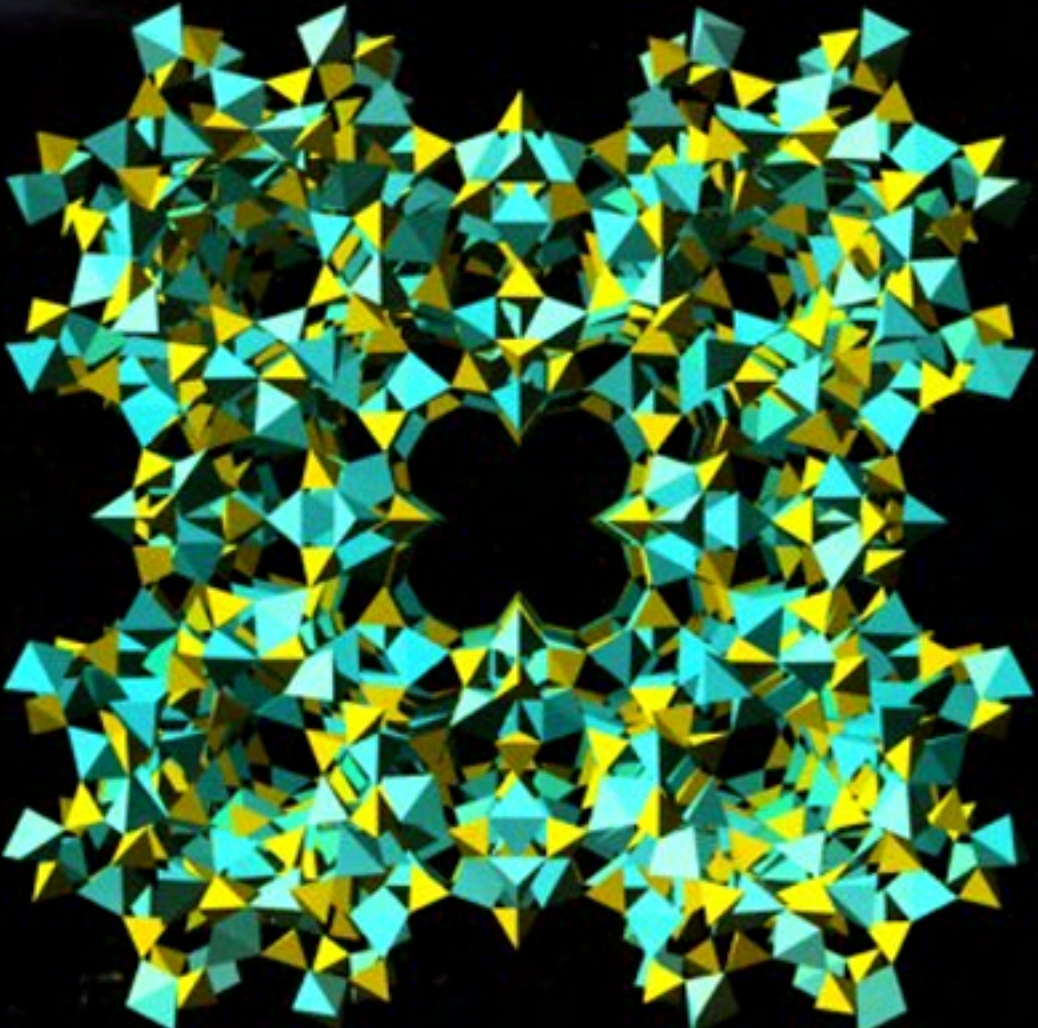

PHYSICAL CHEMISTRY

SECOND EDITION

ROBERT G. MORTIMER

Table of Contents

Preface

The physical chemistry course is the course in which most chemistry students first have the opportunity to synthesize what they have learned in mathematics, physics, and chemistry courses into a coherent pattern of knowledge. The topics of the traditional physical chemistry course can be grouped into several areas: (1) The study of the macroscopic properties of systems of many atoms or molecules; (2) The study of the processes which systems of many atoms or molecules can undergo; (3) the study of the properties of individual atoms and molecules, and (4) the study of the relationship between molecular and macroscopic properties.

The different portions of the book cover different parts of physical chemistry, as follows:

Chapter 1: Introduction to the macroscopic description of large systems.
Chapters 2–9: Thermodynamics and its applications
Chapters 10–13: Nonequilibrium processes
Chapters 14–20: Quantum mechanics and its applications
Chapter 21: Statistical mechanics—the bridge between mechanics and thermodynamics
Chapter 22: The structure of solids and liquids
Chapter 23: Some theories of nonequilibrium processes

The book is constructed so that several different sequences of these topic areas are possible with a minimum of adjustments. Four sequences which should be practical are:

I. As written
II. Ch. 1–9, Ch. 14–20, Ch. 10–13, Ch. 21–23
III. Ch. 1, Ch. 14–20, Ch. 2–9, Ch. 10–13, Ch. 21–23
IV. Ch. 1, Ch. 10–13, Ch. 2–9, Ch. 14–23.

If time does not permit covering the entire book, chapters 22 and 23 can be omitted without loss of continuity.

The book contains several appendixes, designed to improve the usefulness of the book. All of the tables of numerical data in the book are collected into Appendix A. Appendix B is a brief survey of some useful mathematics. Appendix C is a table of integrals and some information about the error function. Appendix D is a brief survey of classical mechanics. Appendix E contains some derivations of thermodynamic formulas. Appendix F presents information about special mathematical functions encountered in quantum mechanics. Appendix G contains a derivation of a formula used in perturbation theory in quantum mechanics. Appendix H is a discussion of the Hückel method of quantum mechanics. Appendix I discusses the matrix representation of symmetry groups. Appendix J is a list of symbols used in the book. Appendix K contains answers to selected numerical exercises and problems.

Each chapter has a list of the principal facts and ideas that are presented in the chapter, as well as objectives for the student. There is also a summary to assist in synthesizing the material of each chapter into a coherent whole. There are also marginal notes throughout the chapters to provide biographical information about some of the important people who originated the ideas that are presented in the book and to assist the student in following the flow of topics in the chapter. 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 the chapter are designed to provide practice in applying techniques and insights obtained through study of the chapter.

The author welcomes feedback from students and instructors; please send your comments and suggestions to the author's attention.

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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.

While writing this edition of this book, I have benefited from the expert advice of many reviewers:

Robert L. Carter	University of Massachusetts Boston
Peter Gold	Pennsylvania State University
James House	Illinois State University
Jaan Laane	Texas A & M University
Jack Opdycke	University of San Diego
J. Bevan Ott	Brigham Young University
Kim Salt	Claremont Colleges

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. I continue to be grateful to the reviewers who assisted with the first edition of this book. The errors which remain are my responsibility, not the responsibility of the reviewers.

I wish to thank the editorial staff at Harcourt/Academic Press for their guidance and help during a rather long and complicated project.

Periodic Table of the Elements

IUPAC groups	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	
Traditional groups (USA)	IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	0	
Periods 1									1 **H** 1.008									2 **He** 4.003	1
2	3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18	2
3	11 **Na** 22.99	12 **Mg** 24.30											13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95	3
4	19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.39	31 **Ga** 69.72	32 **Ge** 72.61	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80	4
5	37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** [98.91]	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3	5
6	55 **Cs** 132.9	56 **Ba** 137.3	71 **Lu** 175.0	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.8	75 **Re** 186.2	76 **Os** 190.1	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.7	83 **Bi** 209.0	84 **Po** [209.0]	85 **At** [210.0]	86 **Rn** [222.0]	6
7	87 **Fr** [223.0]	88 **Ra** [226.0]	103 **Lr** [260.1]	104 **Unq** [261.1]	105 **Unp** [262.1]	106 **Unh** [263.1]	107 **Uns** [262.1]	108 **Uno** [265.1]	109 **Une** [266.1]										7

57 **La** 138.9	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** [144.9]	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.2	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0
89 **Ac** [227.0]	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** [237.0]	94 **Pu** [244.1]	95 **Am** [243.1]	96 **Cm** [247.1]	97 **Bk** [247.1]	98 **Cf** [251.1]	99 **Es** [252.1]	100 **Fm** [257.1]	101 **Md** [258.1]	102 **No** [259.1]

Key

Atomic number	1
Symbol	**H**
Atomic Mass	1.008

Values in brackets are masses of most stable isotopes.

Fundamental Constants and Conversion Factors

From E. R. Cohen and B. N. Taylor, *The 1986 Adjustment of the Fundamental Physical Constants, CODATA Bulletin Number 63*, November 1986

Quantity	Symbol	Value
Avogadro constant	N_{Av}	6.02214×10^{23} mol^{-1}
Bohr magneton	β_e	9.27402×10^{-24} J T^{-1}
Boltzmann constant	k_B	1.38066×10^{-23} J K^{-1}
electron g-factor	g_e	2.0023193044
electron mass	m_e	9.10939×10^{-31} kg
elementary charge	e	1.602177×10^{-19} C
Faraday constant	F	96485.3 C mol^{-1}
molar gas constant	R	8.3145 J K^{-1} mol^{-1}
neutron mass	m_n	1.674929×10^{-27} kg
Newtonian constant of gravitation	G	6.673×10^{-11} m^3 kg^{-1} s^{-2}
nuclear magneton	β_N	5.050787×10^{-27} J T^{-1}
permeability of vacuum	μ_0	$4\pi \times 10^{-7}$ N A^{-2} (exact) $12.566370614 \times 10^{-7}$ N A^{-2}
permittivity of vacuum	ε_0	$8.8545187817 \times 10^{-12}$ C^2 N^{-1} m^{-2}
Planck constant	h	6.62608×10^{-34} J s
proton mass	m_p	1.672623×10^{-27} kg
Rydberg constant	$\Re_\infty$	10973731.53 m^{-1}
	$hc\Re_\infty$	13.60570 eV
	$\Re_H$	10967758.1 m^{-1}
	$hc\Re_H$	13.5983 eV
speed of light in vacuum	c	299792458 m s^{-1} (exact)

Prefixes for SI Units

factor	prefix	abbreviation	factor	prefix	abbreviation
10^{-1}	deci	d	10	deca	da
10^{-2}	centi	c	10^2	hecto	h
10^{-3}	milli	m	10^3	kilo	k
10^{-6}	micro	μ	10^6	mega	M
10^{-9}	nano	n	10^9	giga	G
10^{-12}	pico	p	10^{12}	tera	T
10^{-15}	femto	f	10^{15}	peta	P
10^{-18}	atto	a	10^{18}	exa	E

Conversion Factors for Non-SI Units

unit	abbreviation	value
atmosphere	atm	101325 Pa (definition)
torr	torr	133.322 Pa $= \frac{1}{760}$ atm
atomic mass unit	amu	1.66054×10^{-27} kg
bar	bar	1×10^{5} Pa
electron volt	eV	1.602178×10^{-19} J
poise	P	0.1 kg m^{-1} s^{-1}
liter	L	1×10^{-3} $m^3 = 1$ dm^3
angstrom	Å	1×10^{-10} m
debye	D	3.335641×10^{-30} C m
calorie	cal	4.184 J (definition)
inch	in	0.0254 m (definition)
pound	lb	0.4536 kg

The Greek Alphabet

A	α	alpha	I	ι	iota	P	ρ	rho
B	β	beta	K	κ	kappa	Σ	σ	sigma
Γ	γ	gamma	Λ	λ	lambda	T	τ	tau
Δ	δ	delta	M	μ	mu	Y	υ	upsilon
E	ε	epsilon	N	ν	nu	Φ	ϕ	phi
Z	ζ	zeta	Ξ	ξ	xi	X	χ	chi
H	η	eta	O	o	omicron	Ψ	ψ	psi
Θ	θ	theta	Π	π	pi	Ω	ω	omega

List of Numerical Tables in the Appendix

1

Systems, States, and Processes

OBJECTIVES

After studying this chapter, the student should:

1. understand the relationship between state specification and mathematical functions;
2. understand the relationship between macroscopic and microscopic states;
3. understand and be able to work with the Boltzmann probability distribution;
4. understand the use of Newton's second law as an equation of motion;
5. understand the distinction between reversible and irreversible macroscopic processes.

PRINCIPAL FACTS AND IDEAS

1. The principal goal of physical chemistry is to understand the behavior of systems (portions of the universe) and to apply this understanding in useful ways.
2. The state of a system is specified by the values of a certain number of independent variables.
3. Dependent variables are those whose values are determined by mathematical functions of the independent variables.
4. In a one-phase fluid system of one substance at equilibrium, three macroscopic variables such as temperature, volume, and amount of substance can be independent variables. Other variables, such as the pressure, are dependent variables given as functions of the independent variables.
5. When a system can be described by classical mechanics the microscopic (mechanical) state of a system is specified by the position and velocity of every particle in the system.
6. Macroscopic states are determined by the nature of microscopic states.
7. Many microscopic states correspond to a single macroscopic state, and the properties of the macroscopic state correspond to averages over the microscopic states.
8. In a system of independent molecules, the probability that a molecule will be found in a mechanical state with energy ε is proportional to $e^{-\varepsilon/k_B T}$ (the Boltzmann distribution).

1.1 Scientific Inquiry

Some people have always been curious about the universe, and have sought explanations for the things that they observed. Some devised explanations that we now dismiss as ignorant superstitions once satisfied the need to understand why things happen as well as describing what happens. As cultures evolved, philosophers such as Aristotle attempted to describe and understand the properties of the material universe in a systematic way, and their accumulated knowledge in this area came to be known as **natural philosophy**. As the volume of knowledge widened, it became impossible for any person to study all of natural philosophy, and it began to be divided into what we now call the several natural sciences: astronomy, biology, chemistry, geology, and physics.

Physics has been defined as the study of the properties of matter that are shared by all substances, while chemistry has been defined as the study of the properties of individual substances. Physical chemistry involves both of these approaches and is sufficiently fundamental that its principles underlie the other areas of chemistry.

The first stage in scientific inquiry is **observing** and reporting the properties of particular objects and what they do under specific conditions. The second stage is **generalization**. This means concluding from experimental facts that all systems exhibit some common behavior, and constructing a general statement or **empirical law** that expresses this behavior. The third stage in the scientific method is **explanation**. This means contriving a set of hypotheses about the nature of the physical universe (a theory). The fourth stage of the scientific method is **testing the theory**. One first deduces the consequences of the theory. This process is called **deductive reasoning**, or reasoning from the general case to the specific case. One then compares these predictions with experiment, possibly carrying out new experiments. If the actual behavior and the predictions agree, the theory is likely to be tentatively accepted as a valid explanation of the phenomena.

The early history of modern chemistry provides an important example of the application of the scientific method. At the end of the eighteenth century, chemistry was evolving from the ancient art of alchemy, which included attempts to make gold from something less expensive. There was a body of accumulated knowledge, but it was not organized into a coherent picture. The discovery of three laws of chemistry began the development of an organized field of knowledge. Lavoisier carefully determined that the mass of the products equaled the mass of the reactants in every one of his experiments. He stated the **law of conservation of mass**, which asserts that this equality occurs in every chemical reaction. Such an assertion is strictly speaking a logical error, since no one can examine every possible reaction, but science is largely based on such laws. Proust then announced the law of **constant composition**, also called the **law of definite proportions**, which states that in all samples of a given compound, the ratio of the masses of any two elements is always the same.

Antoine Laurent Lavoisier, 1743–1794, was a French chemist known as the "father of modern chemistry." He was beheaded during the French Revolution because of his investments in his father-in-law's firm, which was employed by the royal government to collect taxes.

Joseph Louis Proust, 1754–1826, was a French chemist who published his law of definite proportions in 1799. He was also the first to isolate sugar from grapes.

John Dalton, 1766–1844, was an English schoolmaster and chemist.

Dalton added the third law of chemistry, the **law of multiple proportions**, which states that if two elements occur in two different compounds, the masses of the first element that combine with a given mass of the second element in the two compounds are in the ratio of small whole numbers. He then proposed an explanation of these laws, which we call **Dalton's atomic theory**. This theory proposes that every element consists of unique, indestructible, indivisible atoms that combine as units to form compounds. Lavoisier has been called the father of modern chemistry, and this is true from an experimental point of view, but Dalton must be regarded as the father of modern chemistry from a theoretical point of view.

There was argument about the validity of Dalton's theory for a century, although various experiments gave results in agreement with its predictions. At the end of the nineteenth century, Ostwald still argued that the concept of atoms was useful but that there was no evidence for their actual existence. However, even Ostwald was convinced by several new pieces of evidence and new theories, including Einstein's 1905 theory of Brownian motion, which ascribed this phenomenon to random bombardment of colloidal particles by solvent molecules.

We now know that the original atomic theory is only approximately correct. Atoms are not indestructible, and atoms of the same element can have different masses. The conservation of mass is not exact if only rest-mass is considered. However, in ordinary chemical processes atoms are neither created nor destroyed, the conservation of mass is valid to about 12 significant digits, and we apply the atomic theory of Dalton in all of our stoichiometric calculations.

Wilhelm Ostwald, 1853–1932, was a German chemist who, among other things, developed the industrial method to make nitric acid. He received the 1909 Nobel Prize in chemistry for this contribution.

Albert Einstein, 1879–1955, was the greatest physicist of the twentieth century, and made fundamental contributions in many branches of physics. He did some of his most important work in 1905 while working at the Swiss patent office and pursuing theoretical physics in his spare time. He received the 1921 Nobel Prize in physics for his explanation of the photoelectric effect.

* *Indicates an exercise or problem with an answer in Appendix K.*

*Exercise 1.1

A typical chemical reaction involves several hundred kilojoules of energy per mole of reactant. Einstein's famous formula for the equivalence of mass and energy is $E = mc^2$, where E is the energy, m is the mass, and c is the speed of light, 2.9979×10^8 m s^{-1}. Calculate the mass equivalent to 400 kJ of energy and compare it to a typical molar mass, say 0.100 kg mol^{-1}.

1.2 Systems and States

In physical chemistry, one studies various properties of matter. We must have clearly in mind what the object of our study is and what properties we are focusing on. In order to talk about this, we must have a common vocabulary.

Systems

The object that we are studying at a given moment is called the **system**. Much of what we do will be centered around three things: (1) the definition of the system; (2) the values of variables that specify the **state of the system**, which means the condition of the system at a given time; and (3) the **processes** that can change the state of the system. These three aspects provide a common theme in all of the areas of physical chemistry.

The portion of the universe that is outside of the system is called the **surroundings**. We must be specific about the boundary between system and surroundings. For example, if we study a sample of liquid or gas confined in a container, we will ordinarily specify that the container is part of the surroundings.

Figure 1.1 shows an example of a **macroscopic system** (a system big enough to see with the unaided eye). The system consists of a fluid (liquid or gas) contained in a cylinder with a movable piston. The cylinder and piston are part of the surroundings. There is a valve between the cylinder and a hose leading to the atmosphere or 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 pass into or out of the system, it is called an **open system**. The cylinder–piston apparatus is immersed in a second part of the surroundings, a constant-temperature bath. If the system were completely insulated from its surroundings so that no heat could pass

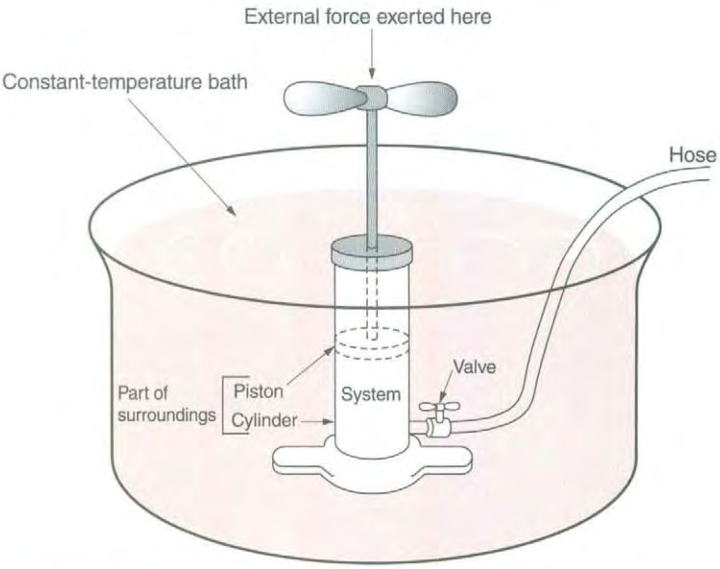

Figure 1.1. A Typical Fluid System Contained in a Cylinder with Variable Volume. Work can be done on the system by displacing the piston, heat can be transferred to the system from the bath in which it is immersed, and matter can be added to the system through the valve if it is open.

between system and surroundings, it would be called an **adiabatic system**, or we would say that it can undergo only **adiabatic processes**. If the system were completely separated from the rest of the universe so that no heat, work, or matter could be transferred, it would be called an **isolated system**.

A **microscopic system** generally consists of a single atom or a single molecule. Microscopic systems cannot be seen with the unaided eye or with ordinary microscopes, and it is only within recent decades that images of individual atoms and molecules have been produced. Our information about microscopic systems is usually indirectly obtained by interpretation of some measurement.

Sometimes we will discuss a **model system**. This is an imaginary system designed to resemble some real system, but which can be described more easily than the real system. Model systems are useful only if we can show that they approximate the behavior of a real system and if we can analyze their behavior in a useful way.

States and State Variables

Specifying the **state of a system** means describing the condition of the system by giving values of a sufficient set of variables. A macroscopic system has two types of states: the **macroscopic state**, or **macrostate**, which involves properties of the entire system, and the **microscopic state**, or **microstate**, which involves molecular properties. A microscopic system possesses only a microscopic state.

Macroscopic States

A macroscopic state is sometimes called a **thermodynamic state**. This state is specified by giving values of macroscopic variables such as the pressure P, the temperature T, the volume V, the amount of substance n, the mass m, the density ρ (equal to m/V), etc. The value of every possible macroscopic variable is not needed to specify the macroscopic state of the system. It is an experimental fact that *when values of enough variables are specified, the values of all other variables are determined as dependent variables by the nature of the system*. When enough variables are specified so that the other macroscopic variables are determined, we say that these variables specify the state of the system. The other variables are mathematical functions of these independent variables. All variables that can either be used to specify the state of the system or that depend on the state of the system are called **state functions** or **state variables**.

Consider a fluid system consisting of a one-phase fluid sample of one substance at equilibrium. If n (the amount of substance), T (the temperature), and P (the pressure) are controlled, the system will take on a volume that is determined by the values of T, P, and n through a mathematical function characteristic of the system. For example, a dilute gas approximately obeys the **ideal gas equation of state**

$$V = V(T, P, n) = \frac{nRT}{P} \tag{1.2-1}$$

where R is a constant known as the **ideal gas constant** or **molar gas constant**.

The statement that only three variables are required to specify the macrostate of a one-component fluid system is restricted to equilibrium states. Nonequilibrium states can be much more complicated. **Equilibrium** is a condition in which there is no tendency for any net change to occur. There can be systems in which no apparent change is observed, even over a long period of time, but which are not at equilibrium. For example, solid carbon can exist as diamond, graphite, or fullerenes ("buckyballs"). In order to be at chemical equilibrium at ordinary pressures, diamond must convert to graphite. However, the *rate* of conversion is very slow, and diamond is said to be in a **metastable state**. A metastable state is not an equilibrium state, and has a tendency to change toward equilibrium. However, a description that applies to equilibrium states can often be applied to metastable states without significant error.

Isaac Newton, 1642–1727, was a great British mathematician and physicist who was also one of the inventors of calculus.

Tycho Brahe, 1546–1601, was a Danish astronomer who made the most accurate astronomical observations ever made without a telescope. He was able to measure angular positions of stars and planets to within 2 minutes of arc (1/30 of a degree).

Microscopic States

A microscopic state pertains to mechanical properties and is sometimes called a **mechanical state**. Mechanics is the branch of physics that deals with energy, forces, and the motions of objects. **Classical mechanics**, sometimes called **Newtonian mechanics**, is the theory of mechanics that dominated physics until the twentieth century. Newton proposed three laws of motion, which explained the motions of celestial bodies observed by Brahe and systematized by Kepler. **Newton's second law** is the most important of these laws:

$$\boxed{\mathbf{F} = m\mathbf{a} = m\frac{d\mathbf{v}}{dt} = m\frac{d^2\mathbf{r}}{dt^2}} \tag{1.2-2}$$

where $\mathbf{F}$ is the force acting upon an object having mass m, $\mathbf{r}$ is its position vector, $\mathbf{v}$ is its velocity, and $\mathbf{a}$ is its acceleration. The force, position, velocity, and acceleration have direction as well as magnitude, so they are vectors.

Important equations that will be used frequently will be enclosed in a screened box.

Johannes Kepler, 1571–1630, was a German astronomer and protégé of Brahe who discovered that Brahe's data implied elliptical planetary orbits and who derived laws of planetary motion.

Classical mechanics is found to apply accurately to systems such as celestial bodies, rifle bullets, rockets, and billiard balls. Like the law of conservation of energy, it is not exact but it is extremely useful. Around the beginning of the twentieth century it was found that classical mechanics failed to explain a number of phenomena. Objects with small masses, such as electrons, must be described using **quantum mechanics**, while objects moving at high speeds must be described by **relativistic mechanics**.

According to classical mechanics, the microstate of a system is specified by giving the position and velocity of every particle in the system. When quantum mechanics is used, we must directly specify which state applies, usually by giving the values of a set of **quantum numbers**. A quantum state requires roughly the same amount of information to specify it as does the analogous classical state. A structureless particle moving in three dimensions requires three coordinates and three velocity components to specify its classical state, and requires three quantum numbers to specify its state of motion quantum mechanically. If we ignore its spin, the state of motion of an electron in a hydrogen atom is specified by the quantum numbers n, l, and m. If we have many particles, the specification of the microscopic state requires a lot of information.

EXAMPLE 1.1

Consider a sample of helium gas consisting of 1.0 mol. Ignoring the motion of electrons inside the atoms and assuming that classical mechanics is an adequate description, estimate the amount of computer paper needed to specify the microscopic state of the system.

Solution

Specification of the state requires a total of 3.6×10^{24} values. If these values were printed on ordinary computer printer paper with the six values for each atom on one line, the values for 66 atoms could be printed on one sheet. With 2500 sheets per box, 3.6×10^{18} boxes would be required for a system of 1.000 mol. At $20 per box, this would cost 1.8×10^{17} dollars for the paper, about 50,000 times the 1999 federal debt of the United States. A computer printer that can print five sheets per minute would require 3.5×10^{15} years to print the values.

***Exercise 1.2**

Specification of the state of electronic motion in a hydrogen atom requires four quantum numbers, n, l, m, and m_s, specifying the electronic energy, the magnitude of the orbital angular momentum, the z component of the angular momentum, and the z component of the spin angular momentum. For a region in interstellar space containing 1.00 nmol of hydrogen atoms, estimate the time required to type all of the values of the quantum numbers into a computer, pretending that the atoms are distinguishable from each other.

1.3 Units of Measurement. SI Units

We will carry out many calculations using state variables and other numerical quantities. The value of any numerical quantity consists of two parts, a number and a specification of the unit of measurement. When writing values of physical quantities, you should always write the unit as well as the numerical part. *To carry out any calculation correctly, you must express all variables in terms of consistent units.* One such set of units is the **international system of units**, or **SI units**. SI stands for *Système International*, the French name for the set of units. The SI units are "mks" units, in which lengths are measured in **meters** (m), masses are measured in **kilograms** (kg), and time is measured in **seconds** (s). There are seven **base units** in the SI. In addition to the

SI units for mass, length, time, the other SI base units are the **kelvin** (K) for absolute temperature, the **ampere** (A) for electrical current, the **candela** (cd) for luminous intensity, and the **mole** (mol) for amount of substance.

In addition to the base units, there are a number of **derived units**. From Newton's second law, Eq. (1.2-2), the units of force must be kg m s^{-2}, and we define the **newton** (N) as the SI unit of force:

$$1\ \mathrm{N} = 1\ \mathrm{kg\ m\ s^{-2}} \quad \text{(definition)} \tag{1.3-1}$$

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

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 while managing his family's brewery.

Pressure is force per unit area, and the **pascal** (Pa) is the SI unit of pressure:

$$1\ \mathrm{Pa} = 1\ \mathrm{N\ m^{-2}} = 1\ \mathrm{kg\ m^{-1}\ s^{-2}} \quad \text{(definition)} \tag{1.3-2}$$

Energy has the units of force times distance. The SI unit of energy is the **joule** (J):

$$1\ \mathrm{J} = 1\ \mathrm{N\ m} = 1\ \mathrm{kg\ m^2\ s^{-2}} \quad \text{(definition)} \tag{1.3-3}$$

We will occasionally use non-SI units, such as the **calorie** (cal), which was originally defined as the amount of heat required to raise the temperature of 1 g of water by 1°C, and is now defined by

$$1\ \mathrm{cal} = 4.184\ \mathrm{J} \quad \text{(exactly, by definition)} \tag{1.3-4}$$

We will use several non-SI units of pressure, especially the atmosphere:

$$1\ \mathrm{atm} = 101{,}325\ \mathrm{Pa} \quad \text{(exactly, by definition)} \tag{1.3-5}$$

$$760\ \mathrm{torr} = 1\ \mathrm{atm} \quad \text{(exactly, by definition)} \tag{1.3-6}$$

$$1\ \mathrm{bar} = 100{,}000\ \mathrm{Pa} \quad \text{(exactly, by definition)} \tag{1.3-7}$$

The average barometric pressure near sea level is approximately equal to 1.00 atmosphere. A pressure equal to 1 torr will raise a column of mercury to a height of very nearly 1 millimeter if the mercury is at a temperature of 273.15 K (0.00°C). One bar is approximately equal to 750.1 torr.

The SI unit of volume is the cubic meter. Chemists are accustomed to using a non-SI unit of volume, the **liter** (L), which is the same as a cubic decimeter:

$$1\ \mathrm{L} = 0.001\ \mathrm{m^3} = 1\ \mathrm{dm^3} \quad \text{(exactly, by definition)} \tag{1.3-8}$$

The **formula unit** of a substance is the smallest amount of substance that retains the identity of the substance. It can be an atom, a molecule, or an electrically neutral set of ions, depending on the substance. The **mole** (abbreviated mol) is the SI unit for the amount of a substance. 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 carbon-12 isotope. Therefore, the number of formula units, N, of a sample of any substance is proportional to the **amount of substance** measured in moles, denoted by n:

$$N = N_{\mathrm{Av}} n \tag{1.3-9}$$

The proportionality constant N_{Av} is **Avogadro's constant**. It is known from experiment to have the value

$$N_{\mathrm{Av}} = 6.02214 \times 10^{23}\ \mathrm{mol}^{-1} \tag{1.3-10}$$

The ideal gas law can be written in terms of the amount of gas or the number of molecules:

$$V = \frac{nRT}{P} = \frac{nN_{\mathrm{Av}}k_{\mathrm{B}}T}{P} = \frac{Nk_{\mathrm{B}}T}{P} \tag{1.3-11}$$

This constant is named for Ludwig Boltzmann, 1844–1906, an Austrian physicist who was one of the inventors of gas kinetic theory.

The constant k_{B} is called Boltzmann's constant. In SI units the molar gas constant is

$$R = 8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}} \tag{1.3-12}$$

so that

$$k_{\mathrm{B}} = \frac{R}{N_{\mathrm{Av}}} = 1.3807 \times 10^{-23}\ \mathrm{J\ K^{-1}} \tag{1.3-13}$$

***Exercise 1.3**

Find the value of the gas constant in $\mathrm{L\ atm\ K^{-1}\ mol^{-1}}$, in $\mathrm{cal\ K^{-1}\ mol^{-1}}$, in $\mathrm{cm^3\ atm\ K^{-1}\ mol^{-1}}$, and in $\mathrm{cm^3\ bar\ K^{-1}\ mol^{-1}}$.

The ideal gas equation of state (ideal gas law) of Eq. (1.2-1) is used to define the **ideal gas temperature scale**, which is one representation of the **absolute temperature scale**. It is found that any gas more and more nearly obeys the ideal gas law as the pressure is made lower and lower. We write

$$T = \lim_{P \to 0} \left(\frac{PV}{nR} \right) \tag{1.3-14}$$

Our interpretation of the limit symbol in Eq. (1.3-14) is that one evaluates the quantity PV/nR at various pressures and then extrapolates the graph of this quantity to zero pressure, identifying the intercept as the limit.

1.4 State Functions

Values of a small set of state variables suffice to specify the equilibrium state of a macroscopic system. All other state variables must be dependent variables whose values are given by mathematical functions of those variables used to specify the state. The ideal gas law provides a familiar example:

$$P = P(T, V, n) = \frac{nRT}{V} \tag{1.4-1}$$

EXAMPLE 1.2

Find the pressure in Pa and in atm of 1.000 mol of an ideal gas at a temperature is 273.15 K (0°C) and a volume of 22.400 L.

Solution

$$\begin{aligned} P &= \frac{(1.000\ \text{mol})(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(273.15\ \text{K})}{(22.400\ \text{L}(1\ \text{m}^3/1000\ \text{L})} \\ &= 1.014 \times 10^5\ \text{J m}^{-3} = 1.014 \times 10^5\ \text{N m}^{-2} = 1.014 \times 10^5\ \text{Pa} \\ &= 101.4\ \text{kPa} = (1.014 \times 10^5\ \text{Pa})\left(\frac{1\ \text{atm}}{101325\ \text{Pa}}\right) = 1.001\ \text{atm} \end{aligned}$$

In this example we have used the factor-label method of converting the units in which a quantity is expressed in order to obtain consistent units. It is important to write the unit as well as the numerical part of any value when applying this method. See almost any general chemistry textbook for a review of the method.

***Exercise 1.4**

If pressure is measured in atmospheres (atm) and volume is measured in liters (L), the value of the gas constant R is equal to 0.08206 L atm K^{-1} mol^{-1}.

a. Find the volume of 2.000 mol of an ideal gas at a temperature of 298.15 K and a pressure of 0.500 atm.

b. Find the pressure of a sample of 1.000 mol of an ideal gas at a volume of 20.00 L and a temperature of 500.0 K.

Exercise 1.4 illustrates the fact that various different sets of three variables can be chosen to specify the state of a fluid system. If n, T, and P are chosen, then V is a dependent variable. If n, V, and T are chosen, then P is a dependent variable. Furthermore, we assert (to be shown later) that other dependent variables such as the energy are functions of the same three variables.

Microscopic States

The situation is similar with microscopic states. If the system obeys classical mechanics, the state of the system is specified by the values of the positions and velocities of all particles. Consider a monatomic gas containing N atoms of a single element. If we can ignore electronic energy, the **kinetic energy** $\mathscr{K}$ is:

$$\mathscr{K} = \tfrac{1}{2}mv_1^2 + \tfrac{1}{2}mv_2^2 + \cdots + \tfrac{1}{2}mv_N^2 = \tfrac{1}{2}m\sum_{i=1}^{N} v_i^2 \tag{1.4-1}$$

If v_{ix} is the x component of the velocity of the ith particle, with similar symbols for the y and z components,

$$v_i^2 = v_{ix}^2 + v_{iy}^2 + v_{iz}^2 \tag{1.4-2}$$

so that we can consider the kinetic energy to be a function of the velocity components:

$$\mathscr{K} = \mathscr{K}(v_{1x}, v_{1y}, v_{1z}, v_{2x}, v_{2y}, v_{2z}, \ldots, v_{Nx}, v_{Ny}, v_{Nz}) \tag{1.4-3}$$

The **momentum** is defined as the mass times the velocity, and is denoted by **p**:

$$\mathbf{p} = m\mathbf{v} \tag{1.4-4}$$

The kinetic energy is given in terms of the momenta by the equation:

$$\mathscr{K} = \frac{1}{2m}p_1^2 + \frac{1}{2m}p_2^2 + \cdots + \frac{1}{2m}p_N^2 = \frac{1}{2m}\sum_{i=1}^{N} p_i^2 \tag{1.4-5}$$

The **potential energy** $\mathscr{V}$ is defined so that a velocity-independent force $\mathbf{F}_i$ on particle number i can be obtained from its partial derivatives, as in Eq. (D-6) of Appendix D:

$$F_{ix} = -\left(\frac{\partial \mathscr{V}}{\partial x_i}\right), \qquad F_{iy} = -\left(\frac{\partial \mathscr{V}}{\partial y_i}\right), \qquad F_{iz} = -\left(\frac{\partial \mathscr{V}}{\partial z_i}\right) \tag{1.4-6}$$

where F_{ix} is the x component of the force $\mathbf{F}_i$, etc. The potential energy $\mathscr{V}$ is a function of the positions of the particles of the system:

$$\mathscr{V} = \mathscr{V}(x_1, y_1, z_1, x_2, y_2, z_2, \ldots, x_N, y_N, z_N) = \mathscr{V}(q) \tag{1.4-7}$$

where the symbol q is an abbreviation for the coordinates of all particles in the system.

An important property of the potential energy can be seen by inspection of Eq. (1.4-6): If any constant is added to the value of $\mathscr{V}$, the forces are unchanged, since the derivative of a constant is equal to zero. Since the forces are the only physically meaningful effects of the potential energy, we state the fact: *An arbitrary constant can be added to a potential energy without any physical effect.*

*Exercise 1.5

Near the surface of the earth, the gravitational potential energy of an object of mass m is given by

$$\mathscr{V}_g = mgz \tag{1.4-8}$$

The acceleration due to gravity at the surface of the earth depends slightly on latitude. We use the value 9.80 m s^{-2}, which applies near 38° of latitude, the latitude of Washington D.C. and San Francisco, California.

where g is the acceleration due to gravity, equal to 9.80 m s^{-2}, and z is the height of the object (the coordinate in the vertical direction). Using Eq. (1.4-6), find the gravitational force on an object with mass 1.000 kg near the surface of the earth. Show that this force is independent of whether the height is measured as the altitude above sea level or as the height above some other position and that different choices of the position at which $z = 0$ correspond to adding different constants to the potential energy.

If we exclude the rest-mass energy, the total energy of a mechanical system is the sum of the kinetic energy and the potential energy:

$$E = \mathscr{K} + \mathscr{V} \tag{1.4-9}$$

Since $\mathscr{K}$ is determined by the velocities of the molecules and $\mathscr{V}$ is determined by the positions of the molecules, the total energy E is a function of positions and velocities of the particles, and is therefore a state function of the microscopic state. We write

$$E = E(v, q) \tag{1.4-10}$$

where we use the letter v without a subscript as an abbreviation for all of the velocities of particles in the system. We can also write

$$E = E(p, q) \tag{1.4-11}$$

where we use the letter p without a subscript as an abbreviation for all of the momenta of particles in the system.

The Macroscopic State

Now consider the macroscopic state of a system of many molecules. The energy of the system is a macroscopic variable as well as a mechanical variable. We will discuss the discovery of this fact by Joule, Rumford, and others when we discuss the first law of thermodynamics in Chapter 3. The fact that the energy can be considered to be a function of the many positions and velocities of the molecules and can alternatively be considered to be a function of a few variables like the volume, pressure, and temperature will be discussed in Chapters 10 and 21.

The kinetic energy of the motion of the system's center of mass is a macroscopic variable, as is the gravitational potential energy of the system. If we denote the mass of the entire system by M, the vertical coordinate of its center of mass by Z_c, and the velocity of the center of mass by $\mathbf{V}_c$, we write an equation defining the internal energy U:

$$E = \tfrac{1}{2}MV_c^2 + MgZ_c + U \tag{1.4-12}$$

When we discuss thermodynamics, we will usually assume that Z_c remains fixed and that the center of the mass of the system is stationary, so that the internal energy is the only contribution to the energy that we need to discuss.

Since we have asserted that the state of a fluid system containing only one substance is specified by only three variables and since the total energy is a state function, the internal energy is also a state function depending on variables such as the temperature, the volume, the pressure, the amount of substance, etc.:

$$U = U(T, V, n) \tag{1.4-13}$$

or

$$U = U(T, P, n) \tag{1.4-14}$$

etc. The internal energy consists of molecular kinetic and potential energy when viewed microscopically, but is a state function of macroscopic variables when viewed macroscopically.

1.5

The Relationship between Macrostates and Microstates

The macroscopic and microscopic states of a given macroscopic system are not independent. For example, the value of the internal energy, U, a macroscopic state variable, is determined by the positions and velocities of the molecules of the system, which specify the microscopic state. We assert a general relationship: *If the microscopic state is known, the macroscopic state is determined.* However, the reverse is not true. Many different sets of positions and velocities of the molecules of a macroscopic system can correspond to the same energy. We assert: *If the macroscopic state is known, many different microscopic states are possible.* For example, if a fluid system is at macroscopic equilibrium, its macrostate does not change over a period of time. However, since the molecules are moving, the microstate changes very rapidly, and the system passes through a very large number of microstates without changing the macroscopic state. The equilibrium value of a macroscopic variable must correspond to an average of the appropriate microscopic variable over these many microstates.

Another argument for associating a macroscopic state with an average over microscopic states is the fact that macroscopic variables are measured with measuring instruments such as thermometers, manometers, etc. Such instruments always require a certain length of time to respond to a change in the measured variable. During this "response time" the system must pass through many microscopic states, and the measured value of the macroscopic variable must correspond to an average over all of the microscopic states that the system occupied during the response time.

Averaging Procedures and Probability Distributions

There are several kinds of averages. The **mean** is the most commonly used type of average, and is commonly meant when one speaks 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** of a set is the most commonly occurring value in the set.

If we have a set of numbers, $w_1,\ w_2,\ w_3,\ w_4, \ldots, w_N$, the mean of this set is defined to be

$$\langle w\rangle = \frac{1}{N}\sum_{i=1}^{N} w_i \quad \text{(definition)} \tag{1.5-1}$$

Assume now that some of the values of w are equal. We arrange the 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 in value 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 only the distinct members of the set

$$\langle w\rangle = \frac{1}{N}\sum_{i=1}^{M} N_i w_i \tag{1.5-2}$$

We must still divide by N, not by M, to get the correct mean value. There are fewer terms in this sum than in the sum of Eq. (1.5-1), unless every N_i equals unity, but the mean value is unchanged. The formula of Eq. (1.5-2) can often enable us to average a large set of values conveniently.

We define

$$p_i = \frac{N_i}{N} \tag{1.5-3}$$

The quantity p_i is the fraction of the entire set equal to w_i, and is 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 a **probability distribution**. We can now write

$$\langle w\rangle = \sum_{i=1}^{M} p_i w_i \tag{1.5-4}$$

From the definition of p_i in Eq. (1.5-3), these probabilities are **normalized**, which means that they sum to unity.

$$\sum_{i=1}^{M} p_i = \frac{1}{N}\sum_{i=1}^{M} N_i = \frac{N}{N} = 1 \quad \text{(normalization)} \tag{1.5-5}$$

*Exercise 1.6

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	2

Find the mean score on the quiz without taking a sum of 50 terms.

We can also get the mean of a function of our values. If $h(w)$ is some function of w, its mean value is

$$\langle h\rangle = \sum_{i=1}^{M} p_i h(w_i) \tag{1.5-6}$$

*Exercise 1.7

For the quiz scores in Exercise 1.6, find the mean of the squares of the scores,

$$\langle w^2\rangle = \sum_{i=1}^{M} p_i w_i^2$$

and the square root of this mean, called the **root-mean-square** score.

The Probability Distribution for Molecular States

Since we must average over very many microscopic states, we require a probability distribution for microscopic states of a system. Assuming that classical mechanics is an adequate approximation, the microscopic states of the entire system can be specified by specifying the positions and velocities of the individual molecules. In a dilute gas, the molecules are relatively far apart and the forces between them are negligible. In this case the state of one molecule is independent of the states of the other molecules.

For a system of independent molecules, we can average over the microstates of the system by averaging over the mechanical states of the individual molecules. However, the average over molecular states is not necessarily an average in which each molecular state occurs with equal probability. We now seek a probability distribution for these molecular states. We make two assumptions that will determine the mathematical form of the molecular probability distribution:

1. *The probability of a molecular state depends only on the energy of the molecular state.*
2. *The same probability distribution applies for all kinds of molecules.*

These assumptions are reasonable, but we must examine the agreement of their consequences with experiment.

Let $p(\varepsilon)$ be the probability that a molecular state of energy ε will occur for a randomly chosen molecule. From the first assumption, p will depend only on ε. From the second assumption, there is only one function p for all types of molecules.

Consider two molecules, identified as molecule 1 and molecule 2, which will be treated as though they were a larger molecule. Its probability distribution P depends on ε, the energy of the pair of particles, which is the sum of the energies of the two particles:

$$P = P(\varepsilon) = P(\varepsilon_1 + \varepsilon_2) \tag{1.5-7}$$

If the molecules do not interact with each other, they are independent. We apply a fact of probability theory: *The probability of the occurrence of two independent events is the product of the probabilities of the two events.* Therefore,

$$P(\varepsilon) = p(\varepsilon_1)p(\varepsilon_2) \tag{1.5-8}$$

Only the exponential function satisfies Eq. (1.5-8), as we will now show.

Differentiate Eq. (1.5-8) with respect to ε_1, treating ε_2 as a constant:

$$\frac{\partial P}{\partial \varepsilon_1} = \left(\frac{dp}{d\varepsilon_1}\right)p(\varepsilon_2) \tag{1.5-9}$$

By the chain rule of differentiation, the left side of this equation is

$$\frac{\partial P}{\partial \varepsilon_1} = \left(\frac{dP}{d\varepsilon}\right)\left(\frac{\partial \varepsilon}{\partial \varepsilon_1}\right) = \frac{dP}{d\varepsilon} \tag{1.5-10}$$

For more information on the chain rule and other identities involving derivatives, see Appendix B. We substitute this expression into Eq. (1.5-9) and divide by P:

$$\frac{1}{P(\varepsilon)}\frac{dP}{d\varepsilon} = \frac{1}{p(\varepsilon_1)}\frac{dp}{d\varepsilon_1} \tag{1.5-11}$$

An analogous equation can be written by differentiating Eq. (1.5-8) with respect to ε_2 instead of ε_1. The left-hand sides of the two equations are identical, so that

$$\frac{1}{p(\varepsilon_1)}\frac{dp}{d\varepsilon_1} = \frac{1}{p(\varepsilon_2)}\frac{dp}{d\varepsilon_2} \tag{1.5-12}$$

In this equation, the variables ε_1 and ε_2 are separated. This statement means that ε_1 occurs only in one term and ε_2 occurs only in the other term. Since they are independent variables, we can keep ε_2 fixed while we allow ε_1 to vary. While ε_2 is held fixed, the right-hand side of the equation is fixed, and the left-hand side must be a constant function of ε_1. A similar argument applies to the right-hand side. Each side of the equation must equal a constant, which we denote by c:

$$\frac{1}{p(\varepsilon_1)}\frac{dp}{d\varepsilon_1}=c \qquad (1.5\text{-}13)$$

Multiplying this equation by $d\varepsilon_1$ and integrating,

$$\ln(p)=c\varepsilon_1+A \qquad (1.5\text{-}14)$$

where A is a constant of integration. Taking antilogarithms,

$$p(\varepsilon_1)=e^{A}e^{c\varepsilon_1}\propto e^{c\varepsilon_1} \qquad (1.5\text{-}15)$$

The symbol $\propto$ means "is proportional to." For now, we omit the evaluation of A and write the proportionality instead of the equality.

We must determine what the parameter c is. We will show in Chapter 21 that

$$c=-\frac{1}{k_{\mathrm{B}}T} \qquad (1.5\text{-}16)$$

where k_{B} is Boltzmann's constant and where T is the absolute (kelvin) temperature.

The probability distribution for molecular states in a dilute gas is thus

$$p(\varepsilon)\propto e^{-\varepsilon/k_{\mathrm{B}}T} \qquad (1.5\text{-}17)$$

This probability distribution is called the **Boltzmann distribution.**

The Boltzmann probability distribution has a number of important properties:

1. *States of higher energy are less probable than states of lower energy.*
2. *At higher temperatures, the difference in population between states of high energy and states of low energy decreases, until as T approaches infinity, all states approach equal probability.*
3. *As T approaches zero on the kelvin scale, only the states of lowest energy are populated.*

We have assumed that the molecules of a gas do not interact. In this case, the energy of a molecule consists of kinetic energy and a potential energy that depends only on the position of the one molecule:

$$\varepsilon=\mathscr{K}+\mathscr{V}=\tfrac{1}{2}mv^2+\mathscr{V}(x,y,z) \qquad (1.5\text{-}18)$$

Near the surface of the earth, the gravitational potential energy depends only on the vertical coordinate z:

$$\mathscr{V}=mgz \qquad (1.5\text{-}19)$$

For a small gaseous system, the molecules are at approximately the same altitude and only the kinetic energy needs to be considered. The coordinate z can be measured from any chosen origin, so that adding a constant to the potential energy has no physical effect. If $\mathscr{V}$ is constant, you can choose that constant so that $\mathscr{V}=0$.

Figure 1.2 shows the Boltzmann probability distribution for a range of molecular energies and for three different temperatures, 100 K, 300 K, and 1500 K. The probability of a state of $\varepsilon=0$ is arbitrarily set equal to 1 in this figure. We will find in Chapters 10 and 21 that the average kinetic energy of molecules of a monatomic gas is equal to $3k_{\mathrm{B}}T/2$, and is independent of the mass of the molecules. The value of this

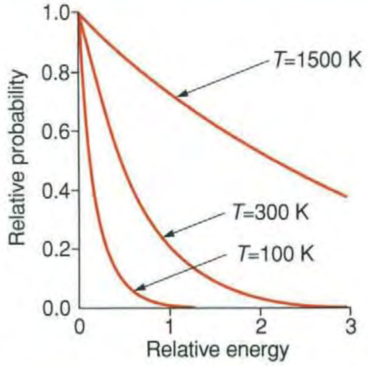

Figure 1.2. The Boltzmann Probability Distribution as a Function of Energy for Three Different Temperatures. This figure illustrates the properties of the Boltzmann distribution as described in the text, with lower probabilities for lower energies, but with the difference becoming smaller at higher temperatures.

quantity at 300 K is equal to 6.21×10^{-21} J. This value is assigned a relative energy = 1 in the figure and corresponds to a probability 22.3% of that of zero energy at 300 K. At 100 K, states of this energy are almost unpopulated, but at 1500 K, they have a probability equal to 74.1% of the probability of a state of zero energy at that temperature.

EXAMPLE 1.3

Assume that the earth's atmosphere is at equilibrium at 298 K (not a very 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 kg mol^{-1}.

Solution

Since the temperature is constant, the average kinetic energies of the molecules are the same at all altitudes (we will show that this is correct in Chapter 10). Representing the high-altitude state as 2 and the sea-level state as 1, the probability ratio is

$$\frac{p_2}{p_1} = \frac{N_2}{N_1} = \frac{P_2}{P_1} = \frac{e^{-(\mathcal{K}_2+\mathcal{V}_2)/k_BT}}{e^{-(\mathcal{K}_1+\mathcal{V}_1)/k_BT}} = \exp\left(-\frac{\mathcal{V}_2-\mathcal{V}_1}{k_BT}\right)$$

The numbers of molecules are proportional to the probabilities, and from the ideal gas law, the pressure is proportional to the number of molecules, so that the pressure is proportional to the population given by the Boltzmann distribution. The kinetic energy terms cancel from our assumption of constant temperature. The gravitational potential energy is $\mathcal{V} = mgz$, where we take z to be the height above sea level.

$$\mathcal{V}_2 - \mathcal{V}_1 = \frac{(0.029\ \text{kg mol}^{-1})(9.80\ \text{m s}^{-2})(8900\ \text{m})}{6.022 \times 10^{23}\ \text{mol}^{-1}} = 4.2 \times 10^{-21}\ \text{J}$$

If $P = 1.00$ atm at sea level, and if we assume that air is an ideal gas:

$$\frac{P}{1.000\ \text{atm}} = \exp\left(\frac{-4.2 \times 10^{-21}\ \text{J}}{(1.3807 \times 10^{-23}\ \text{J K}^{-1})(298\ \text{K})}\right)$$
$$= 0.36$$

***Exercise 1.8**

The altitude of Pike's Peak is 14110 ft. Estimate the barometric pressure on Pike's Peak on a winter day when the temperature is −15°F.

1.6 Processes

A process is an occurrence that changes the state of a system. Since we identified microscopic states and macroscopic states, we identify microscopic and macroscopic processes.

Microscopic (Mechanical) Processes

Consider first the case that classical mechanics is an adequate approximation for the motions of atoms or molecules. If the system is a single particle and if the force on it is determined by its position, Eq. (1.2-2) can be solved to give the position of the particle as a function of time, and its velocity can be derived from the time dependence of its position. It constitutes an **equation of motion** for the particle. If the system consists of two interacting particles, their combined equation of motion can solved, but the equations of motion for three or more particles cannot be solved exactly. Considerable research has been carried out on the numerical simulation of classical equations of motion for systems of several hundred particles, and useful results have been obtained. See Chapter 22.

EXAMPLE 1.4

A particle is moving subject to a constant frictional force in the direction opposite to its velocity, but 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 $x = 0$. Assume that the coefficient of friction is equal to 0.800.

Solution

So long as v_x is nonzero, the frictional force is

$$F_x = -(0.800)(1.000\ \mathrm{kg})(9.80\ \mathrm{m\ s^{-2}}) = -7.84\ \mathrm{kg\ m\ s^{-2}} = -7.84\ \mathrm{N}$$

where N stands for newton, the unit of force. Newton's second law gives

$$F_x = m\frac{d^2x}{dt^2} = m\frac{dv_x}{dt}$$

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 time 0 to time t', a particular time:

$$\int_0^{t'} \frac{dv_x}{dt}\,dt = -(7.84\ \mathrm{m\ s^{-2}})\int_0^{t'} dt$$

$$v_x(t') - v_x(0) = -(7.84\ \mathrm{m\ s^{-2}})t'$$

$$v_x(t') = v_x(0) - (7.84\ \mathrm{m\ s^{-2}})t' = 10.0\ \mathrm{m\ s^{-1}} - (7.84\ \mathrm{m\ s^{-2}})t'$$

This solution applies only until v_x vanishes, at which time the force stops and the particle remains stationary. This occurs when

$$t' = t'' = \frac{10.0\ \mathrm{m\ s^{-1}}}{7.84\ \mathrm{m\ s^{-2}}} = 1.28\ \mathrm{s}$$

The position is given by another integration:

$$x(t') - x(0) = \int_0^{t'} \frac{dx}{dt}\,dt = \int_0^{t'} v_x\,dt = \int_0^{t'} [10.0\ \mathrm{m\ s^{-1}} - (7.84\ \mathrm{m\ s^{-2}}t]\,dt$$

In this equation we have used the expression for the velocity in which t' was replaced by t. This is necessary because we require the velocity as a function of t, not t', in the integrand function. The integration yields

$$x(t) = (10.0\ \mathrm{m\ s^{-1}})t - \tfrac{1}{2}(7.84\ \mathrm{m\ s^{-2}})t^2$$

This solution applies only for values of t no larger than 1.28 s because the formula for the force no longer applies. The position and velocity are shown in Figure 1.3.

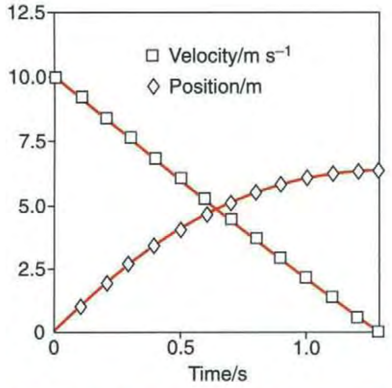

Figure 1.3. Graph for Example 1.4. Position and Velocity as a Function of Time. This figure shows how the velocity decreases linearly to zero and the coordinate attains a constant value.

*Exercise 1.9

Assume that a particle of mass m moves only in the z direction and is subject to a constant force given by $F_z = mg$. 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 z and v_z as functions of time. Hint: This exercise can be solved by carrying out two integrations, as in the previous example.

Reversible and Irreversible Macroscopic Processes

A macroscopic process changes the macroscopic state of a system. The two principal classes of macroscopic processes are reversible and irreversible processes. A **reversible process** is one that can at any time be reversed in direction by an infinitesimal change in the surroundings. Every process has a driving force that causes it to proceed. For example, a temperature difference is the driving force for a flow of heat. The driving force for a reversible process must be infinitesimal in magnitude. For example, if heat is flowing reversibly from a system to its surroundings, the temperatures of the system and the surroundings can differ only infinitesimally, since an infinitesimal change in the temperature of the surroundings must be capable of reversing the direction of heat flow. A process is faster for larger magnitudes of its driving force, so a reversible process must occur infinitely slowly, and the system has time to relax to equilibrium at each stage of the process. During a reversible process, the system passes through a sequence of equilibrium states.

The system is not required to remain in equilibrium states during an **irreversible process**, and the process can occur in a finite time. In Chapters 3 and 4, we will discuss irreversible processes such that the system is in an equilibrium state or metastable state when the process begins and is in an equilibrium state after the process ends. In Chapter 11 we will discuss transport processes, an important class of irreversible processes.

Summary of the Chapter

The state of a system is the numerical specification of the circumstance in which it is found. There are two important kinds of states of macroscopic systems. The first is the macroscopic state, which concerns only variables pertaining to the system as a whole. The second type of state is the microscopic state, which pertains to the mechanical variables of individual molecules.

The equilibrium macroscopic state of a one-phase fluid 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.

If the microscopic state of a macroscopic system is specified, the macroscopic state is completely determined. Many microscopic states can correspond to a single macroscopic state, and a macroscopic state can be represented as an average over very many microscopic states of the system.

Processes are the means by which the state of the system changes. Microscopic processes are governed by Newton's second law if classical mechanics is an adequate approximation. The two principal kinds of macroscopic processes are reversible processes and irreversible processes. The direction of a reversible process can be changed by an infinitesimal change in the surroundings. The system passes through equilibrium states during a reversible process.

PROBLEMS

Problems for Section 1.2

1.10. Assuming a molar mass of 0.100 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 part per million. Compare this energy with a typical chemical bond energy, roughly 400 kJ mol^{-1}.

Problems for Section 1.3

***1.11.** **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.

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

1.12. 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.

Problems for Section 1.4

***1.13.** Express the speed of light in furlongs per fortnight. A furlong is $\frac{1}{8}$ mile, and a fortnight is 14 days.

1.14. 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. Find the conversion factor between ergs and joules, and the conversion factor between dynes and newtons.

***1.15.** In one English system of units, lengths are measured in feet (12 inches ↔ 1 foot, 1 inch ↔ 0.0254 m) and 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 ↔ 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 $(°\text{R})^{-1}$ 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.

Problems for Section 1.5

a. Find the probability of drawing the ace of spades from one 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.

***1.17.** Compute the odds for each possible value of the sum of the two numbers showing when two dice are thrown.

1.18. Assume that air is an ideal gas mixture consisting of 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}.

***1.19.** Calculate the difference in the density of air at the top and bottom of a vessel 0.50 m tall at 298.15 K at sea level. Assume that air is a single ideal gas with average molar mass 0.029 kg mol^{-1}.

1.20. Estimate the difference in barometric pressure between the ground floor of a building and the fifty-first floor, assumed to be 500 feet higher. State any assumptions.

Problems for Section 1.6

1.21. **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 a "friction coefficient" and where $\mathbf{v}$ is the velocity. Obtain a formula for the velocity and position of an object described by this equation moving in the $\mathbf{x}$ direction with initial position $x(0) = x_0$ and initial velocity $v_x(0) = v_0$.

b. Draw a graph of the position of the particle as a function of time for $x_0 = 0$ and $v_0 = 10.0\ \text{m s}^{-1}$. Use a graphing program such as CricketGraph© or Kaleidagraph© if available.

1.22. An object is propelled upward at an initial velocity of 10.0 m s^{-1}. Ignoring air resistance, find the maximum height of the object above its starting point.

1.23. 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.

2

The Equilibrium Macroscopic States of Gases and Liquids

OBJECTIVES

After studying this chapter, the student should:

1. be able to apply the methods of calculus to the macroscopic observables of a simple system;
2. be able to solve problems related to the macroscopic equilibrium properties of gases and liquids;
3. be able to work with various equations of state for gases, including the ideal gas equation of state;
4. understand the behavior of a system at the critical point and be able to work problems related to the critical point.

PRINCIPAL FACTS AND IDEAS

1. In a simple one-phase fluid system of one substance, three variables suffice to specify the macroscopic equilibrium state of the system. At least one of the variables must be an extensive variable.
2. The intensive state, which includes only intensive variables, is specified by only two variables in the case of a simple one-phase fluid system of one substance.
3. The language of mathematics is used to describe the macroscopic equilibrium properties of systems.
4. Nonideal gases and liquids are described mathematically by various equations of state.
5. The coexistence of phases can be described mathematically.
6. The liquid–gas coexistence curve terminates at the critical point, beyond which there is no distinction between liquid and gas phases.
7. The law of corresponding states asserts that in terms of reduced variables, all substances obey the same equation of state.

2.1 Mathematical Functions and the Equilibrium Macroscopic State of a Simple System

In Chapter 1 we introduced the idea that the state of a system is specified by the values of a set of independent variables and that other variables are dependent variables whose values are given by mathematical functions of the independent variables. A mathematical function is a rule that delivers a value for a dependent variable when values of one or more independent variables are specified. It can be represented in various ways: by a formula, by a graph, or by a table with two or more columns of values.

A dilute gas is one that is adequately described by the ideal gas law. If you have a dilute gas at equilibrium and if you choose values for n (the amount of substance in moles), T (the absolute temperature), and P (the pressure) for the system, the nature of the system dictates the value of V, which can be calculated from the ideal gas law contained in Eq. (1.2-1):

$$V = \frac{nRT}{P} \tag{2.1-1}$$

We could also consider n, T, and V to be independent variables so that P is a dependent variable:

$$P = \frac{nRT}{V} \tag{2.1-2}$$

The ideal gas law illustrates the fact that different choices can be made for the independent variables that specify the state of a system. Not only can P be expressed as a function of T, V, and n, but V can be expressed as a function of T, P, and n, and so on.

For any fluid system at equilibrium, whether it is a dilute gas or not, P is some mathematical function of T, V, and n, denoted by

$$P = f(T, V, n) \tag{2.1-3}$$

The pressure P is the dependent variable, and there are three independent variables: T, V, and n. The letter f stands for the functional relationship while the letter P stands for the pressure. Such a functional relation is called an **equation of state.** If a system is not a dilute gas, Eq. (2.1-3) would represent a different function than that of Eq. (2.1-2).

A formula such as that of Eq. (2.1-2) is not the only way to represent a function. Figure 2.1a shows a set of graphical curves that represent the dependence of P on V for an ideal gas, for a fixed value of n (1.000 mol) and for several fixed values of T. Figure 2.1b shows a perspective view of a graphical surface in three dimensions that represents the dependence of P on V and on T for a fixed value of n (1.000 mol). Just as the height of a curve in Figure 2.1a gives the value of P for a particular value of V, the height of the surface in Figure 2.1b gives the value of P for a particular value of T and a particular value of V.

Instead of the notation of Eq. (2.1-3), chemists usually write

$$P = P(T, V, n) \tag{2.1-4}$$

or

$$V = V(T, P, n) \tag{2.1-5}$$

using the same letter for the function and for the dependent variable, even if we use a different set of independent variables. Chemists also use the same letter P to represent

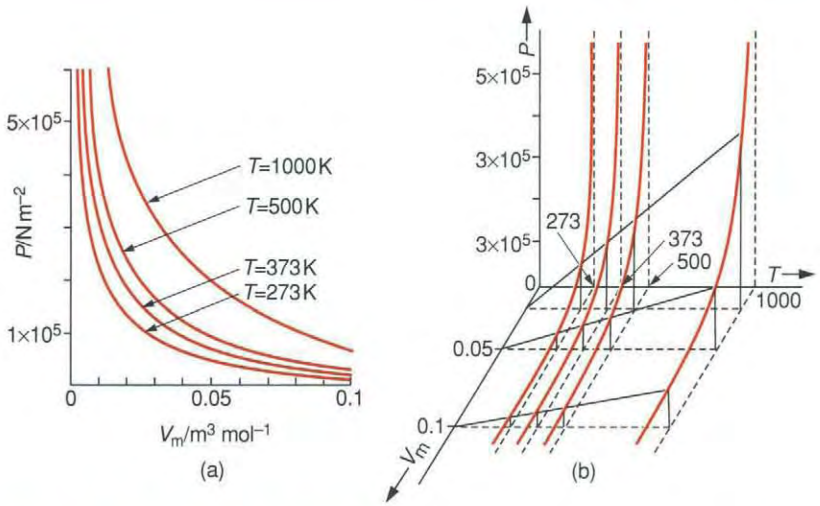

Figure 2.1. The Pressure of an Ideal Gas. (**a**) Pressure as a function of V at constant n and various constant values of T. The curves in this graph conform to the ideal gas equation of state, $PV = nRT$. (**b**) Pressure as a function of V and T at constant n. This three-dimensional graph gives the same information as the set of all curves in part (**a**).

the function delivering a value of P, no matter what independent variables are chosen and whatever representation of the function is used.

***Exercise 2.1**

Assume that the volume of a liquid system 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 using arbitrary symbols for constants and using the symbol V_0 for the volume at some reference temperature T_0, some reference pressure P_0, and some reference amount of substance n_0.

Equilibrium Macroscopic States and State Variables

In addition to P, V, T, and n, there are a number of other variables that depend only on the equilibrium state of the system. We call these variables **state variables** or **state functions**. They must also be mathematical functions of the independent variables used to specify the state of the system. One of the most important is the thermodynamic energy or internal energy, U, introduced but not defined in Chapter 1. We will use the internal energy now as an example of a macroscopic state variable and will define it and study its properties in Chapter 3. Just as P is a function of T, V, and n, or V is a function of T, P, and n, we assume that U is also a function of three independent variables.

There are two principal classes of macroscopic variables: **extensive variables** are proportional to the size of the system, while **intensive variables** are independent of the size of the system. For example, U, V, n, and m (the mass of the system) are extensive variables, while P and T are intensive variables. One test to determine whether a variable is extensive or intensive is to imagine combining a given system with a replica of that system, keeping P and T fixed. Any variable that has twice the value for the combined system as for the original system is extensive, and any variable that is unchanged is intensive. The quotient of two extensive variables is an intensive variable. Examples are the density, $\rho = m/V$, the molar volume, $V_{\mathrm{m}} = V/n$, and the molar internal energy, $U_{\mathrm{m}} = U/n$.

We will denote any molar quantity by a subscript m. *Some authors use a different notation and denote the molar volume by* $\bar{V}$ *or* $\tilde{V}$, *etc. The notation* $\bar{V}$ *was used in the first edition of this book.*

We now make the assertion, which we take as a summary and generalization of experimental fact: *All equilibrium macroscopic state variables of a one-phase fluid system of one substance are mathematical functions of three independent variables, at least one of which must be extensive.* Equivalently, *the equilibrium macroscopic state of a one-component one-phase fluid system is specified by giving the values of three macroscopic variables, of which at least one must be extensive.* One independent variable must be extensive because extensive variables cannot be functions only of intensive variables. The size of the system could be changed without changing the value of any intensive variable, but this must change the values of extensive variables. If two one-component one-phase fluid systems containing the same substance are at equilibrium and have the same values of three macroscopic variables (at least one of which is extensive), then they must have the same values of all other equilibrium macroscopic variables. They are in the same macroscopic state.

One-phase fluid systems that contain several substances have an additional independent variable for each substance beyond the first substance, so that the total number of independent variables at equilibrium is $c + 2$, where c is the number of independent substances (called components). We discuss the definition of a component in Chapter 6, but now consider it to be a substance whose amount can be varied independently of the amounts of the other substances. A system with more than one phase requires more variables to specify its state. A one-phase system whose equilibrium state variables are functions of $c + 2$ variables is called a **simple system**. Fluid (liquid or gas) systems and strain-free solid systems are simple systems. A rubber band or a coil spring is not a simple system, since its length can be an additional independent variable. An electrochemical cell is another example of a nonsimple system.

For a simple one-substance one-phase system, we can write

$$U = U(T, V, n) \tag{2.1-6}$$

or

$$U = U(T, P, n) \tag{2.1-7}$$

We do not always know what the particular functions are that such equations represent, but we can sometimes get useful information without knowing the function, using methods of calculus and measured values of derivatives.

Some Variables Related to Partial Derivatives

A function of several independent variables has several derivatives. For example, the derivative of the internal energy U with respect to the temperature, considering U to be a function of T, P, and n, is denoted by $(\partial U/\partial T)_{P,n}$. The subscripts indicate that P and n are held fixed (treated as constants) when the differentiation is performed. This kind of derivative is called a **partial derivative**. There can be other derivatives of U with respect to T. The derivative of U with respect to the temperature, considering U to be a function of T, V, and n, is denoted by $(\partial U/\partial T)_{V,n}$. The subscripts indicate that V and n are treated as constants when carrying out the differentiation. The two partial derivatives, $(\partial U/\partial T)_{P,n}$ and $(\partial U/\partial T)_{V,n}$, are not identical and can have different values. Some facts about the calculus of functions of several variables are presented in Appendix B, and Eq. (B-7) of Appendix B shows the relationship between two such derivatives.

A commonly measured quantity that is related to a partial derivative is the **isothermal compressibility** κ_T:

$$\kappa_T = -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{T,n} \qquad \text{(definition)} \tag{2.1-8}$$

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

The **coefficient of thermal expansion** α is defined by

(2.1-9)

Like the compressibility, the coefficient of thermal expansion is an intensive quantity. The coefficient of thermal expansion is usually positive. However, water has a negative coefficient of thermal expansion between 0°C and 3.98°C.

A few values of isothermal compressibilities for 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 usually not large and these values can be used over fairly wide ranges of temperature and pressure.

2.2 Real Liquids and Solids

For ordinary calculations, a sample of a liquid or solid can be treated as though its volume is constant. If higher accuracy is needed, values of isothermal compressibilities and coefficients of thermal expansion can be used in approximate calculations such as those of the next two examples.

EXAMPLE 2.1

The isothermal compressibility of liquid water at 298.15 K and 1.000 atm is equal to $4.524 \times 10^{-5}\ \mathrm{bar}^{-1} = 4.524\ \mathrm{Pa}^{-1}$. 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 298.15 K.

Solution

The compressibility is relatively small in magnitude, so we write an approximation analogous to Eq. (B-3) in Appendix B:

$$\Delta V \approx \left(\frac{\partial V}{\partial P}\right)_{T,n} \Delta P = -V\kappa_T\,\Delta P \tag{2.2-1}$$

where we use the standard notation

$$\Delta V = V(\text{final}) - V(\text{initial}) \tag{2.2-2}$$

with a similar equation for ΔP or any other variable, always taking the final value minus the initial value. The fractional change is

$$\frac{\Delta V}{V} \approx -\kappa_T\,\Delta P = -(4.524 \times 10^{-5}\ \text{bar}^{-1})(49.00\ \text{bar}) = -2.217 \times 10^{-3}$$

The formula used in this example applies exactly in the limit that the changes approach zero. You must always determine whether such an approximation gives adequate accuracy for finite changes.

EXAMPLE 2.2

The coefficient of thermal expansion of liquid water at 298.15 K and 1.000 atm is equal to $2.07 \times 10^{-4}\ \text{K}^{-1}$. 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

Since the coefficient of expansion is small, it should be a good approximation to write

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

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 2.2

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

$$\alpha_L = \frac{1}{L}\left(\frac{\partial L}{\partial T}\right)_P \quad \text{(definition)} \tag{2.2-3}$$

where L is the length of the object. This coefficient is usually used for solids, whereas the coefficient of thermal expansion in Eq. (2.1-9) is used more often for liquids. Unfortunately, the symbol α is often used without the subscript L for the coefficient of linear thermal expansion, and the name "coefficient of thermal expansion" is also sometimes used for it. Since the units of both coefficients are the same (reciprocal temperature) there is opportunity for confusion between them.

The linear coefficient is equal to one-third of the coefficient of thermal expansion, as can be seen from the following. Subject a cubical object of length L to an infinitesimal change in temperature, dT. The new length of the object is

$$L(T+dT) = L(T) + \left(\frac{\partial L}{\partial T}\right)_P dT = L(T)[1 + \alpha_L\, dT]$$

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

$$V(T+dT) = L(T)^3[1+\alpha_L\, dT]^3 = L(T)^3[1 + 3\alpha_L\, dT + 3(\alpha_L\, dT)^2 + (\alpha_L\, dT)^3]$$

Since dT is small, the last two terms are insignificant:

$$V(T+dT) = L(T)^3[1 + 3\alpha_L\, dT] \tag{2.2-4}$$

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

$$V(T+dT) = V(T) + \left(\frac{\partial V}{\partial T}\right) dT = V(T)[1 + \alpha\, dT] \tag{2.2-5}$$

Comparison of Eq. (2.2-5) with Eq. (2.2-4) shows that

$$\alpha = 3\alpha_L \tag{2.5-6}$$

EXAMPLE 2.3

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

Solution

$$\begin{aligned} V(25^\circ\mathrm{C}) &= V(20^\circ\mathrm{C})[1 + 3\alpha_L(5.0^\circ\mathrm{C})] \\ &= (2.000000\ \mathrm{L})[1 + 3(3.2 \times 10^{-6})(5.0^\circ\mathrm{C})] = 2.000096\ \mathrm{L} \end{aligned}$$

*Exercise 2.3

Find the volume of the volumetric flask in Example 2.3 at 100.0°C.

Most liquids have a nearly constant volume under ordinary conditions, as in the examples just presented. The volumes of most solids are even more nearly constant. We therefore recommend the following practice for making ordinary calculations: *Unless there is some reason to do otherwise, treat liquids and solids as though they had fixed volumes.* This practice will give adequate accuracy for most purposes.

*Exercise 2.4

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 1.000 bar. Find the molar volume of acetone at this temperature and a pressure of 1.000 bar and at a pressure of 100.0 bar.

2.3 Real Gases

Although most gases obey the ideal gas law to an accuracy of about one percent when near room temperature and one atmosphere, at pressures around 100 atm one must usually seek a better description than the ideal gas law. Several equations of state have been devised to describe the volumetric behavior (relation of pressure, temperature, and volume) of real gases. The **van der Waals equation of state** describes real gases more accurately than does the ideal gas law:

$$\left(P+\frac{an^2}{V^2}\right)(V-nb)=nRT \tag{2.3-1}$$

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.

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

EXAMPLE 2.4

Use the van der Waals equation to predict the pressure of nitrogen gas at 273.15 K and a molar volume of 22.414 L. Compare with the pressure of an ideal gas at the same temperature and molar volume.

Solution

We solve the van der Waals equation for P as a function of T and the molar volume, V_{m}, equal to V/n.

$$P=\frac{nRT}{V-nb}-\frac{an^2}{V^2}=\frac{RT}{V_{\mathrm{m}}-b}-\frac{a}{V_{\mathrm{m}}^2} \tag{2.3-2}$$

$$=\frac{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(273.15\ \mathrm{K})}{0.022414\ \mathrm{m^3\ mol^{-1}}-0.0000391\ \mathrm{m^3\ mol^{-1}}}-\frac{0.1408\ \mathrm{Pa\ m^3\ mol^{-2}}}{(0.022414\ \mathrm{m^3\ mol^{-1}})^2}$$

$$=1.0122\times 10^5\ \mathrm{Pa}=0.9990\ \mathrm{atm}$$

For the ideal gas,

$$P=\frac{RT}{V_{\mathrm{m}}}=\frac{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(273.15\ \mathrm{K})}{0.022414\ \mathrm{m^3\ mol^{-1}}}=1.0132\times 10^5\ \mathrm{Pa}=1.0000\ \mathrm{atm}$$

Notice the fact that P depends on only two independent variables, T and V_{m}. Since P is intensive, it cannot depend on an extensive variable.

*Exercise 2.5

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 percent difference from the pressure of an ideal gas under the same conditions.

c. Find the pressure of 1.000 mol of nitrogen at a volume of 0.500 L and a temperature of 298.15 K using the van der Waals equation of state. Find the percent difference from the pressure of an ideal gas under the same conditions.

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

$$\frac{PV_m}{RT} = 1 + \frac{B_2}{V_m} + \frac{B_3}{V_m^2} + \frac{B_4}{V_m^3} + \cdots \tag{2.3-3}$$

which is a power series in the independent variable $1/V_m$. The B coefficients are called **virial coefficients**. The first virial coefficient, B_1, is equal to unity. The other virial coefficients must be taken as functions of temperature in order to obtain 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**:

$$PV_m = RT + A_2P + A_3P^2 + A_4P^3 + \cdots \tag{2.3-4}$$

The coefficients A_2, A_3, etc., are called **pressure virial coefficients**. It can be shown that A_2 and B_2 are equal.

Exercise 2.6

a. Show that $A_2 = B_2$. Proceed by solving Eq. (2.3-3) for P and substituting this expression for each P in Eq. (2.3-4). Then use the fact that the coefficient of any power of $1/V_m$ must be the same on both sides of the equation.

b. Show that $A_3 = B_3 - B_2^2$.

Table 2.1 displays several additional equations of state. The parameters in these equations of state are constants and values of parameters for several gases are to be 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 the two-parameter equations of state has been evaluated.[1] The Redlich–Kwong equation 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.

Graphical Presentation of Volumetric Data for Gases

Graphs of the **compression factor**, Z, are sometimes used to describe the behavior of gases:

$$Z = \frac{PV_m}{RT} \quad \text{(definition of the compression factor)} \tag{2.3-5}$$

Some older books use a different name, the "**compressibility factor**." We avoid this name since it might be confused with the compressibility, defined in Eq. (2.1-8). Figure 2.2 shows the compression factor for nitrogen gas at several temperatures. At fairly low temperatures, the compression factor decreases below unity for moderate pressures but rises above unity at higher pressure. At higher temperatures the compression factor is larger than unity for all 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 moderate pressures.

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[1] 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).

Table 2.1. Some 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 $\alpha(T)=\left\{1+m[1-(T/T_{\mathrm{c}})^{1/2}]\right\}^{2}$, where m is a 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: The equation is the same as the Soave modification, but $\alpha(T)$ is

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

where X and Y are 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.

O. Redlich and J. N. S. Kwong, *Chem. Rev.*, **44**, 233 (1949).
G. Soave, *Chem. Eng. Sci.*, **27**, 1197 (1972).
R. M. Gibbons and A. P. Laughton, *J. Chem. Soc., Faraday Trans. 2*, **80**, 1019 (1984).
J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1954, pp. 250ff.

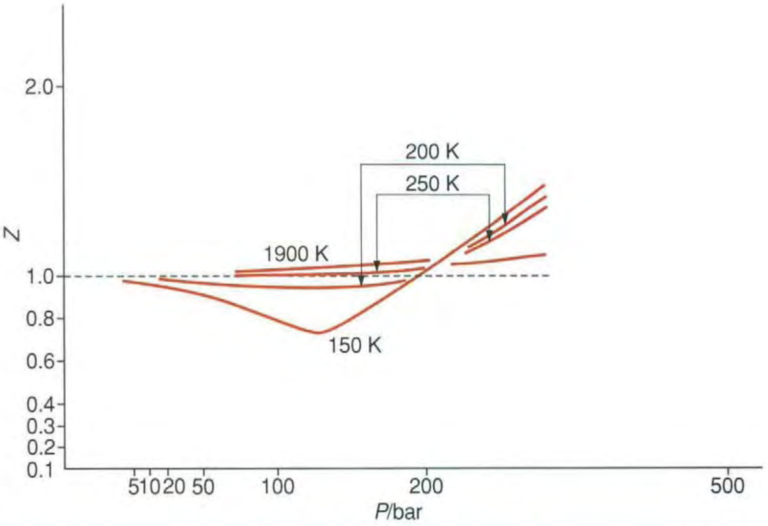

Figure 2.2. The Compression Factor of Nitrogen at Several Temperatures. The behavior of nitrogen is typical. At low temperatures, the value of Z is less than unity for moderate pressures, but rises above unity for larger pressures. At higher temperatures, the value of Z is greater than unity for all pressures.

For a van der Waals gas, the compression factor is

$$Z = \frac{PV_{\mathrm{m}}}{RT} = \frac{V_{\mathrm{m}}}{V_{\mathrm{m}} - b} - \frac{a}{RTV_{\mathrm{m}}} = \frac{1}{1 - by} - \frac{ay}{RT} \qquad (2.3\text{-}6)$$

where $y = 1/V_{\mathrm{m}}$. The variable y is proportional to the pressure at constant temperature if the pressure is small enough. Since a and b are both positive for all known gases, the first term on the right-hand side of Eq. (2.3-6) gives a positive contribution to Z, and the second term gives a negative contribution. The parameter b describes the effect of repulsive intermolecular forces, which make Z larger than it would be for an ideal gas, and the parameter a describes the effect of attractive intermolecular forces, which make Z smaller than it would be for an ideal gas. The first term is independent of the temperature, and the second term is inversely proportional to the temperature. 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. For large values of y, the denominator of the first term is small, making this term dominant even for lower temperatures. For any temperature below the Boyle temperature, there will thus be a nonzero value of the pressure at which $Z = 1$.

EXAMPLE 2.5

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

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

so that

$$T_{\mathrm{Boyle}} = \frac{a}{Rb}$$

b. For nitrogen,

$$T_{\mathrm{Boyle}} = \frac{0.1408\ \mathrm{Pa\ m^6\ mol^{-2}}}{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(3.913 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}})} = 433\ \mathrm{K}$$

*Exercise 2.7

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. (2.3-6) 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.

Gases are fairly well described by the ideal gas equation of state under ordinary conditions. We therefore recommend the following practice for making ordinary calculations: *Unless there is some reason to do otherwise, treat gases as though they were ideal.*

2.4 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, etc., are called **phase transitions** and the samples of matter in the different states are called **phases**. Such transitions take place abruptly and different phases can coexist. If a gas is at a temperature slightly above its condensation temperature at a certain fixed pressure, a small decrease in the temperature can produce coexisting liquid and gas phases, and a further small decrease in the temperature can produce a single liquid phase. Similarly, small increases in the pressure at constant temperature produce the same effects. This remarkable behavior seems to be an exception to the general rule that in nature small causes have small effects and large causes have large effects.

We will discuss the thermodynamics of phase equilibria in Chapter 6. It is found experimentally and understood thermodynamically that for any pure substance the pressure at which any two phases can coexist at equilibrium is a smooth mathematical function of the temperature (or equivalently, that the temperature is a smooth function of the pressure). Figure 2.3 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 or melting) curve at the upper left. The three curves meet at a point called the **triple point**. This point corresponds to 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 one atmosphere is called the **normal melting temperature** or **normal freezing temperature**, and the equilibrium temperature for coexistence of the liquid and gas phases at a pressure equal to one atmosphere is called the **normal boiling temperature**. These temperatures are marked on Figure 2.3. If the triple point happens to lie higher in pressure than one atmosphere the substance does not possess a normal freezing temperature or a normal boiling temperature, but possesses a **normal sublimation temperature** at which the solid and gas coexist at a pressure equal to one atmosphere. Carbon dioxide is such a substance. Its triple point 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. Another substance that can be observed to sublime is iodine. Its sublimation is noticeable because it is colored, but its sublimation pressure is less than 1 atm at room temperature. It has a normal melting temperature of 113.5°C.

The Critical Point

There is a remarkable feature in Figure 2.3: the liquid–vapor coexistence curve terminates at a point called the **critical point**. The temperature, molar volume, and pressure at this point are called the **critical temperature**, denoted by T_c, the **critical**

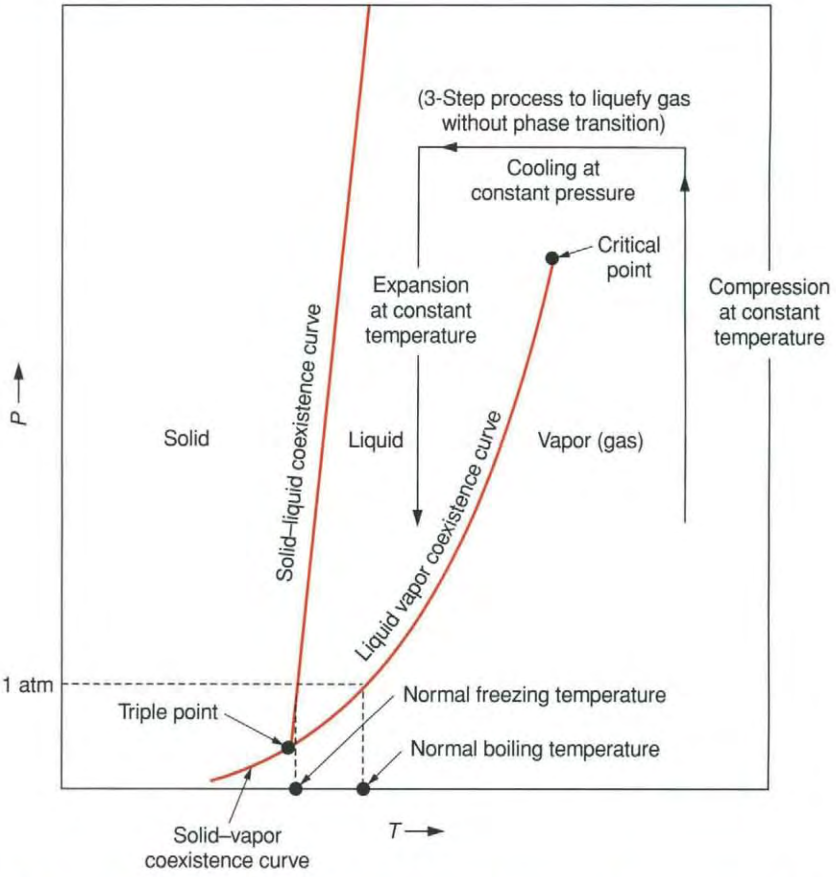

Figure 2.3. The Coexistence Curves for a Typical Pure Substance (Schematic). This diagram is typical of many fluids with relatively simple molecules. The curves represent the coexistence of two phases, and the areas represent possible states for a single phase.

molar volume, denoted by V_{mc}, and the **critical pressure**, denoted by P_c. These three quantities are called the **critical constants**. Table A.5 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, 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 2.3. There has been some speculation about whether the liquid–solid coexistence curve might also terminate at a critical point. Nobody has found such a critical point and some people think 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. There is no such qualitative difference between liquid and gas since both are disordered on the molecular level.

Fluids at supercritical temperatures are often referred to as gases, but such fluids can have liquidlike densities or gaslike densities with no phase transition between these densities. At high densities, multicomponent supercritical fluids can even exhibit phase separations like those of two immiscible liquids. Some industrial extractions, such as decaffeination of coffee, are carried out with supercritical fluids such as carbon dioxide.

We now want to describe the pressure of a simple system as a function of T and V_{m}, the molar volume, over the entire three-phase region. Figure 2.4 schematically shows the pressure as a function of molar volume for several fixed temperatures in the fluid region, with one curve for each fixed temperature. These constant-temperature curves are called **isotherms**. No two isotherms can intersect each other. For temperatures above the critical temperature there is only one fluid phase, and the isotherms are smooth curves. For subcritical temperatures, the liquid–gas phase transition is represented by a horizontal line segment in the isotherm. This line segment is called a **tie line**, and connects the two points representing the molar volumes of the coexisting liquid and gas phases. Tie lines are horizontal because the two phases must be at the same pressure to be at equilibrium. Aside from the tie line, a subcritical isotherm consists of two smooth branches. The liquid branch is nearly vertical since the liquid is nearly incompressible, while the gas branch of the curve is similar to the curve for an ideal gas.

As isotherms for subcritical temperatures closer and closer to the critical temperature are chosen, the tie lines become shorter and shorter until they shrink to zero length at the critical point. The isotherm that passes through the critical point must have a horizontal tangent line at the critical point to avoid crossing any tie line. This point on the isotherm is an inflection point, with a zero value of $(\partial P/\partial V_{\mathrm{m}})_T$ and a zero value of $(\partial^2 P/\partial V_{\mathrm{m}}^2)_T$, corresponding to infinite compressibility.

At the critical point, a fluid exhibits some unusual properties such as strong scattering of light and infinite heat capacity, as well as infinite compressibility. If a sample of a

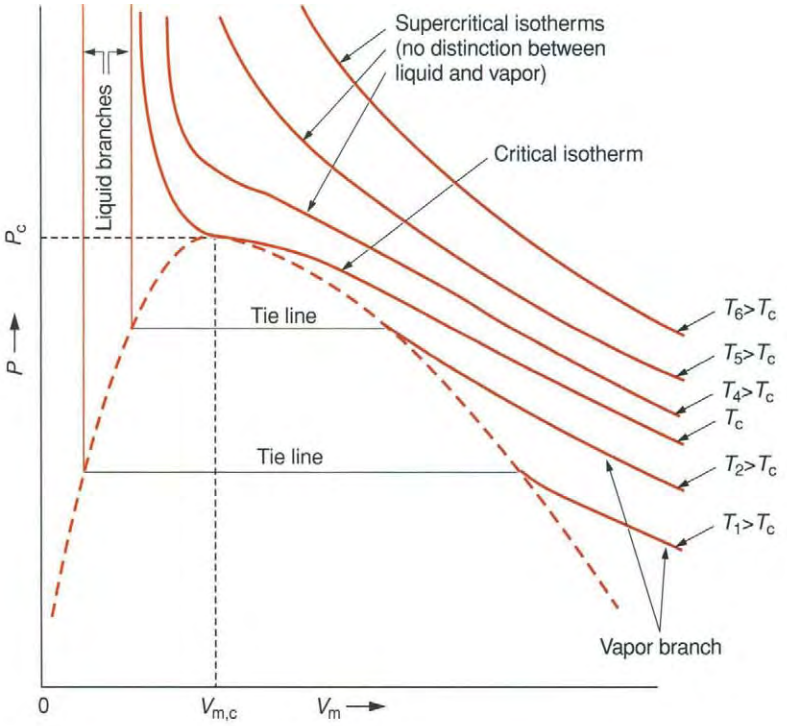

Figure 2.4. Isotherms for a Typical Pure Substance (Schematic). The horizontal line segments (tie lines) for temperatures lower than the critical temperature represent the coexistence of the liquid and gas phases. Only the ends of the tie lines represent possible intensive states. The curves other than line segments represent possible intensive states of a single phase.

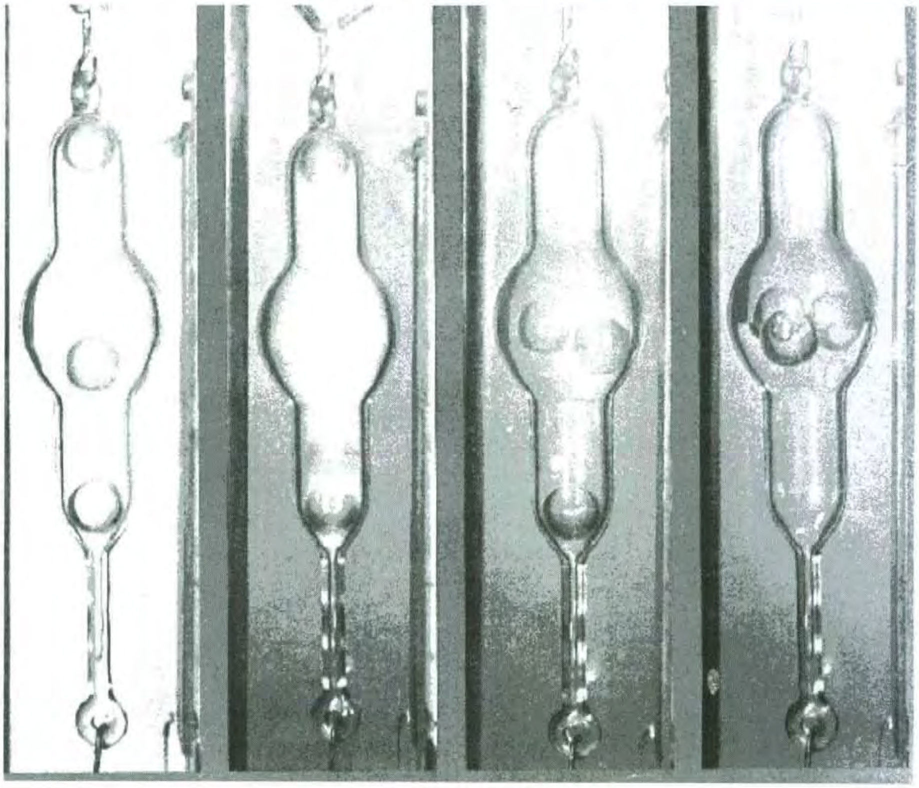

Figure 2.5. Liquid–Gas Equilibrium near the Critical Point. The three balls are slightly different in density, with densities close to the critical density of the fluid, carbon dioxide. (**a**) At a temperature slightly above the critical temperature. The density of the fluid depends slightly on height, 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*, **46** (June 10, 1968), p. 104. Used by permission of the copyright holder.

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 value, the meniscus between the liquid and gas phases becomes diffuse and then disappears at the critical temperature. At this temperature the liquid and gas phases become indistinguishable. Figure 2.5 shows photographs illustrating this behavior in carbon dioxide.[2]

The graphs in Figures 2.3 and 2.4 are projections of a single three-dimensional graph with the pressure as the dependent variable and the temperature and molar volume as the independent variables, as shown schematically in Figure 2.6. (The solid–liquid and solid–gas phase transitions are omitted from the diagram.) As shown in Figure 2.6, there are only two independent variables required to give the pressure as a dependent variable. This is true in general for intensive variables in a one-component fluid system. The **intensive state** of a system is the state so far as only intensive variables are concerned. The size of the system is irrelevant. Specification of the intensive state

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[2] J. V. Sengers and A. L. Sengers, *Chem. Eng. News*, **46**, 54 (June 10, 1968).

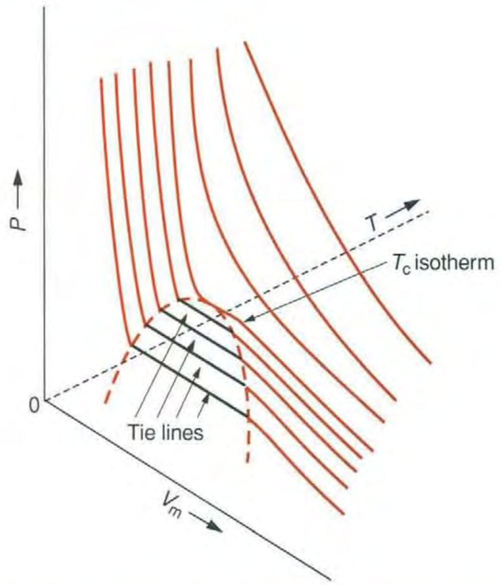

Figure 2.6. Surface Giving Pressure as a Function of Molar Volume and Temperature for a Typical Pure Substance in the Liquid–Vapor Region (Schematic). The three-dimensional diagram gives the same information as the set of all isotherms, of which a few are shown in Figure 2.4.

requires one fewer independent variable than specification of the full macroscopic state. That is, for a one-phase simple system of c components, $c + 1$ intensive variables are independent.

Several isotherms (intersections of the surface with planes of constant T) are drawn on the surface in Figure 2.6. The liquid–gas equilibrium tie lines joining liquid and gas states are seen on 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, being parallel to the direction of viewing. The set of all of them makes up the gas–liquid coexistence curve seen in Figure 2.3. When the three-dimensional graph is viewed in a direction perpendicular to the V_m–P plane, Figure 2.4 results.

Figure 2.7 shows schematically a more complete view of the three-dimensional graph of Figure 2.6, including the solid–liquid and solid–gas phase transitions. There are three sets of tie lines, as labeled in the figure, corresponding to the three curves in Figure 2.3. Since the entire fluid (liquid and gas) surface in Figure 2.6 is connected, it would seem possible to obtain an equation of state that would represent the entire surface accurately, making it unnecessary to use separate equations of state for the liquid and for the gas. Except for the ideal-gas equation, all of the gas-phase 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. 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. In Chapter 6, we will discuss the behavior of the equations of state in the two-phase region, and will discuss the construction of the tie lines. For any representation of the equation of state of a fluid, we can find equations that locate the critical point.

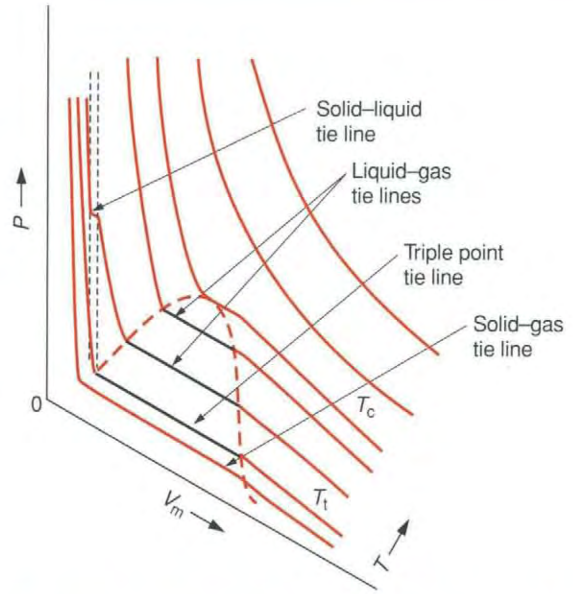

Figure 2.7. Surface Giving Pressure as a Function of Molar Volume and Temperature Showing all Three Phases (Schematic). This figure shows a more complete version of the surface of Figure 2.6, with the solid–liquid phase transition shown as well as the liquid–gas phase transition.

EXAMPLE 2.6

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

$$\left(\frac{\partial P}{\partial V_{\mathrm{m}}}\right)_T = 0 \tag{2.4-1}$$

$$\left(\frac{\partial^2 P}{\partial V_{\mathrm{m}}^2}\right)_T = 0 \tag{2.4-2}$$

The first derivative of Eq. (2.3-1) is

$$\left(\frac{\partial P}{\partial V_{\mathrm{m}}}\right)_T = -\frac{RT}{(V_{\mathrm{m}}-b)^2} + \frac{2a}{V_{\mathrm{m}}^3} \tag{2.4-3}$$

and the second derivative is

$$\left(\frac{\partial^2 P}{\partial V_{\mathrm{m}}^2}\right)_T = \frac{2RT}{(V_{\mathrm{m}}-b)^3} - \frac{6a}{V_{\mathrm{m}}^4} \tag{2.4-4}$$

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}:

$$T_c = \frac{8a}{27Rb}, \qquad V_{\mathrm{mc}} = 3b \tag{2.4-5}$$

Exercise 2.8

Solve the simultaneous equations to verify Eq. (2.4-5). One way to proceed is as follows. Obtain Eq. (I) by setting the right-hand side of Eq. (2.4-3) equal to zero, and Eq. (II) by setting the right-hand side of Eq. (2.4-4) 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 Eq. (2.3-1), the value of the critical pressure for a van der Waals gas is obtained:

$$P_c = \frac{a}{27b^2} \tag{2.4-6}$$

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

$$Z_c = \frac{P_c V_{mc}}{RT_c} = \frac{3}{8} = 0.375 \tag{2.4-7}$$

Exercise 2.9

Verify Eqs. (2.4-6) and (2.4-7).

Equations (2.4-5) and (2.4-6) can be solved for a and b:

$$a = 3V_{mc}^2 P_c = \frac{9RV_{mc}T_c}{8} = \frac{27R^2T_c^2}{64P_c} \tag{2.4-8}$$

$$b = \frac{V_{mc}}{3} = \frac{RT_c}{8P_c} \tag{2.4-9}$$

There are two or three formulas for each parameter, since values for only two variables are needed to obtain values for a and b. Since no substance exactly fits the equation, different values can result from the different formulas. The most accurate fit is obtained using P_c and T_c as independent variables since two-parameter equations of state do not usually give good values of the critical molar volume. The values of the parameters for any two-parameter or three-parameter equation of state can be obtained from critical constants.

Exercise 2.10

a. Show that for the Dieterici equation of state,

$$V_{mc} = 2b, \qquad T_c = \frac{a}{4bR}, \qquad P_c = \frac{a}{4b^2}e^{-2} \tag{2.4-10}$$

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:

$$a = \frac{R^2T_c^{5/2}}{9(2^{1/3}-1)P_c}, \qquad b = \frac{(2^{1/3}-1)RT_c}{3P_c} \tag{2.4-11}$$

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

***Exercise 2.11**

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

The Law of Corresponding States

From Eq. (2.4-7) we see that all substances that obey the van der Waals equation have the same value of the compression factor Z at the critical point, $Z_c = 0.375$. Any two-parameter equation of state gives a characteristic constant value of Z_c for all substances, although the different equations of state do not give the same value, as seen in Exercise 2.10. The Berthelot equation gives the same value as the van der Waals equation, 0.375. The experimental values for many different substances lie between 0.25 and 0.30.

There is an even greater degree of generality, expressed by an empirical law called the **Law of Corresponding States**:[3] *All substances obey the same equation of state in terms of reduced variables.* The reduced variables are defined as follows: The **reduced volume** is defined as the ratio of the molar volume to the critical molar volume:

$$V_r = \frac{V_m}{V_{mc}} \tag{2.4-12}$$

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

$$P_r = \frac{P}{P_c} \tag{2.4-13}$$

and the **reduced temperature** is defined as the ratio of the temperature to the critical temperature:

$$T_r = \frac{T}{T_c} \tag{2.4-14}$$

Using the definitions in Eqs. (2.4-12), (2.4-13), and (2.4-14) and the relations in Eqs. (2.4-5) and (2.4-6) we obtain, for a fluid obeying the van der Waals equation of state,

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

When these relations are substituted into Eq. (2.3-1), the result is

$$\left(P_r + \frac{3}{V_r^2}\right)\left(V_r - \frac{1}{3}\right) = \frac{8T_r}{3} \tag{2.4-15}$$

Exercise 2.12

Carry out the algebraic steps to obtain Eq. (2.4-15)

In Eq. (2.4-15), the parameters a and b have canceled out. 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 van der

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

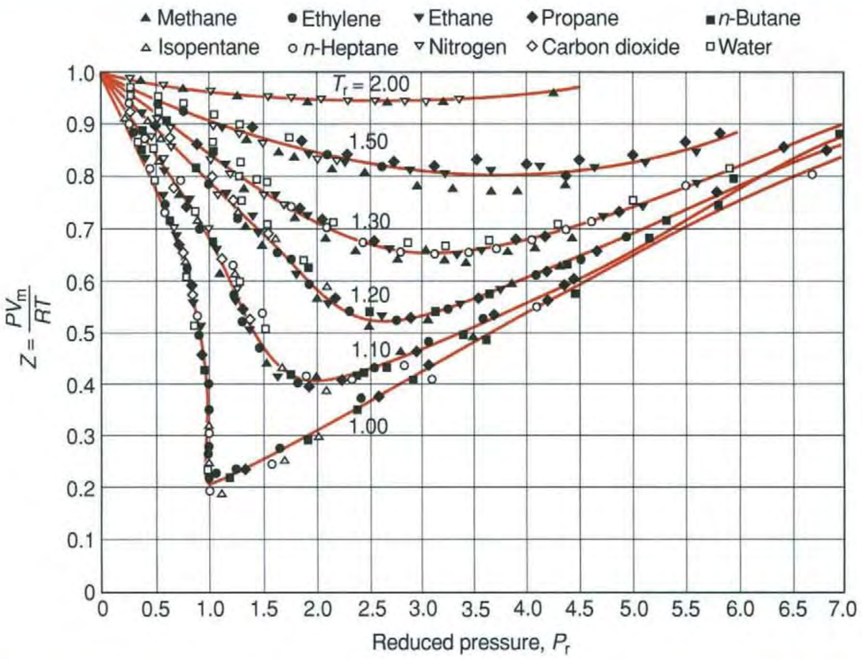

Figure 2.8. The Compression Factor as a Function of Reduced Pressure and Reduced Temperatures for a Number of Gases. This figure shows the extent to which ten substances obey the law of corresponding states. From G.-J. Su, *Ind. Eng. Chem.*, **38**, 803 (1946). Used by permission of the copyright holder.

Waals equation of state thus conforms to the law of corresponding states. Figure 2.8 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 temperatures.[4] The agreement of the data for different substances with the law of corresponding states is better than the agreement of the data with any simple equation of state.

Exercise 2.13

All two-parameter equations of state conform to the law of corresponding states. Show this fact for the Dieterici equation of state by expressing it in terms of the reduced variables.

Summary of the Chapter

The equilibrium macroscopic state of a one-phase simple 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 and liquids was described. A "calculation practice" was introduced. By this practice, gases are treated as ideal unless some specific reason exists for a more accurate treatment. Solids and liquids are treated as

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

though they had constant volume. For cases in which the ideal gas law is not an adequate description, several equations of state were presented.

Phase transitions were introduced. 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 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 when it is expressed in terms of reduced variables.

PROBLEMS

Problems for Section 2.1

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

***2.15.** 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.

2.16. 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 $(\partial P/\partial n)_{T,V}$.

2.17. Evaluate each of the partial derivatives in the previous problem for carbon dioxide at 298.15 K and 10.000 bar.

2.18. Finish the equation

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

2.19. Take $z = ax\cos(y/b)$, 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, Eq. (B-18) of Appendix B.

2.20. a. Find the fractional change in the volume of a sample of liquid water if its temperature is changed from 20.00°C to 40.00°C and its pressure is changed from 1.000 bar to 31.000 bar.

b. Estimate the percent change in volume of a sample of benzene if it is heated from −20°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 100.0 atm.

***2.21. 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.

2.22. 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.)

2.23. For the viral equation of state,

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

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

2.24. 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).

Problems for Section 2.2

***2.25.** 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 cm^3 mol^{-1} at 0°C and 11.0 cm^3 mol^{-1} at 150°C.

2.26. 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.

***2.27.** The volume of a sample of a liquid at constant pressure is sometimes 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.

2.28. The coefficient of thermal expansion of ethanol equals $1.12 \times 10^{-3}\ K^{-1}$ at 20°C and 1.000 atm. Find the volume of 1.000 mol of ethanol at 10°C and at 30°C. The density at 20°C is equal to $0.7893\ g\ cm^{-3}$.

Problems for Section 2.3

2.29. 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.

2.30. **a.** For the van der Waals equation of state temperature temperatures below the Boyle temperature, find an expression for a value of the pressure other than $P = 0$ for which $PV_m = RT$.

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

***2.31.** **a.** By differentiation, find an expression for the isothermal compressibility of a gas obeying the van der Waals equation of state.

b. Find the value of the isothermal compressibility of nitrogen gas at 298.15 K and $V_m = 24.4$ L. Compare with that of an ideal gas.

2.32. **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 $V_m = 24.4$ L.

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

2.34. Manipulate the Dieterici equation of state into the virial form as in Eq. (2.3-3). Use the identity

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

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

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

2.36. Express A_3 in Eq. (2.3-4) in terms of B_2 and B_3 in Eq. (2.3-3).

***2.37.** The experimental value of the compression factor $Z = PV_m/RT$ for hydrogen gas at $T = 273.15$ K and $V_m = 0.1497\ L\ mol^{-1}$ 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.

2.38. **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.

Problems for Section 2.4

2.39. **a.** Use the van der Waals equation of state in terms of reduced variables, Eq. (2.4-15), to calculate the pressure of 2.000 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.

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

2.40. Show that the Dieterici equation of state conforms to the law of corresponding states.

***2.41.** **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.

2.42. The critical temperature of xenon is 289.73 K, and its critical pressure is 5.840 MPa (5.840 megapascals).

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.

2.43. **a.** Show that if the virial equation of state is truncated at the third term,

$$\frac{PV_\mathrm{m}}{RT} = 1 + \frac{B_2}{V_\mathrm{m}} + \frac{B_3}{V_\mathrm{m}^2}$$

a critical point can occur.

b. Find the expressions for the critical pressure, the critical molar volume, and the critical temperature in terms of the virial coefficients.

c. Find the value of the compression factor $Z = pV_\mathrm{m}/RT$ at the critical point. How realistic do you think the representation could be?

General Problems

2.44. **a.** Manipulate the van der Waals equation of state into the virial form of Eq. (2.3-3). Use the identity

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

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.

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

$$V(t_\mathrm{C}) = V(0^\circ\mathrm{C})(1 + \alpha' t_\mathrm{C} + \beta' t_\mathrm{C}^2 + \gamma' t_\mathrm{C}^3 + \delta' t_\mathrm{C}^4)$$

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:

$$\alpha' = -6.4268 \times 10^{-5}(^\circ\mathrm{C})^{-1},$$

$$\beta' = 8.505266 \times 10^{-6}(^\circ\mathrm{C})^{-2},$$

$$\gamma' = -6.78977 \times 10^{-8}(^\circ\mathrm{C})^{-3},$$

$$\delta' = 4.01209 \times 10^{-10}(^\circ\mathrm{C}^{-4}),$$

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

$$\alpha' = -5.3255 \times 10^{-5}(^\circ\mathrm{C})^{-1},$$

$$\beta' = 7.615323 \times 10^{-6}(^\circ\mathrm{C})^{-2},$$

$$\gamma' = -4.37217 \times 10^{-8}(^\circ\mathrm{C})^{-3},$$

$$\delta' = 1.64322 \times 10^{-10}(^\circ\mathrm{C})^{-4}.$$

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.

2.46. **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. Draw 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. Draw 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. Draw 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 relative maximum and a relative 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 are said to be important in bringing water to the top of large trees, since pressure of 1.000 atm can raise liquid water to a height of only 34 ft. What negative pressure would be required to bring water to the top of a giant sequoia tree with height 300 ft? 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. Draw 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. Draw 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 2.1 and 2.2. 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. (A cubic equation must be solved. Get a numerical approximation to the solution by trial and error or other numerical method.) Compare your answer with the correct value, 18.798 $\text{cm}^3\ \text{mol}^{-1}$.

2.47. 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 equation of state 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 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 simple one-phase system containing one substance is specified by the value of three state variables.

g. Two gaseous systems with 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.

3

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

OBJECTIVES

After studying this chapter, a student should:

1. understand the relationship of heat, work and energy;
2. be able to calculate amounts of heat and work and energy changes for various nonchemical processes, using line integrals where appropriate;
3. be able to calculate energy and enthalpy changes for a class of chemical reactions.

PRINCIPAL FACTS AND IDEAS

1. Thermodynamics is a general macroscopic theory of the behavior of matter.
2. Thermodynamics is based on three empirical laws.
3. The first law of thermodynamics is a version of the law of conservation of energy.
4. A change in U, the thermodynamic energy or internal energy of a system, is defined by

   $$\Delta U = q + w$$

   where q is an amount of heat transferred to the system and w is an amount of work done on the system.
5. The first law asserts that the internal energy is a state function.
6. Heat is one way of transferring energy.
7. Work is another way of transferring energy.
8. The enthalpy is a variable whose change in a constant-pressure process is equal to the amount of heat transferred to the system in the process.

3.1 Work and the State of a System

Thermodynamics arose in the nineteenth century, not only as part of the strivings of scientists to understand the physical universe but also as part of the efforts of engineers to improve the efficiency of steam engines. This practical interest produced some important early advances in thermodynamics, but thermodynamics quickly grew to become the accepted general theory of the macroscopic behavior of matter at equilibrium. Thermodynamics is an inherently macroscopic theory. It is possible to discuss thermodynamics without the concepts of atoms and molecules, and its early development in the nineteenth century occurred before the universal acceptance of the atomic theory. It also differs from most of the theories of physics and chemistry in that it is based on empirical laws, not on unproved assumptions.

Thermodynamics is closely connected with the macroscopic state of a system, which we introduced in Chapter 1. We begin with easily defined and measured equilibrium variables such as n, T, V, and P. These variables depend only on the state of the system (and not on its history) and are called **state variables**. These state variables will be augmented by two experimental quantities, heat and work, which are not state variables. We will proceed to the definition of the thermodynamic energy, which is shown by experiment to be a state variable.

The Definition of Mechanical Work

The quantitative measurement of work was introduced by Carnot, who defined an amount of work as being the height an object 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 an object times the distance the object is moved in the direction of the force.* Coriolis' definition of work becomes the same as that of Carnot if the force on the object is that due to gravity. If the force and the displacement of the object are both in the z direction, the work done in an infinitesimal displacement is

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.

$$dw = F_z\, dz \quad \text{(definition of work)} \tag{3.1-1}$$

where dw is the quantity of work done on the object, F_z is the force exerted on the object in the z direction, and dz is an infinitesimal displacement of the object in the z direction. The SI unit of work is the joule, which corresponds to forces measured in newtons and distances measured in meters.

If the force and the displacement are not in the same direction, dw can be written as the **scalar product** of two vectors:

$$dw = \mathbf{F} \cdot d\mathbf{r} = |\mathbf{F}||d\mathbf{r}|\cos(\alpha) \tag{3.1-2}$$

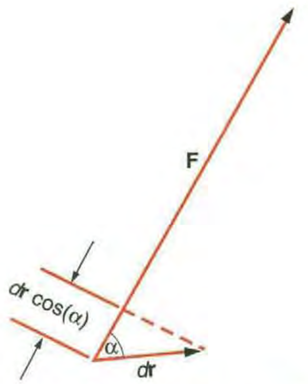

Figure 3.1. A Force and a Displacement. Only the component of the displacement in the direction of the force is effective in determining the amount of work.

where $\mathbf{F}$ is the vector force, where $d\mathbf{r}$ is the vector displacement, and where the angle between the vector $\mathbf{F}$ and the vector $d\mathbf{r}$ is denoted by α. The product $|d\mathbf{r}|\cos(\alpha)$ is the component of the displacement in the direction of the force, as shown in Figure 3.1. The scalar product of the vectors $\mathbf{F}$ and $d\mathbf{r}$, denoted by $\mathbf{F} \cdot d\mathbf{r}$, is defined by Eq. (3.1-2). There is no work done if the object does not move or if the force and the displacement are perpendicular to each other.

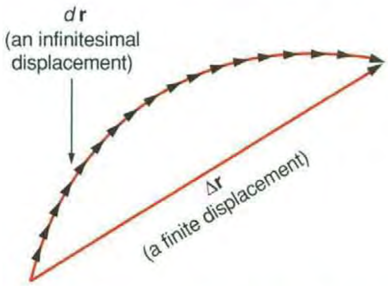

Figure 3.2. A Displacement Divided into Small Steps. If either the displacement or the force changes direction during the process, it must be divided into small steps such that the force and the displacement are constant during each step.

Vectors are discussed briefly in Appendix B. The formula shown in Eq. (3.1-2) can be written in terms of cartesian components as in Eq. (B-32) of Appendix B:

$$dw = F_x\,dx + F_y\,dy + F_z\,dz \tag{3.1-3}$$

We assume now that the force and the displacement are in the z direction, so that Eq. (3.1-3) becomes the same as Eq. (3.1-1). For a process that is not infinitesimal (a finite process) we can divide the displacement into small steps. This division is shown schematically in Figure 3.2 for a process that does not proceed in a single direction. In the limit that the sizes of the steps approach zero, any force is constant during each step, and we can write a version of Eq. (3.1-1) for the work done in each infinitesimal step. The work done on the object in the entire process is obtained by adding the work done in all of the steps making up the process. In the limit of infinitesimal steps, this sum becomes the integral

$$w = \int dw = \int F_z\,dz \tag{3.1-4}$$

where we denote an amount of work done in a finite process by w. In order to use Eq. (3.1-4) for an actual process, we must know how F_z depends on z.

EXAMPLE 3.1

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 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 $z = 10.0$ m.

Solution

Since the force is in the z direction, Eq. (3.1-4) applies:

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

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

The Work Done on a Closed Fluid System

Consider a closed fluid system confined in a vertical cylinder fitted with a piston, as depicted in Figure 1.1. let an external force F_{ext} be exerted downward on the piston (including any force on the piston due to gravity or atmospheric pressure). Since F_{ext} is downward, we assign its value to be negative. Let the height of the piston, z, be changed by the infinitesimal amount dz. If the piston moves downward, dz is negative. We assume that there is no friction, so that all of the force is transmitted to the system. The amount of work done on the system is given by Eq. (3.1-3):

$$dw = F_{\text{ext}}\,dz \tag{3.1-5}$$

We adopt the following convention: *A positive value of w corresponds to work being done on the system by the surroundings. A negative value of w corresponds to work being done on the surroundings by the system.* Equation (3.1-5) conforms to this convention. If dz is negative and F_{ext} is negative, then dw is positive, and work is done on the system.

The amount of work done on the surroundings is the negative of the work done on the system:

$$dw_{\text{surr}} = -dw \tag{3.1-6}$$

In our notation, a quantity without a subscript applies to the system, while a quantity applying to the surroundings is labeled with the subscript "surr." If the area of the piston is $\mathscr{A}$,

$$dw = \frac{F_{\text{ext}}}{\mathscr{A}}\mathscr{A}\,dz = -P_{\text{ext}}\mathscr{A}\,dz$$

where P_{ext} is defined as the magnitude of the external force on the piston divided by its area. Since $\mathscr{A}\,dz$ equals dV, we have

$$dw = -P_{\text{ext}}\,dV \tag{3.1-7}$$

The negative sign in Eq. (3.1-7) comes from the fact that F_{ext} is negative while P_{ext} is defined to be positive. We assert without proof that Eq. (3.1-7) holds for a fluid system with any shape, such as a system confined in a balloon or contained in an open beaker.

A system for which Eq. (3.1-7) holds is called a **simple system** and the work given by Eq. (3.1-7) is called "compression work." A fluid system or a strain-free solid system can be considered to be a simple system for most purposes, but if surface tension must be included, the work done in creating new surface area must be included so that even a fluid system can be a nonsimple system. We discuss surface tension in a later chapter and will find that it is usually negligible for liquids and solids and that it is always negligible for gases. For the present we neglect surface tension and treat all fluid systems as simple systems. A solid system might also have work done on it by bending or stretching it and would then not be a simple system. The "stress–strain" work would have to be added to the expression in Eq. (3.1-7). For a coil spring or a rubber band, the work done on the system is

$$dw = -P_{\text{ext}}\,dV + \tau\,dL \tag{3.1-8}$$

where τ is called the tension and where dL denotes the change in the length of the system. Electrochemical cells, which we discuss in Chapter 9, are also nonsimple systems.

*Exercise 3.1

A sample of a gas is compressed from a volume of 5.00 L to a volume of 1.000 L at a constant external pressure of 1.000 atm (101,325 N m^{-2}). Calculate the work done on the system. Explain why the result does not depend on the temperature or the amount of gas.

The three variables T, V, and n can be used to specify the equilibrium state of a simple one-phase one-component system. Therefore, the location of a point in a three-dimensional space with T, V, and n axes specifies an equilibrium macroscopic state of the system. Conversely, an equilibrium macroscopic state specifies the location of a point in this space. There is a **one-to-one correspondence** between an equilibrium state and a point in the space. The space is called a **state space** of the system, and the point corresponding to the state of the system is called a **state point**. Other choices of independent variables can also be made. For example, P, T, and n can be used and a space with P, T, and n axes becomes the state space.

Reversible Processes

A reversible process is one that can be reversed in direction by an infinitesimal change in the surroundings. The force on the piston in the system of Figure 1.1 due to the pressure of the system balances the external force since an infinitesimal change in the external force must reverse the direction of the process. The system must be at equilibrium, the piston must be stationary, and

$$F_{\mathrm{sys}} = P\mathscr{A} = P_{\mathrm{ext}}\mathscr{A} = -F_{\mathrm{ext}} \quad \text{(equilibrium)} \tag{3.1-9}$$

or

$$P = P_{\mathrm{ext}} \quad \text{(equilibrium)} \tag{3.1-10}$$

where P is the pressure of the system. During an infinitesimal step of a reversible process

$$dw_{\mathrm{rev}} = -P\,dV \quad \text{(simple system)} \tag{3.1-11}$$

Reversible processes are also called **quasi-equilibrium processes** or **quasi-static processes**. Since the system passes through equilibrium states, the process must take place infinitely slowly, and the state point passes through a succession of points in the equilibrium state space, tracing out a curve. Such a curve is schematically represented in Figure 3.3.

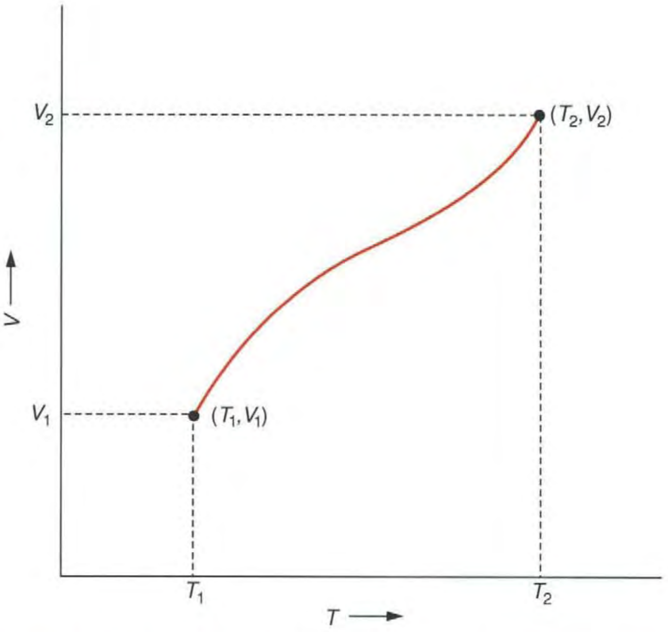

Figure 3.3. A Curve in State Space. During a reversible process the point representing the state of the system moves along a curve in the T–V state space.

Some real processes begin with a system in one equilibrium state (or metastable state) and end with the system in another equilibrium state, although the system passes through nonequilibrium states during the process. This class of real processes can often be discussed by comparison with reversible processes having the same initial and final states. Thermodynamics has also been extended to include irreversible processes by the use of additional assumptions,[1] but we will not discuss this branch of thermodynamics.

Work Done on an Ideal Gas in a Reversible Process

For a finite reversible change in volume on a closed system consisting of n moles of an ideal gas, we can write the work done as the integral of infinitesimal steps using the relation shown in Eq. (3.1-11):

$$w_{\mathrm{rev}} = \int_c dw_{\mathrm{rev}} = -\int_c P\,dV = -nR\int_c \frac{T}{V}\,dV \quad \text{(ideal gas, reversible process)} \tag{3.1-12}$$

Since the integrand in this integral depends on T as well as on V, a particular dependence of T on V must be specified that corresponds to the way in which the process is carried out. This dependence can be represented by a curve in the state space with T and V on its axes, and is used in the integrand function to replace T by the appropriate functions of V. The letter c below the integral sign indicates that a curve is needed to specify this dependence. This kind of integral is called a **line integral**.

If the temperature is constant during a process, the process is called **isothermal**. In a reversible isothermal process in an ideal gas, T can be factored out of the integral:

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

$$w_{\mathrm{rev}} = -nRT\,\ln\left(\frac{V_2}{V_1}\right) \quad \text{(ideal gas, reversible isothermal process)} \tag{3.1-13}$$

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

EXAMPLE 3.2

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

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

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

b. For a sample of ideal gas with fixed n,

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

At constant temperature, $dT = 0$ for each infinitesimal step of the process, so only the dV term contributes. We factor T out of the integral:

$$\Delta P = \int_{V_1}^{V_2} \left(\frac{\partial P}{\partial V}\right)_{T,n} dV = -nRT \int_{V_1}^{V_2} \frac{1}{V^2}\,dV = nRT\left(\frac{1}{V_2} - \frac{1}{V_1}\right)$$

$$= (50.00\text{ g})\left(\frac{1\text{ mol}}{39.938\text{ g}}\right)(8.3145\text{ J K}^{-1}\text{ mol}^{-1})(298.15\text{ K})$$

$$\times\left(\frac{1}{0.01000\text{ m}^3} - \frac{1}{0.005000\text{ m}^3}\right)$$

$$\Delta P = -3.104 \times 10^5\text{ J m}^{-3} = -3.104 \times 10^5\text{ Pa} = -3.063\text{ atm}$$

Exact and Inexact Differentials

The differential of a state function such as dP is called 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 end of the integration curve minus the function evaluated at the initial end of the curve. Therefore, the line integral of an exact differential depends only on the end-points, and not on the curve connecting them.* The integral of dP in part (**b**) of Example 3.2 is equal to the value of P at the end of the process minus the value of P at the beginning of the process:

$$\int_c dP = \Delta P = P_2 - P_1$$

A variety of different curves can have the same initial and final points, but the line integral of an exact differential depends only on the starting point and the final point and is independent of the path between these points. It 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.

Work is Not a State Function

Since w is not a state function, dw is not the differential of a function. A differential such as dw is called an **inexact differential**. The line integral of an inexact differential such as dw depends on the path of integration as well as on the initial point and the final point. *Two processes with the same initial and final states can correspond to different amounts of work done on the system.* We illustrate this important fact by considering a reversible process with the same initial and final states as the process of Example 3.2, but with a different path.

EXAMPLE 3.3

Calculate the work done on the ideal gas system of Example 3.2 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

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

$$w = -(50.0\ \mathrm{g})\frac{1\ \mathrm{mol}}{39.948\ \mathrm{g}}(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(200\ \mathrm{K})\ln\left(\frac{10.00\ \mathrm{L}}{5.000\ \mathrm{L}}\right)$$
$$= -1443\ \mathrm{J}$$

which is not equal to the amount of work in Example 3.2. Since a single case of path dependence is sufficient to show a differential to be inexact, this example shows that dw cannot be an exact differential.

Exercise 3.2

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

b. Calculate the line integral of dP for the process of Example 3.3. Show that the integral is path-independent for the two paths of Example 3.2 and Example 3.3. The integral will have to be done in three sections.

If P_{ext} is a known function, w can be calculated directly for an irreversible process. If P_{ext} is constant,

$$w_{\mathrm{irrev}} = -\int P_{\mathrm{ext}}\,dV = -P_{\mathrm{ext}}\int dV = -P_{\mathrm{ext}}(V_2 - V_1)$$

$$w_{\mathrm{irrev}} = -P_{\mathrm{ext}}\,\Delta V \quad (\text{constant } P_{\mathrm{ext}}) \qquad (3.1\text{-}14)$$

*Exercise 3.3

a. Calculate the amount of work done on the surroundings if the isothermal expansion of Example 3.2 is carried out at a constant external pressure of 1.000 atm instead of reversibly, but with the same initial and final states as in Example 3.2. 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?

For any particular representation of a real gas, the expression for the work done in an isothermal reversible volume change can be obtained by integration, shown in the following example.

EXAMPLE 3.4

Obtain the formula for the work done per mole of gas during an isothermal reversible volume change of a gas whose behavior is represented by the truncated virial equation of state:

$$\frac{PV_{\mathrm{m}}}{RT} = 1 + \frac{B_2}{V_{\mathrm{m}}} \qquad (3.1\text{-}15)$$

where B_2, the second virial coefficient, depends only on the temperature, and where $V_m = V/n$, the molar volume.

Solution

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

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

$$\begin{aligned} w_{\text{rev}} &= -\int_c P\,dV = -nRT\int_{V_1}^{V_2} \frac{1}{V}\,dV + n^2RTB_2\int_{V_1}^{V_2} \frac{1}{V^2}\,dV \\ &= -nRT\ \ln\left(\frac{V_2}{V_1}\right) + n^2RTB_2\left(\frac{1}{V_2} - \frac{1}{V_1}\right) \\ &= -nRT\ \ln\left(\frac{V_{m2}}{V_{m1}}\right) + nRTB_2\left(\frac{1}{V_{m2}} - \frac{1}{V_{m1}}\right) \end{aligned} \tag{3.1-16}$$

Note that w_{rev} is proportional to the size of the system, as expected.

*Exercise 3.4

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 3.4. The second virial coefficient of CO_2 is equal to $-128\ \text{cm}^3\ \text{mol}^{-1}$ at this temperature.

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

c. Calculate the work done if the process is carried out isothermally and irreversibly with a constant P_{ext} equal to 1.000 atm at a constant temperature of 25.00°C, but with the same initial and final volumes. For this calculation, does it matter whether CO_2 is assumed to be ideal or if it is described by another equation of state?

3.2

Heat

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 asserted that heat was a material but "imponderable" fluid called "caloric." This incorrect theory was not fully discredited until several decades after Black's death.

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

Heat Transferred during Temperature Changes

An amount of heat can be measured by determining the change in temperature that it produces in an object of known heat capacity. The **heat capacity**, C, of an object is defined such that

$$dq = C\,dT \tag{3.2-1}$$

where dq is an infinitesimal amount of heat transferred to the object and dT is a resulting infinitesimal change in temperature. It is an experimental fact that heat capacities are never negative. There is no system that lowers its temperature when heat is added. At first glance Eq. (3.2-1) might seem to indicate that C is a derivative of

q with respect to T. This is not the case because dq is an inexact differential like dw. Just as there is no such thing as the work content of a system there is no such thing as the heat content of a system. Therefore, the value of C depends on the way in which we change the temperature of the system. The heat capacity at constant volume is generally different in value from the heat capacity at constant pressure.

The **specific heat** (better called the **specific heat capacity**) is denoted by c and is defined as the heat capacity per unit mass, or C/m, where m is the mass of the object. The specific heat of a substance is an intensive quantity that is characteristic of each material. It generally depends on temperature as well as on the identity of the substance.

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

$$q = \int_c dq = \int_{T_1}^{T_2} C\,dT \tag{3.2-2}$$

where T_2 is the final temperature and T_1 is the initial temperature. If the heat capacity is independent of temperature it can be factored out of the integral:

$$q = C(T_2 - T_1) = C\,\Delta T \tag{3.2-3}$$

Just as with work, a positive value of q indicates heat transferred to the system, and a negative value indicates heat transferred from the system to its surroundings.

*Exercise 3.5

a. Find the amount of heat needed to heat 3.20 mol of liquid water from 25.00°C to 95.00°C. The specific heat of liquid water is nearly independent of temperature and is nearly equal to $1.00\ \mathrm{cal\ K^{-1}\ g^{-1}} = 4.184\ \mathrm{J\ K^{-1}\ g^{-1}}$.

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. Assume that the water and aluminum are insulated from the rest of the universe.

EXAMPLE 3.5

The molar heat capacity (heat capacity per mol) of water vapor at constant pressure of 1.000 atm is represented by

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

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

$$\begin{aligned} q &= (2.000\ \mathrm{mol}) \int_{373.15\ \mathrm{K}}^{773.15\ \mathrm{K}} [30.54\ \mathrm{J\ K^{-1}\ mol^{-1}} + (0.01029\ \mathrm{J\ K^{-2}\ mol^{-1}})T]\,dT \\ &= (2.000\ \mathrm{mol})\{(30.54\ \mathrm{J\ K^{-1}\ mol^{-1}})(400\ \mathrm{K}) \\ &\quad + (0.01029\ \mathrm{J\ K^{-2}\ mol^{-1}})\tfrac{1}{2}[(773.15\ \mathrm{K})^2 - (373.15\ \mathrm{K})^2]\} \end{aligned}$$

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

Heat Transferred during Phase Changes

This heat is sometimes called **latent heat** because it does not change the temperature of the system. The amount of latent heat per unit mass is characteristic of the substance and the phase transition. The latent heat of fusion (melting) of water at 0°C and 1.000 atm equals 79.72 cal g^{-1} or 333.5 kJ kg^{-1}. The latent heat of vaporization (boiling) of water at 100°C and 1.000 atm equals 539.55 cal g^{-1} or 2257.5 kJ kg^{-1}.

***Exercise 3.6**

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

3.3 Internal Energy. The First Law of Thermodynamics

Although Lavoisier discredited the phlogiston theory of combustion, which held that combustion was the loss of a second imponderable fluid called "phlogiston," he was one of the principal promoters of the equally incorrect caloric theory of heat espoused by Black. 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, a dull boring tool produced more heat than a sharp tool. 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. Rumford's results showed that "caloric" was not simply being extracted from the cannon, but that work was being converted to heat.

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

Julius Robert Mayer, 1814–1878, was a German physicist originally trained as a physician. He was apparently the first to espouse the law of conservation of energy, asserting that heat and work are just forms in which energy is transferred, and that energy can neither be created nor destroyed.

Rumford calculated a value for the "mechanical equivalent of heat," or the amount of heat to which a joule of work could be converted. His value was not very accurate. Better values were obtained by Mayer in 1842 and Joule in 1847. Joule carried out experiments in which changes of state were carried out either by doing work or by heating a system. His apparatus is depicted schematically in Figure 3.4. A falling mass turned a stirring paddle in a sample of water, raising the temperature by 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 required for a given change to the heat required for the same change was always the same, approximately 4.18 J of work to 1 cal of heat. The calorie is now defined to be exactly 4.184 J.

***Exercise 3.7**

Calculate the rise in temperature of 100.0 g of water if the falling weight of Figure 3.4 has a mass of 5.00 kg and drops by 0.800 m. Neglect friction in the pulleys, etc.

In Joule's experiments there was no detectable difference in the final state of the system whether its temperature was raised by doing work on it, by heating it, or by some combination of work and heating. This indicates that heat and work are actually two different means of changing a single property of the system, the internal energy U, which is a state function. Based on the work of Rumford, Mayer, Joule, and many others

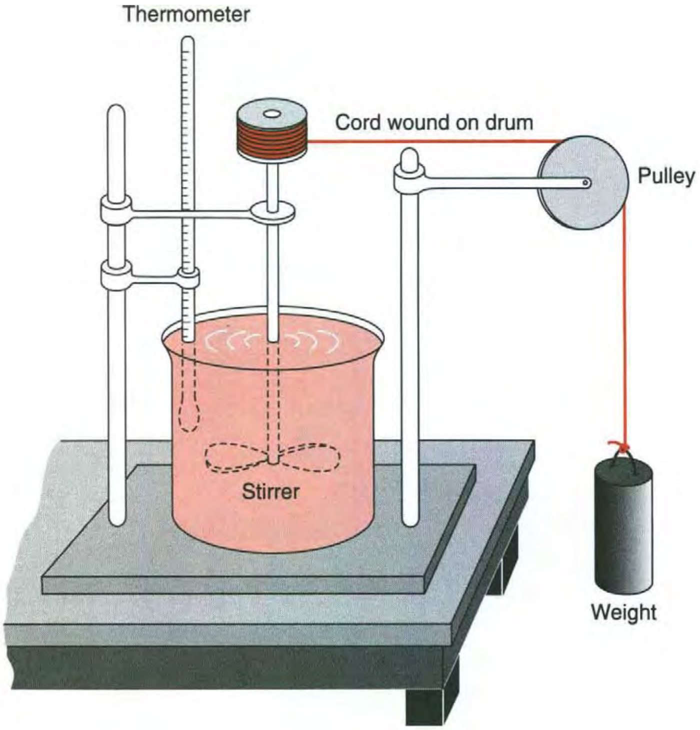

Figure 3.4. Joule's Apparatus for Determining the Mechanical Equivalent of Heat (Schematic). The falling weight does work on the water in the container, changing its energy to an extent that can be determined from the temperature change.

since the time of Joule, we state the **first law of thermodynamics**: *For a closed system and for any process that begins and ends with equilibrium states, ΔU is defined by*

$$\Delta U = q + w \tag{3.3-1}$$

where q is the amount of heat transferred to the system and w is the work done on the system. When so defined, ΔU is equal to the change in value of a state variable U, called the internal energy or the thermodynamic energy:

$$\Delta U = U_{\text{final}} - U_{\text{initial}} \tag{3.3-2}$$

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 Mayer and Joule, the initial credit for announcing the first law of thermodynamics went to Helmholtz.

A state variable is a mathematical function of the independent variables used to specify the state of the system and will from now on be referred to as a **state function**. For a simple equilibrium one-phase system containing one component, the state is specified by the values of three variables. We can write the internal energy as a function of T, V, and n:

$$U = U(T, V, n) \tag{3.3-3}$$

or as a function of a different set of three variables such as T, P, and n:

$$U = U(T, P, n) \tag{3.3-4}$$

Since heat and work are both means of changing the value of the internal energy, they do not maintain separate identities after the transfer of energy is finished. The following analogy has been used:[2] Heat is analogous to rain falling on a pond, work 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 measure how much rain and how much stream flow are in the pond. Like rain, once heat has been transferred to a system it is identifiable only as energy, and no longer as heat. Once work has been done on a system it is no longer identifiable as work, but only as energy. 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. However, like the amount of water in the pond, the energy of the system corresponding to a given equilibrium state is a state function.

Conservation of Energy

The first law of thermodynamics is a version of the **law of conservation of energy** for thermodynamic systems. The law of conservation of energy is a general law of physics to which there are no known exceptions. In fact, apparent violations of energy conservation led particle physicists to search for previously unknown particles that could be carrying energy away from a system, leading to the discovery of the neutrino.[3] In spite of the fact that no exceptions to the first law of thermodynamics have ever been verified, occasionally an unknown inventor announces a machine that will produce more energy than it takes in, violating the first law of thermodynamics. Such machines are known as **perpetual motion machines of the first kind**.

It is the total energy of a system that is governed by the law of conservation of energy. The gravitational potential energy of the system, the kinetic energy of the center of mass of the system, and the rest-mass energy are usually excluded from the internal energy of a chemical system. If so, the total energy is

$$E_{\text{total}} = \frac{1}{2}mv_c^2 + \mathcal{V}_g + m_0c^2 + U \tag{3.3-5}$$

where m is the mass of the system and m_0 is its rest-mass, c is the speed of light, v_c is the speed of its center of mass, $\mathcal{V}_g$ is the gravitational potential energy of the system, and U is the internal energy of the system. Equation (3.3-1) applies only to a closed system whose center of mass is not accelerated and whose gravitational potential energy and rest-mass do not change. These conditions apply to most laboratory systems. In a rocket, energy of combustion is turned into kinetic energy of the whole system, so we must consider the kinetic and potential energy of the system as a whole when we study the internal energy.

The Ideal Gas as an Example System

Thermodynamics applies to all systems, but it is convenient to have a system with simple properties to use for example calculations. The most commonly used example

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

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

system is the ideal gas. A mechanical model system that represents a monatomic ideal gas is a collection of noninteracting point-mass molecules, which have mass but zero size. Point-mass molecules have no internal motions (no electronic motion, no vibration, and no rotation). We will analyze this model system mathematically in Chapter 10 and Chapter 21, once assuming that the molecules' motions are described by classical mechanics and once assuming that they are described by quantum mechanics. Since there are no intermolecular interactions (no intermolecular forces), the potential energy is constant and can be taken as equal to zero. The internal energy of this model system is equal to the kinetic energy of the molecules.

For a model system of point-mass molecules the internal energy is proportional to the amount of the gas and to the temperature:

$$U = \tfrac{3}{2}Nk_{\mathrm{B}}T = \tfrac{3}{2}nRT \quad \text{(gas of point-mass molecules)} \tag{3.3-6}$$

where N is the number of molecules and n is the amount of the gas in moles. It is found that if the factor $\frac{3}{2}$ is included, k_{B} is Boltzmann's constant and R is the gas constant. We assume that we can use Eq. (3.3-6) for a dilute monatomic gas if the electronic energy is ignored. Experimental data for the inert gases (He, Ne, Ar, etc.) conform well to Eq. (3.3-6) at ordinary temperatures. See Chapter 10 and Chapter 21 for discussion of Eq. (3.3-6). We accept it now as an experimental fact.

For molecular gases, rotation and vibration of the molecules must be considered, but the electronic motion can usually be ignored at room temperature. For many gases at ordinary temperatures, the energy of vibrational motion is nearly constant at its minimum value, which can be chosen to equal zero. We will find in Chapter 21 that to a good approximation the rotational energy of a diatomic gas near room temperature is equal to nRT. The rotational energy of a polyatomic gas is approximately equal to $3nRT/2$ if the molecules of the gas are nonlinear (the nuclei do not lie along a straight line) and approximately equal to nRT if the molecules are linear. If the vibrational and electronic contributions can be ignored,

$$U \approx \tfrac{5}{2}nRT \quad \text{(dilute diatomic or linear polyatomic gas)} \tag{3.3-7}$$

$$U \approx 3nRT \quad \text{(dilute nonlinear polyatomic gas)} \tag{3.3-8}$$

Exercise 3.8

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

*__b.__ Find the value of the internal energy of 1.000 mol of argon gas at 298.15 K. Find the ratio of this energy to the rest-mass energy of the system. Find the difference between the observed mass of the system at 298.15 K and at 0 K.

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

3.4 Calculation of Amounts of Heat and Energy Changes

Up to now, we have defined a change in energy as the sum of an amount of heat transferred plus an amount of work done, assuming that both heat and work can be defined and measured satisfactorily. The amount of heat was measured through calorimetry, first defining the heat capacity and using Eq. (3.2-2).

An Alternative Definition of Heat

The first law of thermodynamics provides a means of calculating quantities of heat without using the calorimetric definition of Eq. (3.2-2). If separate means of calculating ΔU and w exist, the value of q can be calculated from

$$q = \Delta U - w \tag{3.4-1}$$

If the first law is assumed as a postulate, Eq. (3.4-1) can be used as the definition of the amount of heat transferred in a process.[4] In order to use Eq. (3.4-1) to define q we find an adiabatic process that has the same initial and final states as the process of interest. Since $q = 0$ for an adiabatic process,

$$\Delta U = w_{\text{adiabatic}} \tag{3.4-2}$$

$$q = w_{\text{adiabatic}} - w \tag{3.4-3}$$

We can regard this as an alternative definition of heat if the first law is accepted as a postulate. This approach is logically different from our original approach, in which it is assumed that heat can be defined and measured and in which the first law of thermodynamics is asserted as experimental fact.

The Energy of an Ideal Gas

The ideal gas gives simpler equations than almost any other system, so we frequently use it as an example system. It is a property of ideal gases at equilibrium that the internal energy depends only on the amount of gas and the temperature, and is independent of the volume or the pressure:

$$U = U(T, n) \quad \text{(ideal gas)} \tag{3.4-4}$$

The ideal gas property of Eq. (3.4-4) is almost as important as $PV = nRT$. We will prove this property in Chapter 5, assuming only that $PV = nRT$. For the present, we take it as an additional defined property of ideal gases. In an isothermal change of state of a closed ideal gas system, ΔU vanishes, so that from Eq. (3.3-1),

$$q = -w = nRT \ln\left(\frac{V_2}{V_1}\right) \quad \text{(ideal gas; reversible isothermal change)} \tag{3.4-5}$$

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[4] Callen, *op. cit.*, pp. 17ff [note 2].

where V_2 is the final volume and V_1 is the initial volume. Equations that apply to an ideal gas usually do not apply to other systems. You must keep in mind which equations apply only to a particular system, and which apply to all systems.

EXAMPLE 3.6

Find the amount of heat put into a system of 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

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

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

Since work is not a state function and since the internal energy is a state function, heat is not a state function. The amount of heat put into a system for a given change of state can depend on the path taken from the initial to the final state, as well as on the initial and final states, just as was the case with an amount of work. The change in the internal energy depends only on the initial and final states.

***Exercise 3.9**

Calculate the amount of heat that is put into the system of Example 3.6 if it expands irreversibly and isothermally at 298.15 K and at a constant external pressure of 1.000 atm (101,325 Pa) from a volume of 20.00 L to a volume of 100.00 L. Hint: ΔU is the same as in Example 3.6.

Energy Changes in a General Closed Simple System

Energy changes can be calculated by carrying out an integration of dU, either following the actual process or following another process with the same initial and final states. For a closed simple system and a reversible process,

$$\Delta U = \int_c \left(\frac{\partial U}{\partial T}\right)_{V,n} dT + \int_c \left(\frac{\partial U}{\partial V}\right)_{T,n} dV \quad \text{(closed simple system)} \qquad (3.4\text{-}6)$$

where c indicates the curve in the state space of the system. This curve is determined by the way in which the process is carried out and can be used to specify V as a function of T or to specify T as a function of V. These dependences are used in the integrands of the line integral of Eq. (3.4-6). The same value for ΔU will result if any curve having the same initial and final points is used for the line integration, so we can use any of these curves for the actual calculation. In addition, ΔU will have the same value for any irreversible process having the same equilibrium initial and final states.

The Heat Capacity at Constant Volume

For an infinitesimal change in a simple system,

$$dq = dU - dw = dU + P_{\text{ext}}\, dV$$

If V is constant, $dV = 0$ and $dw = 0$. Therefore,

$$dq = dU = \left(\frac{\partial U}{\partial T}\right)_{V,n} dT \quad (V \text{ constant, simple system}) \tag{3.4-7}$$

Comparison of this equation with Eq. (3.2-1) shows that

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,n} \tag{3.4-8}$$

where C_V is the *heat capacity at constant volume*. The constant-volume heat capacity is frequently measured for gases, but is seldom measured for liquids and solids because it is difficult to maintain a liquid or solid system at constant volume when the temperature is varied.

The second term on the right-hand side of Eq. (3.4-6) gives the variation of the internal energy with volume at constant temperature. As usual, the ideal gas is the simplest example system. Since U depends only on T and n for an ideal gas,

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = 0 \quad (\text{ideal gas}) \tag{3.4-9}$$

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

$$dU = C_V\, dT \quad (\text{closed system, ideal gas}) \tag{3.4-10}$$

For use in example calculations we apply the properties of our model system of noninteracting molecules from Section 3.3. For a dilute monatomic gas in which electronic and vibrational energy can be neglected, Eqs. (3.3-6), (3.3-7), and (3.3-8) give

$$C_V \approx \tfrac{3}{2}nR \quad (\text{dilute monatomic gas}) \tag{3.4-11}$$

$$C_V \approx \tfrac{5}{2}nR \quad (\text{dilute diatomic or linear polyatomic gas}) \tag{3.4-12}$$

$$C_V \approx 3nR \quad (\text{dilute nonlinear polyatomic gas}) \tag{3.4-13}$$

These equations are satisfactory approximations for some substances, but are not very accurate for others such as bromine, Br_2.

Exercise 3.10

The Euler reciprocity relation, Eq. (B-13), implies

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

Show that Eqs. (3.4-9) and (3.4-11) 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 experiment became known as the **Joule experiment** and was carried out in an apparatus schematically depicted in Figure 3.5. A sample of a gas was placed in one side of the apparatus and the other side of the apparatus was evacuated. The initial temperature of the apparatus was measured and called T_1. The stopcock was then opened to allow the gas to expand irreversibly into the vacuum, after which the final temperature, T_2, was measured.

We define the contents of the apparatus to be the system. Since the surroundings were not affected, 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, Eq. (3.4-1), 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 T_2 would differ from T_1. If the heat capacity of the apparatus and the heat capacity of the gas are known, the change in temperature of the gas, ΔT, could be calculated. The derivative $(\partial U/\partial V)_{T,n}$ could be determined as follows: The Joule experiment would be carried out several times with various volumes for the second chamber. The ratio $\Delta T/\Delta V$ is 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

$$\mu_J = \lim_{\Delta V \to 0}\left(\frac{\Delta T}{\Delta V}\right) = \left(\frac{\partial T}{\partial V}\right)_{U,n} \tag{3.4-14}$$

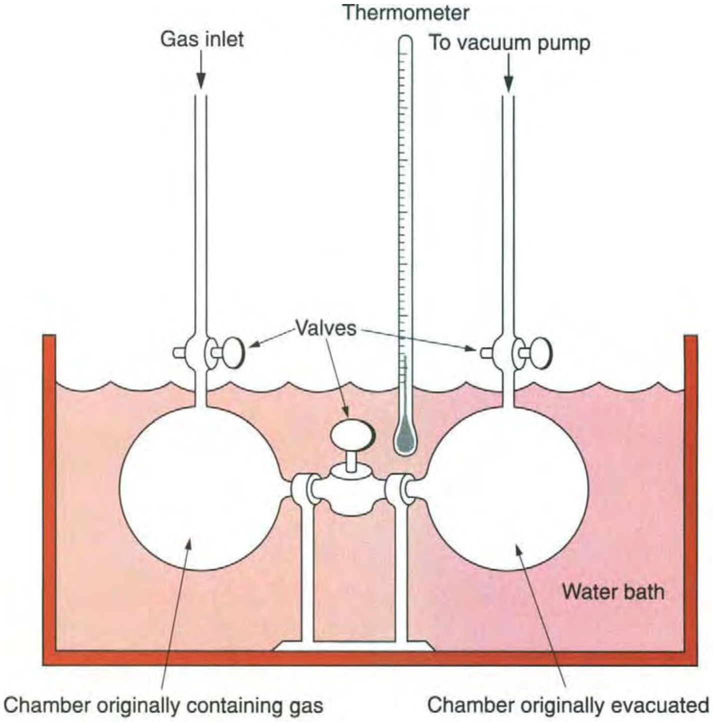

Figure 3.5. The Apparatus for the Joule Experiment (Schematic). The gas is allowed to expand irreversibly into the evacuated side of the apparatus.

We have established that U is fixed in the Joule experiment, and n is fixed because the system is closed, so that the subscripts on the partial derivative are U and n. The quantity μ_J is called the **Joule coefficient**.

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):

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = -\left(\frac{\partial T}{\partial V}\right)_{U,n}\left(\frac{\partial U}{\partial T}\right)_{V,n} = -\mu_J C_V \qquad (3.4\text{-}15)$$

Exercise 3.11

Verify Eq. (3.4-15).

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 the thermometers available at the time, even though he filled the apparatus at pressures up to 22 atm. Later versions of the experiment with better apparatus have given fairly good values of $(\partial U/\partial V)_{T,n}$. After the second law of thermodynamics has been introduced we will present a better way to determine values $(\partial U/\partial V)_{T,n}$.

Calculations of Energy Changes

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, by integration of Eq. (3.4-6).

EXAMPLE 3.7

If the virial equation of state, Eq. (2.4-2), is truncated at the second term, it can be shown that

$$\left(\frac{\partial U_m}{\partial V_m}\right)_{T,n} = \frac{RT^2}{V_m^2}\frac{dB_2}{dT} \qquad (3.4\text{-}16)$$

where R is the gas constant and where V_m is the molar volume. (See Exercise 5.13 for the derivation.) For argon gas at 298.15 K, B_2 is approximately equal to $-15.8\ \mathrm{cm^3\ mol^{-1}}$ and dB_2/dT is approximately equal to $0.25\ \mathrm{cm^3\ mol^{-1}\ K^{-1}}$. The molar constant-volume heat capacity of argon gas is nearly constant and equal to $3R/2$.

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 argon at 298.15 K and a molar volume of 20.000 L.

Solution

Since our system consists of 1.000 mol, we calculate the change in the molar energy, $U_m = U/n$. We also calculate the work done per mole.

a.

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

$$= -(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})^2(0.25\times 10^{-6}\ \mathrm{m^3\ mol^{-1}\ K^{-1}})$$

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

$$= 83\ \mathrm{J\ mol^{-1}}$$

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

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

$$= -(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})\left[\ln\left(\frac{20.0\ \mathrm{L}}{2.00\ \mathrm{L}}\right)\right.$$

$$\left. - (-15.8\ \mathrm{cm^3\ mol^{-1}})\left(\frac{1}{20000\ \mathrm{cm^3\ mol^{-1}}} - \frac{1}{2000\ \mathrm{cm^3\ mol^{-1}}}\right)\right]$$

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

$$q = \Delta U - w = 83\ \mathrm{J\ mol^{-1}} - (-5690\ \mathrm{J\ mol^{-1}}) = 5773\ \mathrm{J\ mol^{-1}}$$

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.

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = (8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})^2\left(\frac{0.25\times 10^{-6}\ \mathrm{m^3\ mol^{-1}\ K^{-1}}}{(0.02000\ \mathrm{m^3\ mol^{-1}})^2}\right)$$

$$= 462\ \mathrm{J\ m^{-3}}$$

$$\mu_\mathrm{J} = -\left(\frac{\partial U}{\partial V}\right)_{T,n}\frac{1}{C_V} = -\frac{462\ \mathrm{J\ m^{-3}}}{12.17\ \mathrm{J\ K^{-1}\ mol^{-1}}} = -38\ \mathrm{K\ (m^3\ mol^{-1})^{-1}}$$

*Exercise 3.12

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 Example 3.7 but with a constant external pressure of 1.000 atm. Compare with the values obtained assuming ideal gas behavior and with values obtained in Example 3.7.

b. Find the change in temperature if 1.000 mol of argon initially at 298.15 K is expanded adiabatically into a vacuum so that its volume changes from 2.000 L to 20.00 L.

A change in internal energy for a nonisothermal process can be calculated by carrying out the line integral in Eq. (3.4-6).

EXAMPLE 3.8

Calculate ΔU for a process that takes 1.000 mol of argon from $T = 298.15$ K and $V = 2.000$ L to $T = 373.15$ K and $V = 20.000$ L.

Solution

Since U is a state function, we can choose any path with the proper end-points to calculate ΔU. We integrate along the path shown in Figure 3.6. The path of the actual process must be used to calculate q and w, since they are path-dependent. The first line segment of the path is that of Example 3.7, so ΔU_1, the change in energy for that part, is equal to 83 J mol^{-1}. For the second line segment,

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

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

where $C_{V,\text{m}}$ is the molar heat capacity at constant volume. Therefore

$$\Delta U = \Delta U_1 + \Delta U_2 = 83\ \text{J} + 935\ \text{J} = 1018\ \text{J}$$

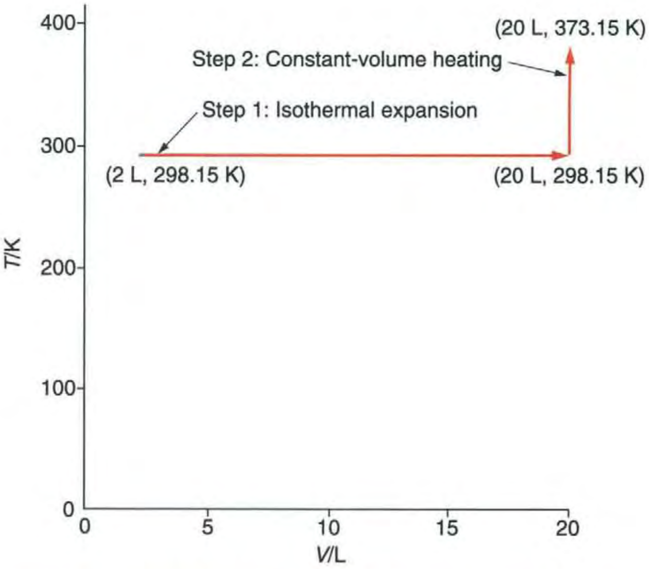

Figure 3.6. The Curve Representing the Path for the ΔU Line Integral. This is a reversible path consisting of an isothermal expansion and a constant-volume change in temperature.

*Exercise 3.13

a. Calculate q and w for the reversible process that follows the path used in Example 3.8.

b. Calculate q and w for the reversible process for 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)?

Adiabatic Processes

In an adiabatic process, q is equal to zero and dq is equal to zero for any infinitesimal step of the process.

$$dU = dq + dw = dw \quad \text{(adiabatic process)} \tag{3.4-17}$$

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

$$dU = C_V\,dT \quad \text{(ideal gas, reversible process)} \tag{3.4-18}$$

Since $PV = nRT$ for an ideal gas,

$$dw = -P\,dV = -\frac{nRT}{V}\,dV \quad \text{(ideal gas, reversible process)} \tag{3.4-19}$$

Equating dU and dw (because $dq = 0$), we obtain

$$C_V\,dT = -\frac{nRT}{V}\,dV \quad \text{(ideal gas, reversible adiabatic process)} \tag{3.4-20}$$

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

To a good approximation, C_V is a constant for many gases at ordinary temperatures. With this assumption we can solve Eq. (3.4-20) by separation of variables. We divide by T to separate the variables:

$$\frac{C_V}{T}\,dT = -\frac{nR}{V}\,dV \tag{3.4-21}$$

We integrate Eq. (3.4-21) from the initial state, denoted by V_1 and T_1, to the final state, denoted by V_2 and T_2:

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

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

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{nR/C_V} = \left(\frac{V_1}{V_2}\right)^{R/C_{V,\mathrm{m}}} \quad \text{(reversible adiabatic process, ideal gas, } C_V \text{ constant)} \tag{3.4-22}$$

If the initial values V_1 and T_1 are given, this equation gives T_2 as a function of V_2 or V_2 as a function of T_2. It is an example of an important general fact: *For a reversible adiabatic process in a simple system, the final temperature is a single-valued function of the final volume for a given initial state.* All of the possible final state points for reversible adiabatic processes lie on a single curve in the state space. Such a curve is called a **reversible adiabat**. This fact will be important in our discussion of the second law of thermodynamics in Chapter 4.

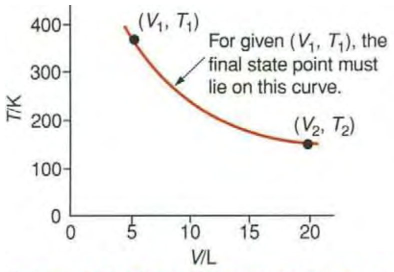

Figure 3.7. Final Temperature as a Function of Final Volume for the Adiabatic Expansion of an Ideal gas. For each initial state, there is only one such curve.

EXAMPLE 3.9

A system consisting of 2.000 mol of argon, assumed ideal with C_V equal to $3nR/2$, 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.

Solution

$$T_2 = T_1\left(\frac{V_1}{V_2}\right)^{nR/C_V} = (373.15\ \mathrm{K})\left(\frac{5.000\ \mathrm{L}}{20.00\ \mathrm{L}}\right)^{2/3} = 148.1\ \mathrm{K}$$

Figure 3.7 represents the final temperature as a function of the final volume for this example.

*Exercise 3.14

a. Find the final temperature for the system of Example 3.9 if the final volume is 10.00 L.

b. Find the volume to which the system of Example 3.9 must be adiabatically and reversibly expanded in order to reach a temperature of 273.15 K.

An equation analogous to Eq. (3.4-20) can be written for any representation of a real gas. For a gas obeying van der Waals equation of state it can be shown (see Problem 5.35) that

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = \left(\frac{\partial U_{\mathrm{m}}}{\partial V_{\mathrm{m}}}\right)_{T,n} = \frac{a}{V_{\mathrm{m}}^2} \qquad (3.4\text{-}23)$$

Exercise 3.15

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

$$C_{V,\mathrm{m}}\,dT = -\frac{RT}{V_{\mathrm{m}} - b}\,dV_{\mathrm{m}} \qquad (3.4\text{-}24)$$

Exercise 3.16

Show that for a reversible adiabatic process in a van der Waals gas with constant $C_{V,\mathrm{m}}$,

$$\left(\frac{T_2}{T_1}\right) = \left(\frac{V_{\mathrm{m1}} - b}{V_{\mathrm{m2}} - b}\right)^{R/C_{V,\mathrm{m}}} \qquad (3.4\text{-}25)$$

EXAMPLE 3.10

Find the final temperature for the process of Example 3.9, using Eq. (3.4-25) instead of Eq. (3.4-22), but still assuming that $C_{V,\mathrm{m}} = 3R/2$.

Solution

From Table A.3, the van der Waals parameter $b = 3.219 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}$ for argon.

$$\begin{aligned} T_2 &= (373.15\ \mathrm{K})\left(\frac{5.000 \times 10^{-3}\ \mathrm{m^3\ mol^{-1}} - 3.22 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}}{20.00 \times 10^{-3}\ \mathrm{m^3\ mol^{-1}} - 3.22 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}}}\right)^{2/3} \\ &= 147.6\ \mathrm{K} \end{aligned}$$

This value differs from ideal behavior by 0.5 K.

If the molar heat capacity of a van der Waals gas is not constant, but can be represented by

$$C_{V,\mathrm{m}} = \alpha + \beta T \qquad (3.4\text{-}26)$$

the equation analogous to Eqs. (3.4-22) and (3.4-25) is

$$\frac{T_2}{T_1}\exp\left(\frac{\beta(T_2 - T_1)}{\alpha}\right) = \left(\frac{V_{\mathrm{m1}} - b}{V_{\mathrm{m2}} - b}\right)^{R/\alpha} \qquad (3.4\text{-}27)$$

Exercise 3.17

Show that Eq. (3.4-27) is correct.

An equation analogous to Eq. (3.4-22) exists for any simple system. 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. The volume and the temperature are not the only choices for independent variables. For an ideal gas with constant heat capacity, we can substitute the ideal gas equation, $T = PV_{\mathrm{m}}/R$, into Eq. (3.4-22) to obtain

$$\frac{P_2}{P_1} = \left(\frac{V_{\mathrm{m}1}}{V_{\mathrm{m}2}}\right)^{1+R/C_{V,\mathrm{m}}} = \left(\frac{V_1}{V_2}\right)^{1+R/C_{V,\mathrm{m}}} \tag{3.4-28}$$

and

$$\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/(C_{V,\mathrm{m}}+R)} \tag{3.4-29}$$

***Exercise 3.18**

The "Santa Ana" winds of the California coast are dry 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 ft above sea level) and a temperature of 25°C and that it is adiabatically and reversibly compressed to a pressure of 1.00 atm. Assume that air is an ideal gas with $C_{V,\mathrm{m}} = 5R/2 = \text{constant}$. Find the final temperature. This treatment ignores other factors that raise the temperature, such as frictional heating as the air passes along the ground.

3.5 Enthalpy—A Convenience Variable

Many chemical systems are contained in vessels that are open to the atmosphere, and are thus maintained at a nearly constant pressure.[5] For analysis of processes taking place under constant-pressure conditions, we define a new variable, denoted by H and called the **enthalpy**:

$$H = U + PV \quad \text{(definition)} \tag{3.5-1}$$

The enthalpy is a state function because U, P, and V are state functions. It is one of a class of variables sometimes called "**convenience variables.**"

Consider a simple system whose pressure remains equal to a constant external pressure. From now on we will refer to these conditions simply as constant-pressure conditions, but we mean also that the pressure is equal to the external pressure. For any such process

$$dw = -P_{\mathrm{ext}}\,dV = -P\,dV \quad \text{(constant pressure)} \tag{3.5-2}$$

---

[5] The Extreme 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.

This expression for dw is the same as that for reversible processes, Eq. (3.1-11). We do not assert that all processes that occur at constant pressure are reversible processes, but only that the same expression for dw applies. For a simple system at constant pressure,

$$\begin{aligned} w &= \int_c dw = -\int_c P_{\text{ext}}\, dV = -\int_c P\, dV = -P(V_2 - V_1) \\ &= -P\,\Delta V \quad \text{(simple system, constant pressure)} \end{aligned} \tag{3.5-3}$$

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

The heat transferred to the system is given by

$$dq = dU - dw = dU + P\,dV \quad \text{(constant pressure)} \tag{3.5-4}$$

From Eq. (3.5-1)

$$dH = dU + P\,dV + V\,dP \tag{3.5-5}$$

At constant pressure, the $V\,dP$ term vanishes, so that

$$dq = dH \quad \text{(constant pressure)} \tag{3.5-6}$$

For a finite process

$$q = \Delta H \quad \text{(constant pressure)} \tag{3.5-7}$$

Although q is generally path-dependent, it is path-independent for constant-pressure processes since for such processes q is equal to the change in the state function H. Since $dw = dU - dq$, w is also path-independent for constant-pressure processes. Enthalpy changes of processes are sometimes called "heats" of the processes.

The Heat Capacity at Constant Pressure

The heat capacity at constant pressure is

$$C_P = \lim_{\Delta T \to 0}\left(\frac{q}{\Delta T}\right)_P = \lim_{\Delta T \to 0}\left(\frac{\Delta H}{\Delta T}\right)_P$$

so that

$$C_P = \left(\frac{\partial H}{\partial T}\right)_{P,n} \tag{3.5-8}$$

The heat capacity at constant pressure is the most commonly measured heat capacity for solids and liquids because C_V is hard to measure for these systems. We now obtain an expression for the difference between C_P and C_V so that C_V can be calculated from C_P. We first substitute the definition of the enthalpy, Eq. (3.5-1), into Eq. (3.5-8):

$$C_P = \left(\frac{\partial H}{\partial T}\right)_{P,n} = \left(\frac{\partial U}{\partial T}\right)_{P,n} + P\left(\frac{\partial V}{\partial T}\right)_{P,n} \tag{3.5-9}$$

There is no $V(\partial P/\partial T)$ term because P is held constant in the differentiation. As an example of the variable-change identity, Eq. (B-7) of Appendix B, we can write

$$\left(\frac{\partial U}{\partial T}\right)_{P,n} = \left(\frac{\partial U}{\partial T}\right)_{V,n} + \left(\frac{\partial U}{\partial V}\right)_{T,n}\left(\frac{\partial V}{\partial T}\right)_{P,n} \tag{3.5-10}$$

We substitute this equation into Eq. (3.5-9) and use the fact that $C_V = (\partial U/\partial T)_{V,n}$ to write

$$C_P = C_V + \left[\left(\frac{\partial U}{\partial V}\right)_{T,n} + P\right]\left(\frac{\partial V}{\partial T}\right)_{P,n} \tag{3.5-11}$$

Equation (3.5-11) takes on a simple form for an ideal gas, because

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

and

$$\left(\frac{\partial V}{\partial T}\right)_{P,n} = \frac{nR}{P} \quad \text{(ideal gas)}$$

so that

$$C_P = C_V + nR \quad \text{(ideal gas)} \tag{3.5-12}$$

The physical explanation for Eq. (3.5-12) is that in heating an ideal gas under constant-volume conditions, no work is done on the surroundings and all of the heat increases the energy of the system. Under constant-pressure conditions, some of the heat is turned into work against the external pressure as the gas expands, so the same amount of heat produces a smaller change in the energy and thus a smaller change in the temperature. Equations (3.4-11) through (3.4-13) give with Eq. (3.5-12)

$$C_{P,\mathrm{m}} \approx \tfrac{5}{2}R \quad \text{(dilute monatomic gases)} \tag{3.5-13a}$$

$$C_{P,\mathrm{m}} \approx \tfrac{7}{2}R \quad \text{(dilute diatomic or linear polyatomic gases without electronic or vibrational excitation)} \tag{3.5-13b}$$

$$C_{P,\mathrm{m}} \approx 4R \quad \text{(dilute nonlinear polyatomic gases without electronic or vibrational excitation)} \tag{3.5-13c}$$

The ratio of the constant-pressure heat capacity to the constant-volume heat capacity is denoted by γ:

$$\gamma = \frac{C_{P,\mathrm{m}}}{C_{V,\mathrm{m}}} = \frac{C_P}{C_V} \quad \text{(definition of } \gamma\text{)} \tag{3.5-14}$$

The values in Eq. (3.5-13) give

$$\gamma \approx \tfrac{5}{3} \quad \text{(dilute monatomic gas)} \tag{3.5-15a}$$

$$\gamma \approx \tfrac{7}{5} \quad \text{(dilute diatomic or linear polyatomic gases without electronic or vibrational excitation)} \tag{3.5-15b}$$

$$\gamma \approx \tfrac{4}{3} \quad \text{(dilute nonlinear polyatomic gases without electronic or vibrational excitation)} \tag{3.5-15c}$$

Table A.6 in Appendix A gives data on the molar constant-pressure heat capacity for several substances. For gases, the data are represented by the polynomial

$$C_{P,\mathrm{m}} = a + bT + cT^{-2} \tag{3.5-16}$$

The temperature dependence in this formula comes from the contributions of vibrational and electronic motions. For liquids and solids near room temperature, heat capacities are nearly constant, so that the values in the table can be used over a range of temperatures. Additional values are found in Table A.8 of Appendix A, which is a general table of thermodynamic data.

For many metallic solids and other solids in which one 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**. A more general property, shared by all substances, is that the heat capacity of any system approaches zero as the temperature approaches 0 K.

Pierre Louis Dulong, 1785–1838, was a French chemist originally trained as a physician. Alexis Thérèse Petit, 1791–1820, was a French physicist.

***Exercise 3.19**

a. Evaluate $C_{P,\mathrm{m}}$ for oxygen gas at 298.15 K and at 1000 K, using the polynomial representation in Table A.6. Find the percent differences between these values and $5R/2$.

b. Find the percent differences between $C_{P,\mathrm{m}}$ of copper and of iron and $3R$ at 298.15 K.

The Joule–Thomson Experiment

William Thomson, 1824–1907, later Lord Kelvin, was a Scottish mathematician and physicist who proposed the absolute temperature scale. He was an early supporter of Joule and became a close personal friend. He had many accomplishments, including the introduction of the Bell telephone into Great Britain, but is reported to have stated around 1880 that all possible discoveries in physics had already been made.

This experiment was carried out by Joule and Thomson in the 1850s in a second attempt to determine a difference between the behavior of real gases and ideal gases. For an ideal gas the enthalpy depends only on T and n:

$$H = U + PV = U(T, n) + nRT = H(T, n)$$

$$H = H(T, n) \quad \text{(ideal gas)} \tag{3.5-17}$$

Therefore,

$$\left(\frac{\partial H}{\partial P}\right)_{T,n} = 0 \quad \text{(ideal gas)} \tag{3.5-18}$$

In order to determine the value of $(\partial H/\partial P)_{T,n}$ for real gases, Joule and Thomson used an apparatus equivalent to the one schematically shown in Figure 3.8. This apparatus consists of two cylinders fitted with pistons and with a porous 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. By pushing in on the left piston and pulling out on the right piston, a steady flow of gas can be maintained through the porous plug. If the pressure on each side is kept fixed, a time-independent nonequilibrium state (a steady state) will be attained with a different constant temperature on each side. Several experiments are carried out on a given gas with different values of the pressure difference. The Joule–Thomson coefficient is defined as the extrapolated limit

$$\mu_{\mathrm{JT}} = \lim_{P_{\mathrm{R}} \to P_{\mathrm{L}}} \left(\frac{T_{\mathrm{R}} - T_{\mathrm{L}}}{P_{\mathrm{R}} - P_{\mathrm{L}}}\right) = \lim_{\Delta P \to 0} \left(\frac{\Delta T}{\Delta P}\right) \quad \text{(definition)} \tag{3.5-19}$$

where the subscripts R and L indicate right and left. The limit in Eq. (3.5-19) is a partial derivative, but we must determine what variable is held fixed in the differentiation.

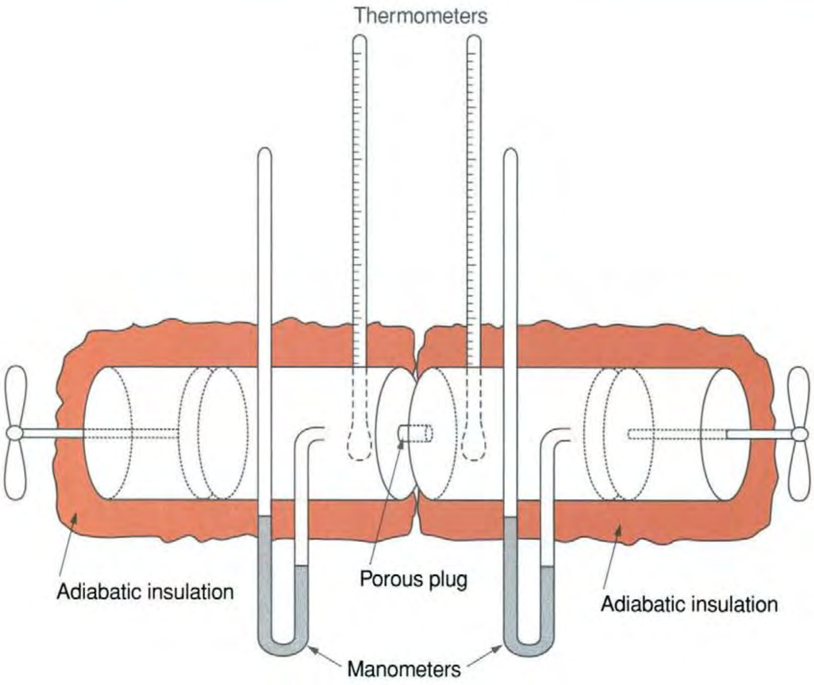

Figure 3.8. The Apparatus for the Joule–Thomson Experiment (Schematic). During the experiment, one of the pistons is moved into its cylinder and the other piston is withdrawn in a way so that the pressure on each side remains constant as the gas flows irreversibly through the porous plug.

We choose as our system a sample of n moles of gas that flows through the porous plug after the steady state is established. We assume that all irreversible processes take place within the porous plug, so that the gas inside each chamber is at equilibrium and is at a pressure equal to the external pressure on that side. This set of assumptions allows us to use our technique of discussing nonequilibrium processes with equilibrium initial and final states.

The work done on the gas on the left side is given by

$$w_{\mathrm{L}} = -\int_{V_{\mathrm{L1}}}^{V_{\mathrm{L2}}} P_{\mathrm{L}}\, dV_{\mathrm{L}} = -P_{\mathrm{L}}(V_{\mathrm{L2}} - V_{\mathrm{L1}}) \tag{3.5-20}$$

and the work done on the gas on the right side is given by

$$w_{\mathrm{R}} = -\int_{V_{\mathrm{R1}}}^{V_{\mathrm{R2}}} P_{\mathrm{R}}\, dV_{\mathrm{R}} = -P_{\mathrm{R}}(V_{\mathrm{R2}} - V_{\mathrm{R1}}) \tag{3.5-21}$$

where the subscript 1 denotes the initial value and the subscript 2 denotes the final value of each quantity. The process that we consider is the complete transfer of the system from one side of the apparatus to the other. 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:

$$V_1 = V_{\mathrm{L1}} - V_{\mathrm{L2}} \tag{3.5-22}$$

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:

$$V_2 = V_{R2} - V_{R1} \tag{3.5-23}$$

From Eqs. (3.5-20) through (3.5-23), the total work done on the system is

$$w = w_L + w_R = P_1V_1 - P_2V_2 = -\Delta(PV) \tag{3.5-24}$$

Exercise 3.20

a. Show that for any change in state

$$\Delta(PV) = P_1\,\Delta V + V_1\,\Delta P + (\Delta P)(\Delta V) \tag{3.5-25}$$

b. When can $\Delta(PV)$ equal $P\,\Delta V$? When can it equal $V\,\Delta P$? When can it equal $P\,\Delta V + V\,\Delta P$?

Since 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, since the chamber on the right is then at the same temperature at which the gas exits from the plug. Therefore,

$$q = 0 \tag{3.5-26}$$

$$\Delta U = q + w = -\Delta(PV) \tag{3.5-27}$$

$$\Delta H = \Delta U + \Delta(PV) = 0 \tag{3.5-28}$$

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:

$$\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_{H,n} \tag{3.5-29}$$

We can use the cycle rule, Eq. (B-15) of Appendix B, to write

$$\left(\frac{\partial H}{\partial P}\right)_{T,n} = -C_P\mu_{JT} \tag{3.5-30}$$

Exercise 3.21

Show that Eq. (3.5-30) is correct.

The Joule–Thomson coefficient of an ideal gas vanishes because $(\partial H/\partial P)_{T,n}$ vanishes for an ideal gas. 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 temperatures below room temperature. This means that for some range of temperature any gas cools upon expansion through a porous plug. It will also be cooled in an irreversible expansion through a nozzle or other aperture, which approximates the Joule–Thomson process. 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 3.11

The Joule–Thomson coefficient of air at 300 K and 25 atm is equal to 0.173 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

$$\Delta T \approx \left(\frac{\partial T}{\partial P}\right)_{H,n} \Delta P = (0.173\ \text{K atm}^{-1})(49\ \text{atm}) = 8\ \text{K}$$

$$T_2 \approx 292\ \text{K}$$

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. If no heat is added, the kinetic energy and the temperature must decrease. If the Joule–Thomson coefficient is negative, the repulsive intermolecular forces must be more important than the attractive forces.

3.6 Calculation of Enthalpy Changes for Non-Chemical Processes

The simplest calculations of ΔH are for constant-pressure processes in closed systems. In this case $\Delta H = q$. If no phase change or chemical reaction occurs,

$$\begin{aligned}\Delta H = q = \int_c dH &= \int_{T_1}^{T_2}\left(\frac{\partial H}{\partial T}\right)_{P,n} dT \\ &= \int_{T_1}^{T_2} C_P\, dT\end{aligned} \quad \begin{array}{l}\text{(constant } n \text{ and } P\text{, no phase} \\ \text{transition, no chemical reaction)}\end{array} \tag{3.6-1}$$

EXAMPLE 3.12

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 $C_{P,\mathrm{m}}$ is represented by

$$C_{P,\mathrm{m}} = a + bT + cT^{-2}$$

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.

$$\begin{aligned}\Delta H = q &= n\int_{T_1}^{T_2}(a + bT + cT^{-2})\, dT \\ &= n\left[a(T_2 - T_1) + \frac{b}{2}(T_2^2 - T_1^2) - c\left(\frac{1}{T_2} - \frac{1}{T_1}\right)\right]\end{aligned}$$

b. Using parameter values from Table A.6,

$$\Delta H = q = (2.000\ \text{mol})\Big[(30.0\ \text{J K}^{-1}\ \text{mol}^{-1})(75.00\ \text{K}\mathrm{]}$$
$$+\tfrac{1}{2}(4.18\times 10^{-3}\ \text{J K}^{-2}\ \text{mol}^{-1})[(373.15\ \text{K})^2-(298.15\ \text{K})^2]$$
$$-(-1.67\times 10^{5}\ \text{J K mol}^{-1})\left(\frac{1}{373.15\ \text{K}}-\frac{1}{298.15\ \text{K}}\right)\Big]$$
$$=(2.000\ \text{mol})(2250\ \text{J mol}^{-1}+105\ \text{J mol}^{-1}-113\ \text{J mol}^{-1})=4484\ \text{J}$$

Enthalpy Changes for Reversible Phase Transitions

The values of enthalpy changes of constant-pressure phase transitions for many common substances can be found in published tables. Table A.7 gives specific enthalpy changes (enthalpy changes per gram) for reversible fusion (melting) and vaporization (boiling) transitions for a number of pure substances at a constant pressure of 1.000 atm. These enthalpy changes are sometimes called latent heats of fusion or of vaporization, or heats of fusion or vaporization. The enthalpy changes for freezing or condensation processes are the negatives of these values. It is best not to call enthalpy changes by the name "heat," since enthalpy changes are equal to amounts of heat only if the pressure is constant.

EXAMPLE 3.13

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

$$q=\Delta H=(3.000\ \text{mol})(18.02\ \text{g mol}^{-1})(-333.5\ \text{J g}^{-1})=-1.202\times 10^{4}\ \text{J}$$

Since H is a state function, ΔH for any process is equal to ΔH for any other process having the same initial and final states.

EXAMPLE 3.14

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 $C_{P,\text{m}} = 5R/2$ and assume the gas to be ideal.

Solution

For purposes of calculation, assume that the gas first expands isothermally 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 on n and T only, ΔH for the first step vanishes. For the second step

$$\Delta H_2=\int_{T_1}^{T_2} C_P\,dT = nC_{P,\text{m}}\,\Delta T$$
$$=(1.000\ \text{mol})\left(\tfrac{5}{2}\right)(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(75.00\ \text{K})=1559\ \text{J}$$
$$\Delta H=\Delta H_1+\Delta H_2=0+1559\ \text{J}=1559\ \text{J}$$

Although ΔH is the same for any process with the same initial and final states as the overall process in Example 3.14, q and w are dependent on the path of a particular process.

EXAMPLE 3.15

Find q and w for the process used in the calculation of Example 3.14.

Solution

We first find V_2 and P_2, the volume and pressure at the end of step 1. From the ideal gas law,

$$V_2 = (10.00\ \mathrm{L})\frac{298.15\ \mathrm{K}}{373.15\ \mathrm{K}} = 7.990\ \mathrm{L}$$

$$P_2 = \frac{(1.000\ \mathrm{mol})(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})}{0.007990\ \mathrm{m^3}} = 3.103 \times 10^5\ \mathrm{Pa}$$

$$q_1 = (1.000\ \mathrm{mol})(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})\ \ln\left(\frac{7.990\ \mathrm{L}}{5.000\ \mathrm{L}}\right) = 1162\ \mathrm{J}$$

Because the pressure was constant during step 2,

$$q_2 = \Delta H_2 = 1559\ \mathrm{J}$$

$$q = q_1 + q_2 = 1162\ \mathrm{J} + 1559\ \mathrm{J} = 2721\ \mathrm{J}$$

Note that q is not equal to ΔH for the overall process, since the entire process is not a constant-pressure process. For the first step,

$$w_1 = \Delta U_1 - q_1 = -q_1 = -1162\ \mathrm{J}$$

For the second step, we let V_3 be the final volume,

$$w_2 = -\int_{V_2}^{V_3} P\,dV = -P\int_{V_2}^{V_3} dV = -P\,\Delta V$$

$$w_2 = -(3.103 \times 10^5\ \mathrm{Pa})(0.01000\ \mathrm{m^3} - 0.007990\ \mathrm{m^3}) = -623.6\ \mathrm{J}$$

$$w = w_1 + w_2 = -1162\ \mathrm{J} - 624\ \mathrm{J} = -1786\ \mathrm{J}$$

*Exercise 3.22

a. Find ΔU for the process of Example 3.15.

b. Find ΔH, q, and w for the process in which the system of Examples 3.14 and 3.15 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

We consider irreversible processes that begin with an equilibrium or metastable state and end 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 equate it to ΔH for the irreversible process.

EXAMPLE 3.16

Find ΔH and q if 2.000 mol of supercooled liquid water at −15.00°C freezes irreversibly at a constant pressure of 1.000 atm to ice at −15.00°C. Assume the molar heat capacity of liquid water to be constant and equal to 76.1 $\mathrm{J\ K^{-1}\ mol^{-1}}$, and that of ice to be constant and equal to 37.15 $\mathrm{J\ K^{-1}\ mol^{-1}}$.

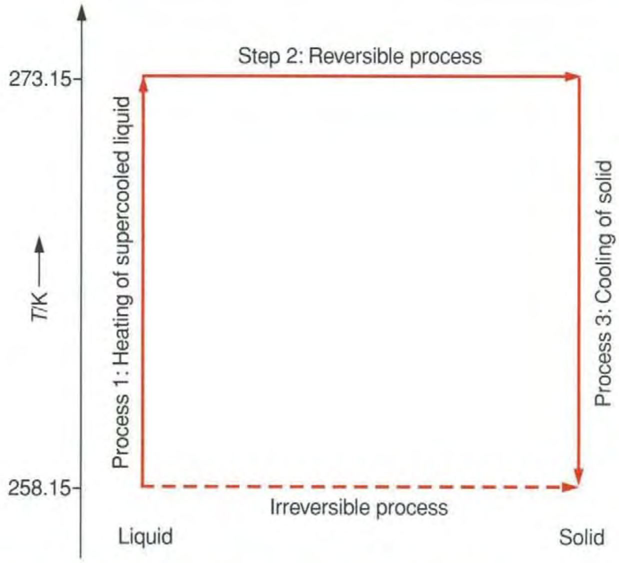

Figure 3.9. Irreversible and Reversible Paths for Example 3.16. The enthalpy change for the irreversible process is equal to the sum of the enthalpy changes for processes 1, 2, and 3.

Solution

We calculate ΔH along the reversible path shown in Figure 3.9. Step 1 is the reversible heating of the system to 0.00°C, the equilibrium freezing temperature at 1.000 atm. Step 2 is the reversible freezing of the system at 0.00°C, and step 3 is the reversible cooling of the system to −15.00°C. Supercooled water is in a metastable state, which is sufficiently like an equilibrium state that we can treat step 1 like a reversible process.

$$\Delta H_1 = \int_{258.15\text{ K}}^{273.15\text{ K}} C_P(\mathrm{l})\,dT = C_P(\mathrm{l})\,\Delta T$$

$$= (3.000\text{ mol})(67.1\text{ J K}^{-1}\text{ mol}^{-1})(15.00\text{ K}) = 2013\text{ J}$$

The enthalpy change of step 2 is just like that of Example 3.13:

$$\Delta H_2 = -1.202 \times 10^4\text{ J}$$

The enthalpy change of step 3 is similar to that of step 1.

$$\Delta H_3 = \int_{273.15\text{ K}}^{258.15\text{ K}} C_P(\mathrm{s})\,dT = C_P(\mathrm{s})\,\Delta T$$

$$= (3.000\text{ mol})(37.15\text{ J K}^{-1}\text{ mol}^{-1})(-15.00\text{ K}) = -1114\text{ J}$$

$$\Delta H = \Delta H_1 + \Delta H_2 + \Delta H_3 = -1.112 \times 10^4\text{ J}$$

Since the process is at constant pressure, $q = \Delta H$.

3.7 Calculation of Enthalpy Changes for 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, so nearly every constant-temperature chemical reaction is accompanied by energy and enthalpy changes. If the system gives off heat when the reaction takes place at constant temperature and pressure, the reaction is called **exothermic**, and if the system absorbs heat, the reaction is called **endothermic**.

In this chapter we will consider only chemical reactions of a restricted class, in which every reactant or product is either a gas or a pure liquid or solid. Three reactions in this class are

$$2H_2(g) + O_2(g) \rightarrow 2H_2O(l) \tag{3.7-1}$$

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \tag{3.7-2}$$

$$N_2O_4(g) \rightarrow 2NO_2(g) \tag{3.7-3}$$

The label "s" refers to solid, the label "l" refers to liquid, and the label "g" refers to gas.

We now choose to write chemical reaction equations with the symbols for all substances on the right-hand side, and with the → symbol replaced by an equals sign. The three reactions of Eq. (3.7-3) become

$$0 = 2H_2O(l) - 2H_2(g) - O_2(g) \tag{3.7-4}$$

$$0 = CaO(s) + CO_2(g) - CaCO_3(s) \tag{3.7-5}$$

$$0 = 2NO_2(g) - N_2O_4(g) \tag{3.7-6}$$

In order to write an equation that applies to any chemical equation, we denote the stoichiometric coefficient of substance number i by v_i. If substance number i is a product, we specify that $v_i > 0$ and if substance number j is a reactant we specify that $v_j < 0$. In Eq. (3.7-6) if NO_2 is substance number 1 and N_2O_4 is substance number 2, then $v_1 = 2$ and $v_2 = -1$. We number the substances from 1 to c, and any chemical reaction equation can now be represented by the equation

$$0 = \sum_{i=1}^{c} v_i \mathscr{F}_i \tag{3.7-7}$$

where $\mathscr{F}_i$ is an abbreviation for the chemical formula of substance number i. The form of this equation will enable us to write a compact general formula for the enthalpy change of any chemical reaction.

We can express the enthalpy change for a reaction in our restricted class in terms of the enthalpies of pure substances. These enthalpies depend on the state of the substance. 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 designate by P°. The standard-state pressure was until recent years chosen as 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 a set of data. The actual substance at pressure P° is the standard state for solids and liquids, but the standard state for a gas is defined to be the ideal gas at pressure P°. This choice means that corrections must be made for the difference between the real gas and an ideal gas. These corrections are small, and we will learn how to calculate them in a later chapter.

According to Dalton's law of partial pressures, each ideal gas in a mixture behaves as though the other gases were absent. If all substances are either pure condensed phases or ideal gases, if surface tension effects can be ignored, and if each substance is in an equilibrium or metastable state, the enthalpy of the system is a sum of contributions of the separate substances

$$H = \sum_{i=1}^{c} n_i H_{\mathrm{m}}(i) \tag{3.7-8}$$

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. If the substance number i is in its standard state, its molar enthalpy is denoted by $H_{\mathrm{m}}(i)^{\circ}$.

Consider a chemical reaction that begins with all substances in equilibrium or metastable states at some particular temperature and pressure and ends with all substances in equilibrium states at the same temperature and pressure. The enthalpy change of the reaction is given by

$$\Delta H = H_{\mathrm{final}} - H_{\mathrm{initial}} = \sum_{i=1}^{c} \Delta n_i H_{\mathrm{m}}(i) \tag{3.7-9}$$

where Δn_i is the change in the amount of substance number i. We say that **one mole of reaction** occurs if

$$\Delta n_i = \nu_i$$

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 disappears that is equal to the magnitude of its stoichiometric coefficient. For one mole of reaction

$$\Delta H = \sum_{i=1}^{c} \nu_i H_{\mathrm{m}}(i) \tag{3.7-10}$$

This enthalpy change depends on the way in which the reaction equation is balanced. For example, if all stoichiometric coefficients are doubled, ΔH for the reaction doubles. When we give a value of ΔH, etc., for a reaction, it is always for one mole of the reaction, *as written*.

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°. If values for standard-state molar enthalpies were available, Eq. (3.7-10) could be used to calculate ΔH° for a reaction. However, actual values for standard-state molar enthalpies cannot be found in tables, since an arbitrary constant can be added to each internal energy without any physical effect. The **standard-state enthalpy change of formation** of substance i, $\Delta_{\mathrm{f}} H^{\circ}(i)$, is defined to be the enthalpy change of the chemical reaction to form one mole of substance i in the specified phase from the appropriate elements in their most stable forms, with all substances in their standard states. The superscript ° denotes the standard state, and although we do not append a subscript m, the enthalpy change of formation is defined to be a molar quantity. Standard-state enthalpy changes of formation for a number of substances are listed in Table A.8 of Appendix A.

The enthalpy change for one mole of any standard-state reaction in our restricted class is given by

$$\Delta H^{\circ} = \sum_{i=1}^{c} \nu_i \Delta_{\mathrm{f}} H^{\circ}(i) \tag{3.7-11}$$

We can show this equation to be correct as follows: Let process 1 convert the reactants into elements in their most stable form. The standard-state enthalpy change for process 1 is

$$\Delta H_1^\circ = H_{\text{elements}} - H_{\text{reactants}} = \sum_{\substack{i=1 \\ \text{(reactants only)}}}^{c} \nu_i \Delta_f H^\circ(i) \tag{3.7-12}$$

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. (3.7-12) is positive because the stoichiometric coefficients are negative.

Let process 2 be the production of the products of the reaction of interest from the elements produced in process 2. The standard-state enthalpy change of process 2 is

$$\Delta H_2^\circ = \sum_{\substack{i=1 \\ \text{(products only)}}}^{c} \nu_i \Delta_f H^\circ(i) \tag{3.7-13}$$

We now invoke **Hess's law**,[6] which states that: *The enthalpy change of any process that is equivalent to the successive carrying out of two other processes is equal to the sum of the enthalpy changes of those two processes.* This law is a simple 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,

$$\begin{aligned}\Delta H &= H_{\text{products}} - H_{\text{reactants}} = H_{\text{elements}} - H_{\text{reactants}} + [H_{\text{products}} - H_{\text{elements}}] \\ &= \Delta H_1 + \Delta H_2\end{aligned}$$

The products and the reactants of any reaction contain the same number of atoms of each element, because atoms are neither destroyed or created in a chemical reaction. The two "element" terms cancel, and

$$\Delta H^\circ = \sum_{\substack{i=1 \\ \text{(reactants only)}}}^{c} \nu_i \Delta_f H^\circ(i) + \sum_{\substack{i=1 \\ \text{(products only)}}}^{c} \nu_i \Delta_f H^\circ(i) = \sum_{i=1}^{c} \nu_i \Delta_f H^\circ(i) \tag{3.7-14}$$

where the final sum includes all substances involved in the reaction. We have established Eq. (3.7-11).

EXAMPLE 3.17

Find the standard-state enthalpy change of the reaction of Eq. (3.7-6) at 298.15 K, using values of enthalpy changes of formation from Table A.8.

Solution

$$\begin{aligned}\Delta H^\circ &= 2\Delta_f H^\circ(\mathrm{NO_2}) + (-1)\Delta_f H^\circ(\mathrm{N_2O_4}) \\ &= (2)(33.18\ \mathrm{kJ\ mol^{-1}}) + (-1)(9.16\ \mathrm{kJ\ mol^{-1}}) = 57.20\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

We use dimensionless stoichiometric coefficients, so that the enthalpy change for the reaction has the units of joules per mole (meaning per mole of the reaction *as written*). One can think of the units of ν_i as moles of substance i per mole of reaction. If the way in which the reaction equation is balanced changes, the value of ΔH° changes. For

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[6] Germain Henri Hess, 1802–1850, Swiss-Russian chemist whose law first indicated that thermodynamics applies to chemistry.

example, if all stoichiometric coefficients are doubled, the equation is still balanced, but the value of ΔH doubles.

*Exercise 3.23

Using values in Table A.8, find the standard-state enthalpy change of the reaction of Eq. (3.7-6) at 298.15 K.

If the formation reaction for a substance cannot be carried out, the enthalpy change of formation can be calculated from the enthalpy change of a reaction that can be carried out, if the enthalpy changes of formation of the other substances in the reaction are known.

EXAMPLE 3.18

The standard-state enthalpy change of combustion of methane at 298.15 K equals $-890.36\ \text{kJ mol}^{-1}$, with liquid water as one of the products. Find the enthalpy change of formation of methane at 298.15 K.

Solution

The balanced reaction equation is

$$0 = CO_2(g) + 2H_2O(l) - CH_4(g) - 2O_2(g)$$

so that

$$-890.36\ \text{kJ mol}^{-1} = \Delta_f H^\circ(CO_2) + 2\Delta_f H^\circ(H_2O) + (-1)\Delta_f H^\circ(CH_4) + (-2)\Delta_f H^\circ(O_2)$$

Since gaseous O_2 is the most stable form of oxygen at 298.15 K, $\Delta_f H^\circ(O_2) = 0$. Therefore, using values of the enthalpy changes of formation of the other substances from Table A.9 in Appendix A,

$$\begin{aligned}\Delta_f H^\circ(CH_4) &= 890.36\ \text{kJ mol}^{-1} + (-393.522\ \text{kJ mol}^{-1}) \\ &\quad + 2(-285.830\ \text{kJ mol}^{-1}) + (-2)(0\ \text{kJ mol}^{-1}) \\ &= -74.82\ \text{kJ mol}^{-1}\end{aligned}$$

Enthalpy Changes at Various Temperatures

An enthalpy change for a temperature other than the temperature found in a table can be calculated from heat capacity data using the fact that an enthalpy change is path-independent. Consider the processes shown in Figure 3.10. The reaction at temperature T_2 is the process whose enthalpy change we want to find. Call it process 2. An alternate pathway for 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, whose enthalpy change is assumed to be known. Process 4 is the change in temperature of the products from T_1 to T_2. According to Hess's law:

$$\Delta H_2 = \Delta H(T_2) = \Delta H_3 + \Delta H_1 + \Delta H_4 = \Delta H_3 + \Delta H(T_1) + \Delta H_4 \qquad (3.7\text{-}15)$$

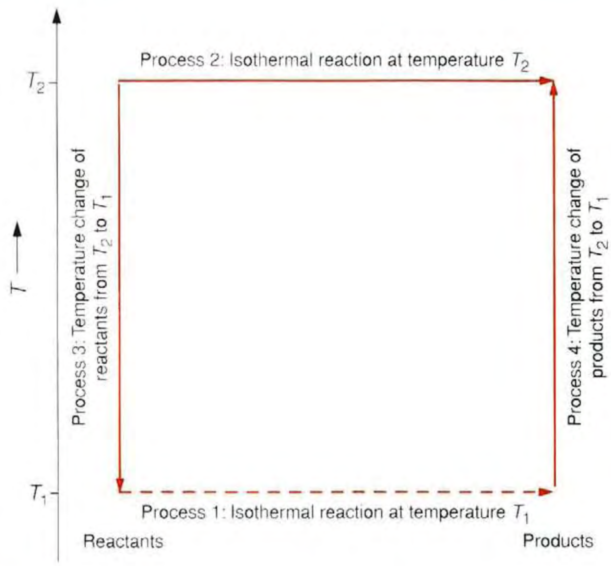

Figure 3.10. The Process to Calculate $\Delta H(T_2)$ from $\Delta H(T_1)$. $\Delta H(T_2)$ is equal to the sum of the enthalpy changes of processes 3, 1, and 4.

For one mole 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

$$\Delta H_3 = \underset{\text{(reactants only in sum)}}{\int_{T_2}^{T_1} \sum_{i=1}^{c} |\nu_i| C_{P,\mathrm{m}}(i)\, dT} = \underset{\text{(reactants only in sum)}}{\int_{T_1}^{T_2} \sum_{i=1}^{c} \nu_i C_{P,\mathrm{m}}(i)\, dT} \tag{3.7-16}$$

where $C_{P,\mathrm{m}}(i)$ is the molar heat capacity of substance i. The second equality comes from interchanging the limits of integration and realizing that the stoichiometric coefficients are negative. Process 4 is the change in temperature of the products from T_1 to T_2, so that

$$\Delta H_4 = \underset{\text{(products only in sum)}}{\int_{T_1}^{T_2} \sum_{i=1}^{c} \nu_i C_{P,\mathrm{m}}(i)\, dT} \tag{3.7-17}$$

The sums in Eqs. (3.7-16) and (3.7-17) can be combined to give the expression

$$\Delta H(T_2) = \Delta H(T_1) + \int_{T_1}^{T_2} \Delta C_P\, dT \tag{3.7-18}$$

where

$$\Delta C_P = \sum_{i=1}^{c} \nu_i C_{P,\mathrm{m}}(i) \tag{3.7-19}$$

All reactants and products are included in this sum. Since reactants have negative stoichiometric coefficients, ΔC_P is the heat capacity of the products minus the heat capacity of the reactants. If Eq. (3.7-18) is applied to the standard-state reaction, then ΔC_P and each ΔH are replaced by the appropriate standard-state quantities.

EXAMPLE 3.19

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. (3.7-6).

Solution

$$\begin{aligned}\Delta C_P^\circ &= 2C_{P,\mathrm{m}}^\circ(\mathrm{NO_2}) + (-1)C_{P,\mathrm{m}}^\circ(\mathrm{N_2O_4})\\ &= 2(37.20\ \mathrm{J\ K^{-1}\ mol^{-1}}) + (-1)(77.28\ \mathrm{J\ K^{-1}\ mol^{-1}})\\ &= -2.88\ \mathrm{J\ K^{-1}\ mol^{-1}} = -0.00288\ \mathrm{kJ\ K^{-1}\ mol^{-1}}\end{aligned}$$

Using the value of $\Delta H^\circ(298.15\ \mathrm{K})$ from Example 3.17,

$$\begin{aligned}\Delta H^\circ(298.15\ \mathrm{K}) &= 57.2\ \mathrm{kJ\ mol^{-1}} + \int_{298.15\ \mathrm{K}}^{373.15\ \mathrm{K}} (-0.00288\ \mathrm{kJ\ K^{-1}\ mol^{-1}})\, dT\\ &= 57.2\ \mathrm{kJ\ mol^{-1}} - 0.216\ \mathrm{kJ\ mol^{-1}} = 57.0\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

*Exercise 3.24

Find the value of the standard-state enthalpy change of the reaction of Eq. (3.7-6) at 200°C. State any assumptions.

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 not large. The enthalpy of an ideal gas does not depend on the pressure, and real gases behave nearly like ideal gases for moderate pressures. 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 really great accuracy we will use the value of the standard-state enthalpy change for the enthalpy change for a reaction at ordinary pressures.

Adiabatic 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. If an adiabatic reaction takes place at constant pressure, the enthalpy change is equal to zero. In order to compute the final temperature of a system in which a chemical reaction takes place adiabatically, we consider the processes shown in Figure 3.11. Process 1 is the actual reaction, for which ΔH is equal to zero. Process 2 is the isothermal reaction. Process 3 is the change in temperature of the products plus

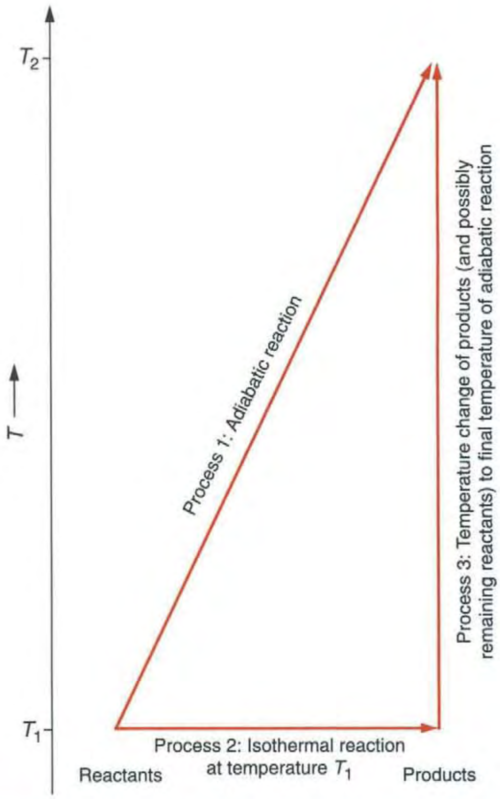

Figure 3.11. The Process to Calculate the final Temperature of an Adiabatic Reaction. The enthalpy change of process 1 is equal to the sum of the enthalpy changes of processes 2 and 3.

any remaining reactants to the same final state as process 1. Since enthalpy is a state function,

$$\Delta H_1 = \Delta H_2 + \Delta H_3 = 0 \tag{3.7-20}$$

If a stoichiometric mixture is taken and if the reaction proceeds to completion, there are no remaining reactants, and we can write

$$\Delta H_3 = \underset{\text{(products only in sum)}}{\int_{T_1}^{T_2} \sum_{i=1}^{c} \nu_i C_{P,\mathrm{m}}(i)\, dT} = \Delta H_2 \tag{3.7-21}$$

This equation can be solved for T_2. If there are remaining amounts of some reactants, their heat capacities must be added to Eq. (3.7-21). If the reaction comes to equilibrium short of completion, the equilibrium can shift as the temperature changes (see Chapter 8) and the calculation is more complicated. We will not discuss that case.

EXAMPLE 3.20

Find the final temperature if the reaction of Eq. (3.7-1), the combustion of hydrogen gas, 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. Assume that the value of ΔH at 298.15 K can be used over the range of temperature encountered.

Solution

$$\Delta H^\circ(298.15\text{ K}) = 2\Delta_f H^\circ(\mathrm{H_2O}) - 0 - 0$$

$$= 2(-241.818\text{ kJ mol}^{-1}) = -483.636\text{ kJ mol}^{-1} = -483636\text{ J mol}^{-1}$$

$$C_P = (2)(51.18\text{ J K}^{-1}\text{ mol}^{-1}) = 102.36\text{ J K}^{-1}\text{ mol}^{-1}$$

$$\int_{298.15\text{ K}}^{T_2} (102.36\text{ J K}^{-1}\text{ mol}^{-1})\,dT - 483636\text{ J mol}^{-1} = 0$$

$$(102.36\text{ J K}^{-1}\text{ mol}^{-1})(T_2 - 298.15\text{ K}) = 483636\text{ J mol}^{-1}$$

$$T_2 = 5023\text{ K} \approx 5000\text{ K}$$

*Exercise 3.25

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. The dependence of ΔH on temperature can also be included, as in Eq. (3.7-18) with T_2 replaced by a variable T. This leads to a nonlinear equation, which might have to be solved by trial and error or by other numerical techniques.

*Exercise 3.26

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 3.20.

3.8

Energy Changes of Chemical Reactions

Energy changes of chemical reactions could be calculated from energy changes of formation in exactly the same way as enthalpy changes. However, tables of energy changes of formation are not commonly used because it is possible to calculate the energy change of a chemical reaction from the enthalpy change of the reaction. From the definition of the enthalpy, Eq. (3.5-1),

$$\Delta U = \Delta H - \Delta(PV) \tag{3.8-1}$$

Ordinarily, $\Delta(PV)$ is much smaller than ΔH, so that it can be calculated approximately while ΔH is calculated accurately. 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 $\Delta(PV)$. For the class of reactions that we considered in the previous section,

$$PV = P[V(\mathrm{s}) + V(\mathrm{l}) + V(\mathrm{g})] \tag{3.8-2}$$

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. We ignore the volume of the solid and liquid phases and write

$$\Delta(PV) \approx \Delta[PV(\mathrm{g})] \tag{3.8-3}$$

If the products and reactants are at the same temperature and if we use the ideal gas equation as an approximation,

$$\Delta[PV(\mathrm{g})] \approx [\Delta n(\mathrm{g})]RT \tag{3.8-4}$$

If one mole of reaction occurs, then

$$\Delta n(\mathrm{g}) = \Delta\nu(\mathrm{g}) = \sum_{\substack{i=1 \\ \text{(gases only)}}}^{c} \nu_i \tag{3.8-5}$$

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 3.21

Find $\Delta(PV)$ and ΔU° for the reaction of Eq. (3.7-1) at 298.15 K.

Solution

$$\Delta(PV) \approx \Delta\nu(\mathrm{g})RT = (-3)(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})$$

$$\Delta(PV) \approx -7437\ \mathrm{J\ mol^{-1}} = -7.437\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta H^\circ = 2\Delta_f H^\circ(\mathrm{H_2O}) - 0 - 0 = -571.660\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta U^\circ = -571.660\ \mathrm{kJ\ mol^{-1}} - (-7.437\ \mathrm{kJ\ mol^{-1}}) = -564.223\ \mathrm{kJ\ mol^{-1}}$$

***Exercise 3.27**

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 Example 3.21.

***Exercise 3.28**

Find ΔU° for the reaction of Eq. (3.7-6) at 298.15 K.

Calorimetry

The most common procedure for the determination of enthalpy changes of formation of combustible substances is to carry out the combustion reaction in a constant-volume calorimeter. The enthalpy change of combustion is determined and the enthalpy change of formation is calculated as in Example 3.18. Figure 3.12 depicts a constant-volume calorimeter known as a **bomb 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 filled with a measured amount of water, and the water is stirred until a steady temperature is attained. The system, consisting of the solid

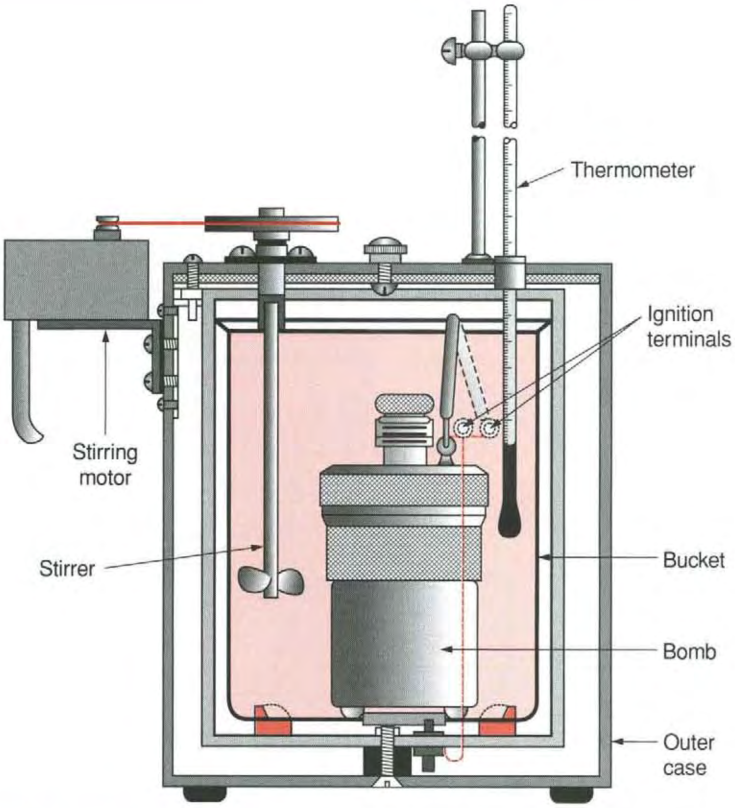

Figure 3.12. A Bomb Calorimeter. The bomb is immersed in a metal bucket that contains a fixed amount of water. The system consists of the substances inside the bomb, and the bomb, bucket, and water are the surroundings. (Courtesy of the Parr Instrument Co.)

reactant and the oxygen, is in a metastable state that can be treated as though at equilibrium. The system is ignited electrically and the bomb, water, and bucket are allowed to approach equilibrium at a new temperature several degrees higher than the initial temperature. The amount of heat transferred to the calorimeter (bomb, water, and bucket) is calculated from knowledge of the heat capacity of the calorimeter. If this heat capacity is independent of temperature (an excellent approximation for a temperature change of only a few degrees)

$$q = -q_{\mathrm{cal}} - C_{\mathrm{cal}}\,\Delta T \tag{3.8-6}$$

Since the system is at constant volume, $w = 0$ and

$$q = \Delta U \tag{3.8-7}$$

From the amount of solid reactant present, ΔU for one mole of reaction is calculated, allowing ΔH for one mole of reaction to be calculated from equation (3.8-4). This value of ΔH is not quite equal to ΔH°, because neither the final pressure nor the initial pressure is equal to the standard-state pressure, and the gases present are not ideal. Also, 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 if needed for highly accurate work. In most calorimeters 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 fuse must be included in the calculation.

EXAMPLE 3.22

A pellet of naphthalene of mass 1.234 g is burned in a bomb calorimeter with $C_{\text{cal}} = 14{,}225\ \text{J K}^{-1}$ (assume constant). If the initial temperature is 298.150 K and the final temperature is 301.634 K, find ΔU and ΔH for one mole 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

$$C_{10}H_8(s) + 12O_2(g) \rightarrow 10CO_2(g) + 4H_2O(l)$$

$$q = -q_{\text{cal}} = -(14225\ \text{J K}^{-1})(3.484\ \text{K}) = -4.956 \times 10^4\ \text{J}$$

For one mole of reaction,

$$\Delta U = -\frac{(4.956 \times 10^4\ \text{J})}{(1.234\ \text{g})}\left(\frac{128.19\ \text{g}}{1\ \text{mol}}\right) = -5.148 \times 10^6\ \text{J mol}^{-1}$$

$$\Delta H = -5.148 \times 10^6\ \text{J mol}^{-1} + (-2)(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})$$

$$= -5.153 \times 10^6\ \text{J mol}^{-1} = -5153\ \text{kJ mol}^{-1}$$

This value is in good agreement with the published value, $\Delta H^\circ = -5156.8\ \text{kJ mol}^{-1}$.

We can determine the error due to the inequality of the temperatures of the reactant and products. 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 $6.55\ \text{J K}^{-1}$. The heat required to bring the products back to 298.15 K is

$$q_2 = (6.55\ \text{J K}^{-1})(3.484\ \text{K}) = 22.9\ \text{J} = 0.0229\ \text{kJ}$$

This means that $q_{\text{cal}} = 4.956 \times 10^4\ \text{J} + 22.9\ \text{J} = 4.958 \times 10^4\ \text{J}$ for the reaction with the products at the same temperature as the reactants, for a difference of about 0.04%.

*Exercise 3.29

What will be the rise in temperature of the calorimeter in Example 3.22 if a pellet of anthracene of mass 1.345 g is burned? The enthalpy change of combustion of anthracene is $-7114.5\ \text{J mol}^{-1}$.

The calorimetry of substances reacting in solutions is commonly carried out at constant pressure. In this case, q is equal to ΔH, and no calculation of $\Delta(PV)$ is necessary to determine enthalpy changes of reactions.

Average Bond Energies

Chemical reactions involve the breaking and forming of chemical bonds. If it were possible to determine exactly the energy required to break every type of chemical bond, it would be possible to calculate standard-state energy changes of a gaseous chemical reaction from bond energies. One problem is that breaking chemical bonds between the same pair of elements in different compounds requires slightly different amounts of energy. 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, one uses the relationship

$$\Delta U \approx \text{(sum of all bond energies in reactants)} - \text{(sum of all bond energies in products)} \tag{3.8-8}$$

The calculation can be simplified if one omits from both terms those bonds that occur in both reactants and products, since their contributions cancel.

EXAMPLE 3.23

Estimate the energy change of the reaction

$$C_2H_4(g) + H_2(g) \rightarrow C_2H_6(g)$$

Compare with the value obtained from enthalpy changes of formation.

Solution

For one mole 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.

$$\begin{aligned}\Delta U &= 613\ \text{kJ mol}^{-1} + 436\ \text{kJ mol}^{-1} - 348\ \text{kJ mol}^{-1} - 2(413\ \text{kJ mol}^{-1})\\ &= -125\ \text{kJ mol}^{-1}\end{aligned}$$

The 4 mol of C—H bonds that occur both in the products and the reactants are omitted from the calculation. For comparison, we calculate ΔH from enthalpy changes of formation at 298.15 K:

$$\begin{aligned}\Delta H_{298.15\,\text{K}} &= \Delta_f H^\circ(C_2H_6) - \Delta_f H^\circ(C_2H_4) - \Delta_f H^\circ(H_2)\\ &= -84.68\ \text{kJ mol}^{-1} - (52.26\ \text{kJ mol}^{-1}) - 0 = -136.94\ \text{kJ mol}^{-1}\\ \Delta U_{298.15\,\text{K}} &= -136.94\ \text{kJ mol}^{-1} - (-1)(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})\\ &= -136.94\ \text{kJ mol}^{-1} + 2.48\ \text{kJ mol}^{-1} = -134.46\ \text{kJ mol}^{-1}\end{aligned}$$

In practice, this method is used only if enthalpy changes of formation are not available, since the results are only approximately correct. The error of 9 kJ mol^{-1} in Example 3.23 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 cannot be used for reactions involving solids or liquids, where intermolecular forces also 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 3.30

Using average bond energy values, estimate ΔH for the reaction

$$C_2H_2(g) + H_2(g) \rightarrow C_2H_4(g)$$

Compare your value with the correct value of ΔH obtained from enthalpy changes of formation.

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[7] See, for example, D. W. Smith, *J. Chem. Soc., Faraday Trans.*, **94**, 3087 (1998).

Summary of the Chapter

This chapter introduced thermodynamics and discussed the first law of thermodynamics, which 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.

The enthalpy, H, was defined through

$$H = U + PV$$

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.

PROBLEMS

Problems for Section 3.1

3.31. If dw_{rev} is written for a closed fluid system as

$$dw_{\text{rev}} = M\,dV + N\,dT$$

then $M = -P$ and $N = 0$. Show that the requirement for dw_{rev} to be an exact differential is not met.

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

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

where x is the length of the spring, x_0 is the equilibrium length, and κ 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

$$\mathcal{V} = \frac{1}{2}\kappa(x - x_0)^2$$

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

***3.33.** **a.** Obtain a formula for the work done in 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 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. 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.

Problems for Section 3.2

3.34. 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.

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

Problems for Section 3.3

3.36. 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 0.917 g mL^{-1}.

***3.37.** 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.

Problems for Section 3.4

3.38. **a.** Calculate the Joule coefficient for carbon dioxide at 298.15 K. Approximate dB_2/dT by the quotient of finite differences of the values for 0°C and 50°C. Use the value of $C_{P,\text{m}}$ in Table A.6 to obtain a value of $C_{V,\text{m}}$. State any assumptions or approximations.

b. Estimate the temperature difference if carbon dioxide at 298.15 K and 133 atm is expanded into a vacuum.

3.39. 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 $C_{V,\mathrm{m}} = 5R/2$.

3.40. 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 $C_{V,\mathrm{m}} = 5R/2$.

***3.41.** 1.000 mol of carbon dioxide is expanded adiabatically and reversibly from 298.15 K and a molar volume of 5.000 L to a volume of 20.00 L.

a. Find the final temperature, assuming the gas to be ideal with $C_{V,\mathrm{m}} = 5R/2 = \text{constant}$.

b. Find the final temperature, assuming the gas to be described by the van der Waals equation with $C_{V,\mathrm{m}} = 5R/2 = \text{constant}$.

3.42. 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 $10.00\ \mathrm{L\,mol^{-1}}$ to a molar volume of $20.00\ \mathrm{L\,mol^{-1}}$. Assume the gas to be ideal with $C_{V,\mathrm{m}} = 5R/2 = \text{constant}$.

b. Repeat the calculation of part (**a**) for argon instead of oxygen. Assume that $C_{V,\mathrm{m}} = 3R/2 = \text{constant}$.

c. Explain in physical terms why your answers for parts (**a**) and (**b**) are as they are.

Problems for Section 3.5

3.43. Show that if $dU = dq + dw$, if dU is exact, and if dq is inexact, then dw must be inexact.

3.44. For constant-pressure processes, what is the function whose differential is equal to dw? Why is dw not equal to the differential of this function for processes in which pressure is not constant?

***3.45.** For a nonsimple system such as a spring or a rubber band governed by Eq. (3.1-8), 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. (3.5-11) relating $C_{P,\tau}$ and $C_{P,L}$.

3.46. Express the exponents in Eqs. (3.4-24), (3.4-34), and (3.4-35) in terms of the heat-capacity ratio γ, defined in Eq. (3.5-14). Use Eq. (3.5-12) to simplify your results.

***3.47.** The Joule–Thomson coefficient of nitrogen gas at 50 atm and 0°C is equal to $0.044\ \mathrm{K\,atm^{-1}}$.

a. 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 $(\partial H_\mathrm{m}/\partial P)_T$ for nitrogen gas at 50 atm and 0°C. State any assumptions.

Problems for Section 3.6

3.48. 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**).

***3.49.** 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.

3.50. The enthalpy change of fusion of mercury is $2331\ \mathrm{J\,mol^{-1}}$. Find ΔH for converting 100.0 g of solid mercury at −75.0°C to liquid mercury at 250.0°C at a constant pressure of 1.000 atm.

3.51. 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 $2331\ \mathrm{J\,mol^{-1}}$.

Problems for Section 3.7

3.52. Calculate ΔH° and ΔU° for the reactions at 298.15 K:

a. $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$
b. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
c. $SO_3(g) + H_2O(g) \rightarrow H_2SO_4(l)$
d. $4CuO(s) \rightarrow 2Cu_2O(s) + O_2(g)$
e. $2CO(g) + O_2(g) \rightarrow 2CO_2(g)$
f. $C_2H_5OH(l) + 3O_2(g) \rightarrow 2CO_2(g) + 3H_2O(l)$

***3.53.** Calculate ΔH° for the reactions of the previous problem at 75°C.

3.54. a. Using the value of the enthalpy change of vaporization of water and the result of part (**a**) of the previous problem, find ΔH° of this reaction for the case that the water is vapor.

b. Recalculate this quantity using the enthalpy change of formation of water vapor and compare with your result of part (**a**).

***3.55. 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:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

c. Find the standard-state enthalpy change of the reaction of part (**b**), using Eq. (3.7-18). Comment on the comparison of your answer with that of part (**b**).

3.56. **a.** The molar enthalpy change of combustion of sucrose, $C_{12}H_{22}O_{11}$, at 298.15 K is equal to $-5640.9 \text{ kJ mol}^{-1}$. Calculate its enthalpy change of formation at 298.15 K. Calculate ΔU° 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 $-11280.6 \text{ kJ mol}^{-1}$. Calculate its enthalpy change of formation at 298.15 K. Compare its enthalpy change of combustion per gram with that of sucrose.

Problems for Section 3.8

***3.57.** **a.** Calculate the value of ΔU_f° for carbon dioxide and for carbon monoxide at 298.15 K.

b. Calculate ΔU° for the reaction at 298.15 K, using the results of part (**a**).

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

c. Calculate ΔH° using Eq. (3.8-4) and compare with your result from part (**a**).

3.58. **a.** Calculate ΔH° for the reaction at 298.15 K:

$$CH_4(g) + O_2(g) \rightarrow CO_2(g) + H_2O(l)$$

(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 $V = 18.0 \text{ cm}^3 \text{ mol}^{-1}$ for liquid water.

***3.59.** **a.** Estimate the enthalpy change of the following reaction, using average bond energies:

$$2C_2H_6(g) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(g)$$

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:

$$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$$

3.60. 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. $N_2O_4(g) \rightarrow 2NO_2(g)$
b. $2SO_2(g) + O_2(g) \rightarrow 2SO_3(g)$
c. $SO_3(g) + H_2O(g) \rightarrow H_2SO_4(g)$
d. $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$
e. $H_2(g) + F_2(g) \rightarrow 2HF(g)$

General Problems

3.61. 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 K to a volume of 20.00 L. Assume that N_2 is ideal, with $C_{V,\mathrm{m}} = 5R/2$.

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

$$w_{\mathrm{rev}} = -\int_c P\,dV$$

is carried out using Eq. (3.4-28), the same value of w is obtained as is obtained from

$$w = \Delta U - q = \Delta U$$

3.62. It is shown in the theory of hydrodynamics[8] that the speed of sound in a fluid, v_s, is given by

$$v_s^2 = \frac{V_\mathrm{m} C_P}{M\kappa_T C_V} = \frac{V_\mathrm{m}\gamma}{M\kappa_T}$$

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 $0.029 \text{ kg mol}^{-1}$ and $C_{V,\mathrm{m}} = 5R/2$.

b. Find the speed of sound in helium at 298.15 K and 1.000 atm.

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[8] H. Lamb, *Hydrodynamics*, 6th ed., Cambridge University Press, New York, 1932.

c. The speed of sound in ethane at 10°C is equal to 308 m s^{-1}. Find the values of $C_{P,\text{m}}$ and of $C_{V,\text{m}}$ for ethane at this temperature.

***3.63.** **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.

3.64. **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) isooctane (2,2,4-trimethylpentane), 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 kJ mol^{-1}.

b. Liquefied propane is sold as a fuel for heating houses, isooctane is a component of gasoline, and is the substance used as the reference compound for "octane numbers." (It is "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.

***3.65.** 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. $dw = -P\,dV$ is correct for all simple systems.

d. The fact that reversible processes cannot occur in the real world makes calculations of reversible processes useless.

e. Since 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 close to each other for chemical reactions.

h. The difference between C_P and C_V can be neglected in gases.

i. The process of the Joule experiment is a useful way of studying nonideality of gases.

4

The Second and Third Laws of Thermodynamics: Entropy

OBJECTIVES

After studying this chapter, a student should:

1. understand the various statements of the second law of thermodynamics as statements that govern possible spontaneous processes;
2. understand the reason why a heat engine cannot have an efficiency as large as unity;
3. have a basic understanding of the physical meaning of the entropy of a system;
4. be able to calculate entropy changes for a variety of processes that begin and end with equilibrium states;
5. be able to calculate absolute entropies;
6. have a basic understanding of the relationship between thermodynamic entropy and statistical entropy and be able to calculate simple statistical entropies.

PRINCIPAL FACTS AND IDEAS

1. There are two principal physical statements of the second law of thermodynamics:
   1 It is impossible for a system in a cyclic process to turn heat completely into work.
   2 Heat cannot flow spontaneously from a cooler to a hotter object if nothing else happens.
2. The mathematical statement of the second law establishes a new state function, the entropy.
3. The mathematical statement provides a means of calculating the entropy change of any process that begins and ends at equilibrium states.
4. The second law of thermodynamics governs whether any macroscopic process can occur spontaneously. The criterion is that the entropy of the universe cannot decrease.
5. Entropy is connected with lack of information through the definition of the statistical entropy due to Boltzmann:

$$S_{\mathrm{st}} = k_{\mathrm{B}} \ln(\Omega)$$

   where k_{B} is Boltzmann's constant and Ω is the number of mechanical states in which the system might exist if it is known to be in a given thermodynamic state.
6. The third law of thermodynamics allows the entropy of a pure crystalline substance to be set equal to zero at absolute zero of temperature.
7. The second and third laws of thermodynamics imply that zero temperature on the kelvin scale is unattainable.

4.1

The Second Law of Thermodynamics and the Carnot Heat Engine

Like the first law of thermodynamics, the second law of thermodynamics is based on experimental fact. It can be stated both verbally and mathematically.

Physical Statements of the Second Law

There are two important physical (verbal) statements of the second law of thermodynamics that are generalizations of experimental fact. The **Kelvin statement** of the second law of thermodynamics 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 in a cyclic process to turn heat completely into work done on the surroundings.*

Rudolf Julius Emmanuel Clausius, 1822–1888, was a German physicist who is generally considered to be the discoverer of the second law of thermodynamics.

The **Clausius statement** of the second law of thermodynamics 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.

No violation of either physical statement of the second law of thermodynamics has ever been observed in a properly done experiment. 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**. Such a machine cannot exist. However, heat can be completely turned into work if the process is not cyclic. In an isothermal expansion of an ideal gas ΔU vanishes, so that

$$w_{\text{surr}} = -w = q \quad \text{(ideal gas, isothermal volume change)} \tag{4.1-1}$$

Since w_{surr} is the amount of work done on the surroundings by the system and since q is the amount of heat put into the system, heat transferred to the system has been completely turned into work done on the surroundings. However, the system has not been restored to its original state. 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 4.1a. 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 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 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.

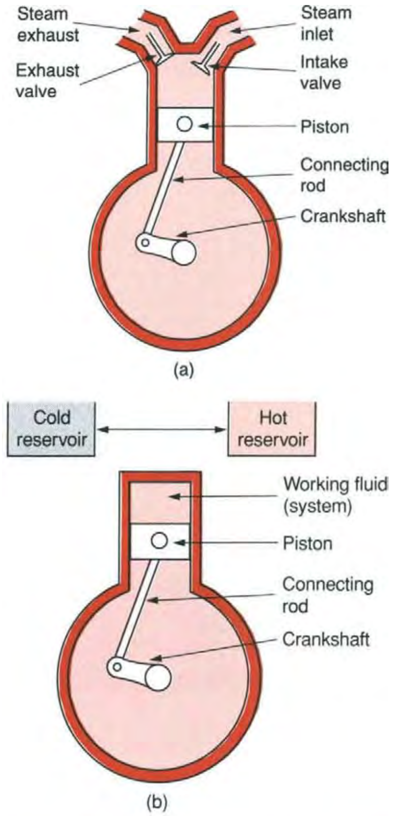


Figure 4.1. Comparison of a Simple Steam Engine and a Carnot Engine (Schematic). (a) A Simple steam engine. High-pressure steam enters through the intake valve, and can push the piston, doing work on the surroundings. **(b) A Carnot heat engine.** The working fluid is a closed system that can accept heat from a hot reservoir, give up heat to a cool reservoir, and push on the piston.

The Carnot engine is depicted in Figure 4.1b. The cylinder contains a gaseous "working fluid," which we define to be the system. This engine has no valves, so the system is closed. We define the cylinder, piston, crankshaft, reservoirs, etc., to be the surroundings. 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. Like the simple steam engine, the Carnot engine operates with a two-stroke cycle, but it is defined to operate reversibly and without friction. We begin the cycle at top dead center with the hot reservoir in contact with the cylinder. The first stroke is expansion, which we break into two steps. The first step is an isothermal reversible expansion of the system at the temperature of the hot reservoir. We stop this expansion with the piston only part of the way toward bottom dead center and remove the hot reservoir from the cylinder. The termination point 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 the cylinder in contact with the cold reservoir. The third step ends at such a volume 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. This state is the same state as the beginning of the cycle and the engine is ready to repeat the cycle.

Figure 4.2a shows the path that the state point of the system follows in the state space as the engine undergoes one cycle, using V and T as the independent variables. Figure 4.2b shows the same cycle using V and P as the independent variables. The state at the beginning of each step is labeled with the same number as is that step. Since the second and fourth steps of the Carnot cycle are adiabatic,

$$q_2 = q_4 = 0 \tag{4.1-2}$$

For the entire cycle,

$$q_{\text{cycle}} = q_1 + q_2 + q_3 + q_4 = q_1 + q_3 \tag{4.1-3}$$

The internal energy U is a state function and the cycle begins and ends at the same state, so that

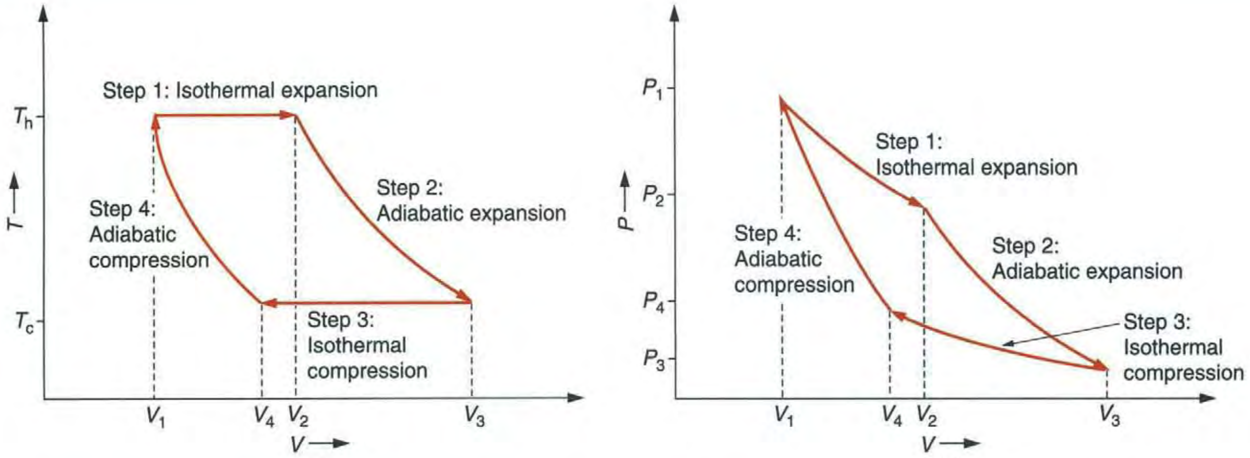
$$\Delta U_{\text{cycle}} = 0 \tag{4.1-4}$$

and

$$w_{\text{cycle}} = \Delta U_{\text{cycle}} - q_{\text{cycle}} = -q_1 - q_3 \tag{4.1-5}$$

The efficiency, η_c, 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 reckoned as a negative part of the heat input.

$$\eta_c = \frac{w_{\text{surr}}}{q_1} = \frac{-w_{\text{cycle}}}{q_1} = \frac{q_{\text{cycle}}}{q_1} = \frac{q_1 + q_3}{q_1} = 1 + \frac{q_3}{q_1} \tag{4.1-6}$$



(a) (b)

Figure 4.2. The Path of the State Point During a Carnot Cycle. (a) In the *V–T* plane. A Carnot cycle must consist of an isothermal expansion, an adiabatic expansion, an isothermal compression, and an adiabatic compression that leads back to the initial state of the isothermal expansion. **(b) In the *V–P* plane.**

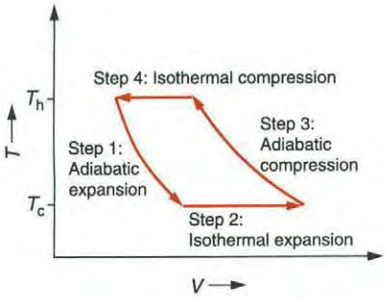


Figure 4.3. The Path of the State Point in the *V–P* Plane during a Carnot Heat Pump Cycle. This cycle is exactly the reverse of the Carnot engine cycle.

From the Kelvin statement of the second law, the efficiency must be less than unity, so that q_3 is negative and q_1 is positive. It is not possible to run a Carnot engine without exhausting some heat to a cool reservoir.

The ratio q_3/q_1 has the same value for all reversible engines that produce work from heat, no matter what the working fluid is, so long as heat reservoirs at the same two temperatures are used. We show this assertion to be fact by considering a **Carnot heat pump**, which is our original Carnot heat engine run backward by another engine. Figure 4.3 represents a reversible Carnot heat pump cycle, which is just the reverse of the cycle of Figure 4.2. We denote the amount of heat put into the hot reservoir by q_4' and the amount of heat taken from the cold reservoir by q_2'. Then, since both cycles are reversible and since we are considering the same Carnot engine run backward,

$$q_4' = -q_1 \tag{4.1-7}$$

and

$$q_2' = -q_3 \tag{4.1-8}$$

Since 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 if the same two reservoirs are used for both cycles:

$$w'_{\text{cycle}} = -w_{\text{cycle}} = w_{\text{surr}} \tag{4.1-9}$$

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** and denoted by η_{hp}. It is analogous to an efficiency:

$$\begin{aligned}\eta_{\text{hp}} &= \frac{|q_4'|}{w'_{\text{cycle}}} = -\frac{q_4'}{-q_2' - q_4'} = \frac{q_1}{q_1 + q_3} \\ &= \frac{1}{1 + q_3/q_1} = \frac{1}{\eta_c}\end{aligned} \tag{4.1-10}$$

This coefficient of performance equals the reciprocal of the Carnot efficiency, since the input and output are reversed in their roles as well as their signs. 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. A real heat pump must have a lower coefficient of performance than a reversible heat pump but will likely have a coefficient of performance greater than unity.

We now prove that any reversible heat engine has the same efficiency as the Carnot engine if it exchanges heat with the same two reservoirs. 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 incorrect. This technique is often used in the proof of mathematical theorems. However, we now seek a contradiction with experimental fact while a mathematician seeks a contradiction with an earlier theorem or with an axiom. Assume that a reversible heat engine does exist with a greater efficiency than a Carnot engine. This is the assumption that we want to show to be false. 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

$$1+\frac{q_3(\mathrm{s})}{q_1(\mathrm{s})} > 1+\frac{q_3(\mathrm{c})}{q_1(\mathrm{c})} \tag{4.1-11}$$

Now use the superengine to drive the Carnot engine as a heat pump between the same two heat reservoirs as used by the superengine. If there is no friction all of the work done by the engine is transmitted to the heat pump:

$$w(\mathrm{s}) = -w'(\mathrm{c}) \tag{4.1-12}$$

From Eq. (4.1-10) 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,

$$q_1(\mathrm{s}) < -q_4'(\mathrm{c}) \quad \text{(statement contrary to fact)}$$

and a larger amount of heat has been put into the hot reservoir by the heat pump than has been removed from it by the superengine. This contradicts the Clausius statement of the second law of thermodynamics, which means that our assumption must be false. *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.*

Exercise 4.1

Carry out the mathematics to show that a reversible engine cannot have a smaller efficiency than a Carnot engine if it uses the same heat reservoirs.

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. If the efficiency of the irreversible engine were greater than the Carnot efficiency it could violate the second law if used to drive a Carnot heat pump. Our conclusion pertaining to real steam engines, internal combustion engines, etc. is: *Any real heat engine cannot be more efficient than a Carnot engine operating between the same two reservoirs, but it can be less efficient.*

The Thermodynamic Temperature and the Zeroth Law of Thermodynamics

The **zeroth law of thermodynamics** is a summary and generalization of experimental fact, like the other laws of thermodynamics. It states that 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 fact is important enough to be called a law of thermodynamics, and it is so basic that it needs to precede the other laws, but the other laws had already been numbered before people figured out how important this law is, so it is called the zeroth law.

The temperature is the variable that has the same value in all objects at thermal equilibrium with each other, so we assert that any other reservoir at the same temperature could be substituted for one of our reservoirs without any change in our analysis. The value of the ratio q_3/q_1 therefore depends only on the temperatures of the reservoirs. The **thermodynamic temperature**, θ, is defined by the relation

$$\frac{\theta_c}{\theta_h} = \left|\frac{q_3}{q_1}\right| \quad \text{(definition)} \tag{4.1-13}$$

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

$$\eta_c = 1 - \frac{\theta_c}{\theta_h} \tag{4.1-14}$$

The thermodynamic temperature scale is not related to any particular kind of substance and is therefore more fundamental than the ideal gas temperature scale. 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. (3.4-5)

$$q_1 = nRT_h \ln(V_2/V_1) \tag{4.1-15}$$

For the third step,

$$q_3 = nRT_c \ln(V_4/V_3) \tag{4.1-16}$$

We can now locate the states at which steps 1 and 3 terminate by using Eq. (3.4-22) twice:

$$\frac{T_c}{T_h} = \left(\frac{V_2}{V_3}\right)^{nR/C_V} \tag{4.1-17}$$

and

$$\frac{T_c}{T_h} = \left(\frac{V_1}{V_4}\right)^{nR/C_V} \tag{4.1-18}$$

These two equations imply that

$$\frac{V_1}{V_2} = \frac{V_4}{V_3} \tag{4.1-19}$$

When this relation is substituted into Eq. (4.1-16),

$$q_3 = nRT_c \ln(V_4/V_3) = nRT_c \ln(V_1/V_2) = -nRT_c \ln(V_2/V_1) \tag{4.1-20}$$

Equation (4.1-20) and Eq. (4.1-15) are substituted into Eq. (4.1-5) to give

$$w_{\text{cycle}} = -q_1 - q_3 = nR(-T_h + T_c)\ln(V_2/V_1) \tag{4.1-21}$$

and

$$\eta_c = \frac{w_{\text{surr}}}{q_1} = \frac{T_h - T_c}{T_h} = 1 - \frac{T_c}{T_h} \tag{4.1-22}$$

By comparison of Eqs. (4.1-14) and (4.1-22),

$$\frac{\theta_c}{\theta_h} = \frac{T_c}{T_h} \tag{4.1-23}$$

Since the two reservoirs can be at any temperatures so long as $T_h > T_c$, temperatures on the thermodynamic and ideal gas temperature scales are proportional to each other for any value of the temperature. The two scales coincide if the unit on the thermodynamic temperature scale is chosen as the kelvin, and the symbol T will from now on stand for the temperature on both the thermodynamic scale and the ideal gas scale. We will call both scales the absolute temperature scale or the kelvin temperature scale. The thermodynamic temperature is a fundamental quantity like mass, length, and time, and the kelvin is one of the "base units" of the SI. We will later show as a consequence of the second and third laws of thermodynamics that zero temperature on the thermodynamic scale is unattainable.

*Exercise 4.2

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

$$\eta_{\text{hp}} = \frac{1}{\eta_{\text{c}}} = \frac{1}{1 - T_{\text{c}}/T_{\text{h}}} \tag{4.1-24}$$

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:

$$\eta_{\text{r}} = \frac{q_2'}{w_{\text{cycle}}} = \frac{q_2'}{-q_2' - q_4'} = -\frac{q_3}{q_1 + q_3}$$

$$\eta_{\text{r}} = \frac{1}{-q_1/q_3 - 1} = \frac{1}{T_{\text{h}}/T_{\text{c}} - 1} \tag{4.1-25}$$

For Carnot heat pumps the coefficient of performance is always greater than unity, and for Carnot refrigerators the coefficient of performance exceeds unity if $T_{\text{h}}/T_{\text{c}} < 2$.

***Exercise 4.3**

a. Calculate the coefficient of performance of a reversible heat pump operating between a high temperature of 70.0°F and a low temperature of 40.0°F.

b. 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.

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 (a).

d. Calculate the cost per joule of heating the house of part (c) with an electrical resistance heater.

4.2 The Mathematical Statement of the Second Law. Entropy

The first law defines the internal energy as a state function in a direct manner, but the physical statements of the second law have no obvious connection with a state function. The second law of thermodynamics can be stated mathematically in a way that defines a new state function: *If one defines the differential dS*

$$dS = \frac{dq_{\text{rev}}}{T} \quad \text{(definition)} \tag{4.2-1}$$

then dS is an exact differential and S is a state function, called the entropy. For an irreversible process

$$dS > \frac{dq_{\text{irrev}}}{T_{\text{surr}}} \tag{4.2-2}$$

where T_{surr} is the temperature of the surroundings.

The argument that the mathematical statement of the second law follows from a physical statement of the second law consists of three parts. The first part is to establish that in the state space of the system only one reversible adiabat passes through any given point, so that two such curves cannot intersect. 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:

$$dS = y\, dq_{\text{rev}} \tag{4.2-3}$$

The third part of the proof is to show that $y = 1/T$ is a valid choice for an integrating factor.[1] We present only the first part of the proof here and sketch the rest in Appendix E.

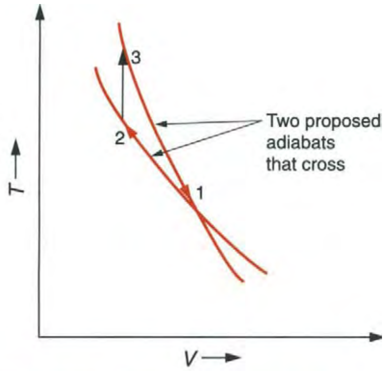


Figure 4.4. Two Reversible Adiabats That Cross (Assumption to Be Proved False). This diagram represents a situation that cannot happen without violating the second law of thermodynamics.

To show that two reversible adiabats cannot cross, 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 such that the curves coincide at state number 1, as depicted in Figure 4.4. The axes of the state space are labeled with V and T but our argument applies if other axes are chosen. We choose a state on each reversible adiabat, labeled states number 2 and number 3 such that the reversible process leading from state 2 to state 3 has $q > 0$. (If we happen to number the states so that $q < 0$ for this process, we must renumber the states.) Now consider a reversible cyclic process $1 \rightarrow 2 \rightarrow 3 \rightarrow 1$. Since steps 1 and 3 are adiabatic,

$$q_{\text{cycle}} = q_2 > 0 \tag{4.2-4}$$

Since $\Delta U = 0$ in any cyclic process,

$$w_{\text{surr}} = -w_{\text{cycle}} = -\Delta U_{\text{cycle}} + q_{\text{cycle}} = q_{\text{cycle}} = q_2 \tag{4.2-5}$$

Heat transferred to the system has been converted completely to work done on the surroundings in a cyclic process, 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.

We now need to show that the fact that two reversible adiabats cannot cross leads to the conclusion that dq_{rev} possesses an integrating factor, and that $1/T$ is such an integrating factor. This argument is sketched in Appendix E. It is first shown that the cyclic integral of dq_{rev}/T vanishes around a Carnot cycle and then that the cyclic integral of dq_{rev}/T vanishes around any cycle. If dS is equal to dq_{rev}/T then dS is an exact integral and S is a state function, establishing Eq. (4.2-1). For a simple system of one phase and one substance, we can write

$$S = S(T, V, n) \tag{4.2-6}$$

or we can write that S is a function of any other set of three state variables, at least one of which must be extensive. However, since Eq. (4.2-1) defines dS and not S any constant can be added to the value of the entropy without any physical effect (the differential of a constant equals zero). As with the energy, only changes in the entropy are well defined, but the third law of thermodynamics will provide a conventional assignment of zero entropy.

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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, pp. 31ff; J. deHeer, *Phenomenological Thermodynamics*, Prentice-Hall, Englewood Cliffs, NJ, 1986, pp. 123ff.

Entropy Changes for Adiabatic Processes

Consider a reversible adiabatic process for any kind of a system. We integrate Eq. (4.2-1) along the curve representing the process. Since $dq_{\mathrm{rev}} = 0$ for every step of the process,

$$\Delta S_{\mathrm{rev}} = \int \frac{dq_{\mathrm{rev}}}{T} = 0 \quad \text{(reversible adiabatic process)} \tag{4.2-7}$$

A reversible adiabatic process does not change the entropy of the system. Our next task is to show that if a system undergoes an irreversible adiabatic process its entropy increases and that Eq. (4.2-2) follows. The assertion that entropy increases in irreversible adiabatic processes is the most important consequence of the second law and is often considered to be a statement of the second law. Since the universe presumably undergoes only irreversible adiabatic processes, the entropy of the universe must increase.

Figure 4.5 shows schematically a change in state 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. At any time 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. Reversible adiabatic processes beginning with a given state must lead to states lying on a single curve, and Figure 4.5 shows such a curve passing through state 1. Let an irreversible adiabatic process lead to state 2. If state 2 does not lie on the curve, either it will lie below the curve as in Figure 4.6a or above the curve as in Figure 4.6b.

We first assume that state 2 lies below the curve as in Figure 4.6a. We now show that this assumption leads to a contradiction with the second law, and cannot be correct. Let state 3 be the state on the curve that has the same volume as state 2. After the

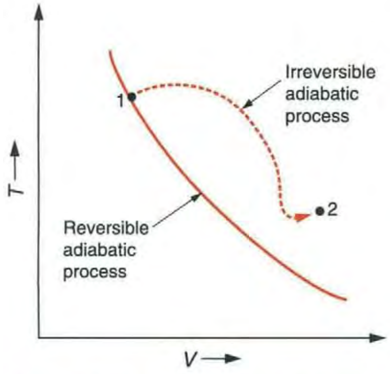
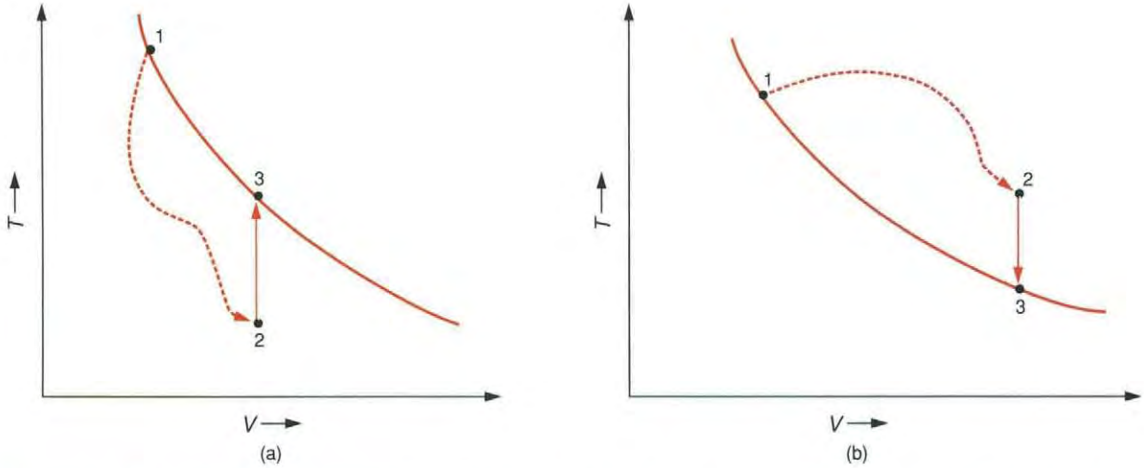


Figure 4.5. An Irreversible Adiabat. An irreversible adiabat does not proceed through a sequence of equilibrium states, even if the inital and final states are equilibrium states.



(a)

(b)

Figure 4.6. Reversible and Irreversible Adiabats. (a) Impossible case. It is shown that an irreversible adiabatic process cannot lead to the low-temperature side of the reversible adiabat. **(b) Possible case.** It is shown that the irreversible adiabatic process can lead to the high-temperature side of the reversible adiabat.

irreversible process has occurred, we carry out a reversible constant-volume step from state 2 to state 3 (step 2). For a constant-volume process,

$$q_2 = \int_c dq = \int_c C_V\, dT \tag{4.2-8}$$

It is an experimental fact that the heat capacity of any system is positive. Therefore, $q > 0$ for the step $2 \rightarrow 3$ 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 (the irreversible process) and step 3 are both adiabatic, so that

$$q_{\text{cycle}} = q_2 > 0 \tag{4.2-9}$$

Since U is a state function

$$\Delta U_{\text{cycle}} = 0 \tag{4.2-10}$$

The work done on the surroundings in the cycle is

$$w_{\text{surr}} = -w_{\text{cycle}} = -\Delta U_{\text{cycle}} + q_{\text{cycle}} = -\Delta U_{\text{cycle}} + q_2 = q_2 \tag{4.2-11}$$

Heat transferred to the system has been completely turned into work done on the surroundings in a cyclic process, which is a violation of the second law. The process is not possible: an irreversible adiabatic process cannot lead to a state below the reversible adiabatic curve.

If state 2 is above the reversible adiabatic curve as in Figure 4.6b, 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, since state 2 is at a higher temperature than state 3,

$$q_{\text{cycle}} = q_2 < 0 \tag{4.2-12}$$

so that

$$w_{\text{surr}} = -w_{\text{cycle}} = -\Delta U_{\text{cycle}} + q_{\text{cycle}} = -\Delta U_{\text{cycle}} + q_2 = q_2 < 0 \tag{4.2-13}$$

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 since the surroundings do not undergo a cyclic process. The process of Figure 4.6b is possible. 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 irreversible adiabatic process from state 1 to state 2 that was depicted in Figure 4.6b. Since S is a state function,

$$\Delta S_{\text{cycle}} = \Delta S_1 + \Delta S_2 + \Delta S_3 = 0 \tag{4.2-14}$$

Since step 3 is reversible and adiabatic, $\Delta S_3 = 0$, and

$$\Delta S_1 = -\Delta S_2 \tag{4.2-15}$$

Since step 2 is reversible, we can integrate Eq. (4.2-1) for this step:

$$\Delta S_2 = \int_{T_2}^{T_3} \frac{dq_{\text{rev}}}{T} = \int_{T_2}^{T_3} \frac{C_V}{T}\, dT < 0 \tag{4.2-16}$$

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. From Eq. (4.2-15) $\Delta S_1 > 0$. Therefore,

$$\Delta S_{\mathrm{irrev}} = \Delta S_1 > 0 \quad \text{(irreversible adiabatic processes)} \tag{4.2-17}$$

Combining Eqs. (4.2-7) and (4.2-17),

$$\Delta S \geq 0 \quad \text{(adiabatic processes)} \tag{4.2-18}$$

where the equality holds for reversible processes. *For any adiabatic process, the entropy of the system cannot decrease.*

Entropy Changes for Nonadiabatic Processes

Consider a closed system and its surroundings arranged as in Figure 4.7. Assuming surface tension effects between system and surroundings to be negligible,

$$S_{\mathrm{combination}} = S + S_{\mathrm{surr}} \tag{4.2-19a}$$

$$\Delta S_{\mathrm{combination}} = \Delta S + \Delta S_{\mathrm{surr}} \tag{4.2-19b}$$

where the system plus surroundings is called the combination. Since the combination is isolated from the rest of the universe, it can undergo only adiabatic processes, and Eq. (4.2-18) applies to it:

$$dS_{\mathrm{combination}} = dS + dS_{\mathrm{surr}} \geq 0 \tag{4.2-20}$$

For reversible process the entropy change of the system and the entropy change of the surroundings cancel, and for irreversible processes the sum of dS and dS_{surr} must be positive. Since the combination is the only part of the universe involved in the process,

$$dS_{\mathrm{universe}} = dS_{\mathrm{combination}} \geq 0 \tag{4.2-21}$$

The most important consequence of the second law of thermodynamics is: *In any reversible process, the entropy of the universe remains constant. In any irreversible process, the entropy of the universe increases.*

In order to focus on the system, we rewrite Eq. (4.2-20) in the form

$$dS \geq -dS_{\mathrm{surr}} \tag{4.2-22}$$

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 $dS + dS_{\mathrm{surr}}$ is not negative. We make the simplest possible assumption about the surroundings: we assume that the heat capacity and the thermal conductivity of the surroundings are so large that the surroundings remain at equilibrium during any process and that the temperature of the surroundings does not change. This means that we can apply Eq. (4.2-1) or (4.2-14) to the surroundings:

$$dS_{\mathrm{surr}} = \frac{dq_{\mathrm{surr}}}{T_{\mathrm{surr}}} = -\frac{dq}{T_{\mathrm{surr}}} \tag{4.2-23}$$

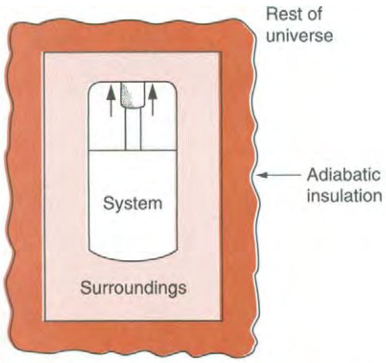


Figure 4.7. A System and Its Surroundings (a "Combination") Adiabatically Insulated from the Rest of the Universe. This combination is used because all of the properties of an adiabatically isolated system can be ascribed to the combination.

where the second equality comes from the fact that any heat transferred to the surroundings must come from the system. Equation (4.2-22) now gives

$$dS \geq \frac{dq}{T_{\text{surr}}} \tag{4.2-24}$$

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. (4.2-24). This equation is the mathematical statement of the second law, with Eqs. (4.2-1) and (4.2-2) combined, and it has been obtained from a physical statement of the second law. The opposite procedure is also possible: if the mathematical statement is taken as a postulate, the physical statements can be derived from it.[2]

Exercise 4.4

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.

Since no violations of the second law of thermodynamics have ever been observed, there is no reason to doubt its universal applicability, but 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 some day begins to contract instead of expanding). This idea is unsupported speculation, and we have every reason to apply the second law of thermodynamics to any process in any macroscopic system and have no reason to assume that it might be violated.[3]

4.3 The Calculation of Entropy Changes

The most direct way to calculate entropy changes is by carrying out the appropriate integral of dS. For any process that begins at an equilibrium state (state 1) and ends at an equilibrium state (state 2) the entropy change is given by

$$\Delta S = S_{\text{final}} - S_{\text{initial}} = \int_c dS = \int_c \frac{dq_{\text{rev}}}{T} \tag{4.3-1}$$

Equation (4.3-1) is a general working equation. The integral must be carried out along a curve in the equilibrium state space of the system beginning at the point representing

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[2] Kirkwood and Oppenheim, *op. cit.* [note 1].

[3] See S. Frautschi, Entropy in an Expanding Universe, *Science*, **217**, 592 (1982).

the initial state and ending at the point representing the final state. The actual process does not have to be a reversible process so long as it has equilibrium initial and final states, but *the path on which the line integral is calculated must correspond to a reversible process*. If you can find a more convenient path with the same initial and final states as a process for which you want to calculate ΔS, use the more convenient path for your integration.

Entropy Changes for Isothermal Reversible Processes

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:

$$\Delta S = \int_c \frac{dq_{\text{rev}}}{T} = \frac{1}{T}\int_c dq_{\text{rev}} = \frac{q_{\text{rev}}}{T} \quad \text{(isothermal process)} \tag{4.3-2}$$

For isothermal reversible volume changes in a system consisting of an ideal gas, q_{rev} is given by Eq. (3.4-5), so that

$$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right) \quad \text{(ideal gas, reversible isothermal process)} \tag{4.3-3}$$

EXAMPLE 4.1

Find ΔS and ΔS_{surr} 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, $\Delta S + \Delta S_{\text{surr}} = 0$:

$$\Delta S_{\text{surr}} = -\Delta S = -40.14\ \text{J K}^{-1}$$

Exercise 4.5

Find ΔS and ΔS_{surr} if 1.000 mol of argon (assumed to be ideal) is expanded reversibly and isothermally from a volume of 50.0 L to a volume of 250.0 L at 298.15 K. Explain the comparison between your answer and that of Exercise 4.1.

EXAMPLE 4.2

For a nonideal gas, the entropy change of a reversible isothermal volume change can be calculated from Eq. (4.3-2) if an expression for q_{rev} is obtained. 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 (the process of Example 2.7a). Argon is represented by the truncated virial equation of state as in that example.

Solution

Using the result of Example 2.7a,

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{5773\ \text{J}}{298.15\ \text{K}} = 19.36\ \text{J K}^{-1}$$

Entropy Changes for Processes That Start and End at the Same Temperature

Since the entropy is a state function, ΔS has the same value for two processes if they have the same initial state and the same final state. If a process has a final temperature that is equal to its initial temperature, Eq. (4.3-2) can be applied to it even if the temperature of the system changes during the process and even if the process is not reversible. We must use q_{rev} for the isothermal reversible process to do the calculation, and not the value of q for the actual process if it differs from q_{rev}.

EXAMPLE 4.3

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 K, condensed to a liquid and then cooled further to 2 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

The entropy change is the same as for an isothermal 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, $PV = \text{constant}$.

$$\Delta S = (2.000\ \text{mol})(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})\ln\left(\frac{1.000\ \text{bar}}{0.500\ \text{bar}}\right) = 11.5\ \text{J K}^{-1}$$

Entropy Changes for Reversible Phase Changes

Two phases of a single substance can be at equilibrium with each other at a temperature that depends on the pressure. Liquid and gaseous water can be at equilibrium with each other at 100.00°C if the pressure is 1.000 atm, and can be at equilibrium with each other at 25.00°C if the pressure is 23.756 torr. If a phase change is carried out reversibly at constant pressure, the temperature is constant and Eq. (4.3-2) applies. Since the pressure is constant, $q = \Delta H$, and

$$\Delta S = \frac{q_{\text{rev}}}{T} = \frac{\Delta H}{T} \quad \text{(reversible phase change)} \tag{4.3-4}$$

EXAMPLE 4.4

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

$$\Delta S = \frac{(3.000\ \mathrm{mol})(18.02\ \mathrm{g\ mol^{-1}})(79.7\ \mathrm{cal\ g^{-1}})(4.184\ \mathrm{J\ cal^{-1}})}{273.15\ \mathrm{K}}$$

$$= -66.0\ \mathrm{J\ K^{-1}}$$

Since the process is reversible,

$$\Delta S_{\mathrm{surr}} = -\Delta S = 66.0\ \mathrm{J\ K^{-1}}$$

***Exercise 4.6**

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 kJ $\mathrm{mol^{-1}}$ and the boiling temperature at 1.000 atm is 78.5°C.

Entropy Changes for Reversible Changes in Temperature

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. (3.5-6) and (3.5-8) give

$$dq = dH = C_P\, dT \quad \text{(closed system, constant pressure)} \qquad (4.3\text{-}5)$$

so that Eq. (4.3-2) becomes

$$\Delta S = \int_{T_1}^{T_2} \frac{C_P}{T}\, dT \quad \text{(closed system, constant pressure)} \qquad (4.3\text{-}6)$$

where T_1 is the initial temperature and T_2 is the final temperature.

EXAMPLE 4.5

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 atm.

Solution

The specific heat capacity of liquid water is nearly constant and equal to 1.000 cal $\mathrm{K^{-1}\ g^{-1}} = 4.184\ \mathrm{J\ K^{-1}\ g^{-1}}$.

$$\Delta S = \int_{273.15\ \mathrm{K}}^{373.15\ \mathrm{K}} \frac{C_P}{T}\, dT = C_P \int_{273.15\ \mathrm{K}}^{373.15\ \mathrm{K}} dT = C_P \ln\left(\frac{373.15\ \mathrm{K}}{273.15\ \mathrm{K}}\right)$$

$$= (2.000\ \mathrm{mol})(18.02\ \mathrm{g\ mol^{-1}})(4.184\ \mathrm{J\ K^{-1}\ g^{-1}}) \ln\left(\frac{373.15\ \mathrm{K}}{273.15\ \mathrm{K}}\right) = 47.03\ \mathrm{J\ K^{-1}}$$

The process is reversible, so

$$\Delta S_{\mathrm{surr}} = -\Delta S = -47.03\ \mathrm{J\ K^{-1}}$$

***Exercise 4.7**

For a gas whose molar constant-pressure heat capacity is represented by

$$C_{P,\mathrm{m}} = a + bT + cT^{-2}$$

derive a formula for ΔS if the temperature is changed from T_1 to T_2 at constant pressure.

For temperature changes at constant volume, Eqs. (3.4-7) and (3.4-8) give

$$dq = dU = C_V\, dT \quad \text{(closed system, constant volume)} \tag{4.3-7}$$

so that Eq. (4.3-2) becomes

$$\Delta S = \int_{T_1}^{T_2} \frac{C_V}{T}\, dT \quad \text{(closed system, constant volume)} \tag{4.3-8}$$

***Exercise 4.8**

Calculate the entropy change if 2.500 mol of neon gas is heated from 80.0°C to 250.0°C at a constant volume of 100.0 L. State any assumptions.

The Entropy Change of an Irreversible Process

The system depicted in Figure 4.8a contains one large object at temperature T_1 and another large object at a higher temperature T_2. These objects are insulated from the surroundings and from each other, except for a thin bar connecting the objects. If the objects are very large compared with the bar, they will have nearly uniform and

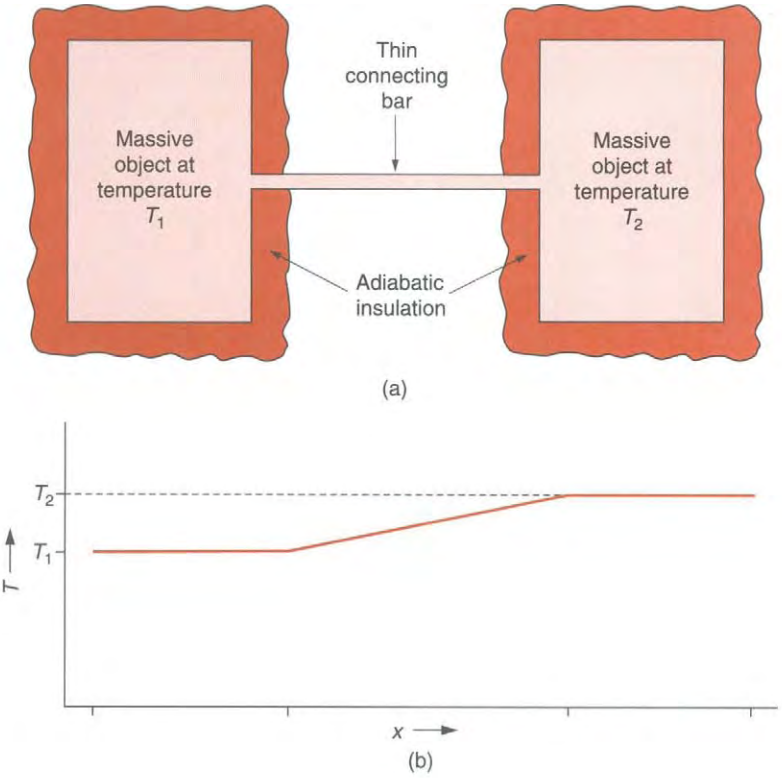

Figure 4.8. An Example Irreversible Process. (a) The system. It is assumed that the large objects at temperature T_1 and temperature T_2 remain at constant temperature, while the thin connecting bar, although not at equilibrium, remains in a steady state. **(b) The temperature distribution in the system.** It is assumed that this temperature distribution is time-independent.

constant temperatures, and the system will come to a **steady state**, in which the properties of the system do not depend on time although an irreversible process is taking place. The bar will have a temperature that depends on position but not on time, as depicted in Figure 4.8b. Consider a period of time Δt, during which a quantity of heat q passes through the bar. Since the nonequilibrium state of the bar is time-independent, the amount of heat entering one end of the bar is equal to the amount of heat leaving the other end of the bar. We assume that the entropy of the bar is a function of its nonequilibrium state, and since the nonequilibrium state of the bar is time-independent, the entropy of the bar does not change.

Since object 1 essentially remains at equilibrium, its entropy change is

$$\Delta S = \int \frac{dq_1}{T_1} = \frac{q_1}{T_1} \tag{4.3-9}$$

where q_1 is the amount of heat transferred in the time Δt. The entropy change of object 2 is

$$\Delta S_2 = \frac{q_2}{T_2} = -\frac{q_1}{T_2} \tag{4.3-10}$$

The entropy change of the system is

$$\Delta S = q_1\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{4.3-11}$$

Since the system is adiabatically insulated from its surroundings, the entropy change of the surroundings vanishes, and the entropy change of the universe is equal to the entropy change of the system.

The time rate of change of the entropy of the universe is called the **entropy production**. It is the rate at which new entropy is being generated. For our steady-state process, the entropy production is

$$\frac{dS_{\text{univ}}}{dt} = \left(\frac{dq}{dt}\right)\left(\frac{1}{T_1} - \frac{1}{T_2}\right) = \left(\frac{dq}{dt}\right)\left(\frac{\Delta T}{T_1 T_2}\right) \tag{4.3-12}$$

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, specifies the rate of the process, and the second factor, $\Delta T/(T_1 T_2)$, specifies the extent to which the system deviates from equilibrium. In irreversible thermodynamics the first factor is called a "flux," and the second factor is called a "force," and it is generally found that the entropy production is a sum of terms that are products of this sort.

***Exercise 4.9**

For the system of Figure 4.8, 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 J of heat flows in 30 s.

Entropy Changes for Irreversible Processes That Begin and End with Equilibrium States

Many of the irreversible processes begin with the system in one equilibrium or metastable state and end with the system in another equilibrium state. Since entropy is a state function, 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. If the entropy change of the surroundings is required, a separate calculation is necessary, since the final state of the surroundings will not necessarily be the same in the reversible process as in the irreversible process.

EXAMPLE 4.6

Calculate ΔS, ΔS_{surr}, and ΔS_{univ} if 2.000 mol of argon (assumed 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 the surroundings remain at thermal 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

$$\Delta S = \frac{q_{\text{rev}}}{T} = (2.000 \text{ mol})(8.3145 \text{ J K}^{-1} \text{ mol}^{-1}) \ln\left(\frac{40.00 \text{ L}}{10.00 \text{ L}}\right) = 23.05 \text{ J K}^{-1}$$

In the ΔS calculation we must use q_{rev}, not the actual value of q. However, since the surroundings remain at equilibrium, $q_{\text{surr,rev}} = q_{\text{surr,actual}}$, and this is used in the calculation of ΔS_{surr}. Since $\Delta U = 0$ for an isothermal process in an ideal gas, and since P_{ext} is constant,

$$q_{\text{surr}} = -q = w = -P_{\text{ext}}\,\Delta V = -(101325 \text{ N m}^{-2})(0.030 \text{ m}^3) = -3040 \text{ J}$$

$$\Delta S_{\text{surr}} = -\frac{3040 \text{ J}}{298.15 \text{ K}} = -10.20 \text{ J K}^{-1}$$

$$\Delta S_{\text{univ}} = 23.05 \text{ J K}^{-1} - 10.20 \text{ J K}^{-1} = 12.85 \text{ J K}^{-1}$$

*Exercise 4.10

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 4.7

Calculate ΔS, ΔS_{surr}, and ΔS_{univ} if the process of Example 4.5 is carried out irreversibly at constant pressure with an arrangement similar to that of Figure 4.8, such that the system and the surroundings are connected only by a thin rod. 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 4.5:

$$\Delta S = 47.03 \text{ J K}^{-1}$$

$$\Delta S_{\text{surr}} = \int_c \frac{dq_{\text{surr}}}{T_{\text{surr}}} = \frac{q_{\text{surr}}}{T_{\text{surr}}} = \frac{-q}{T_{\text{surr}}}$$

Since the process was carried out at constant pressure, $q = \Delta H$, and is the same as for the reversible process in Example 4.5.

$$\Delta S_{\text{surr}} = -\frac{(2.000 \text{ mol})(18.01 \text{ g mol}^{-1})(4.184 \text{ J K}^{-1} \text{ g}^{-1})(100 \text{ K})}{374.15 \text{ K}}$$

$$= -40.28 \text{ J K}^{-1}$$

$$\Delta S_{\text{univ}} = \Delta S + \Delta S_{\text{surr}} = 6.73 \text{ J K}^{-1}$$

Metastable supercooled or superheated phases 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, treating metastable initial states as though they were equilibrium states.

EXAMPLE 4.8

Calculate the entropy change of the system, the surroundings, and the universe for the process of Example 3.16. Assume that the surroundings remain at equilibrium at −15.00°C.

Solution

We use the same reversible path as in Example 3.16:

$$\Delta S_1 = \int_{258.15\ \mathrm{K}}^{273.15\ \mathrm{K}} \frac{C_P(\mathrm{l})}{T}\,dT = C_P(\mathrm{l})\ln\left(\frac{273.15\ \mathrm{K}}{258.15\ \mathrm{K}}\right)$$

$$= (2.000\ \mathrm{mol})(67.1\ \mathrm{J\ K^{-1}\ mol^{-1}})\ln(1.0581) = 7.58\ \mathrm{J\ K^{-1}}$$

$$\Delta S_2 = \frac{\Delta H_2}{T} = \frac{-1.202\times 10^4\ \mathrm{J}}{273.15\ \mathrm{K}} = -44.00\ \mathrm{J\ K^{-1}}$$

$$\Delta S_3 = \int_{273.15\ \mathrm{K}}^{258.15\ \mathrm{K}} \frac{C_P(\mathrm{s})}{T}\,dT = C_P(\mathrm{s})\ln\left(\frac{258.15\ \mathrm{K}}{273.15\ \mathrm{K}}\right)$$

$$= (2.000\ \mathrm{mol})(37.15\ \mathrm{J\ K^{-1}\ mol^{-1}})\ln(0.9451) = -4.20\ \mathrm{J\ K^{-1}}$$

$$\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = -40.62\ \mathrm{J\ K^{-1}}$$

$$\Delta S_{\mathrm{surr}} = \frac{q_{\mathrm{surr}}}{T_{\mathrm{surr}}} = -\frac{q}{T_{\mathrm{surr}}} = -\frac{\Delta H}{T_{\mathrm{surr}}} = \frac{1.112\times 10^4\ \mathrm{J}}{258.15\ \mathrm{K}} = 43.08\ \mathrm{J\ K^{-1}}$$

$$\Delta S_{\mathrm{univ}} = \Delta S + \Delta S_{\mathrm{surr}} = -40.62\ \mathrm{J\ K^{-1}} + 43.08\ \mathrm{J\ K^{-1}} = 2.46\ \mathrm{J\ K^{-1}}$$

The Entropy Change of Mixing Ideal Gases

According to Dalton's law of partial pressures, each gas in a mixture of ideal gases acts as though it were alone in the volume containing the mixture. 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, etc. The number of substances is denoted by s. To create the mixture we imagine an initial state with each substance confined in a separate compartment of a container, as shown in Figure 4.9. We arrange the system so that each gas is at the temperature and the pressure of the final mixture by letting

$$V_i = \frac{n_i RT}{P} \qquad (i = 1, 2, 3, \ldots, s) \tag{4.3-13}$$

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 desired temperature and pressure.

The gases are mixed by withdrawing the partitions between compartments, so that each gas expands irreversibly and isothermally into the entire volume. Since ideal gases act as though each were present by itself, each expansion has the same initial and final states as an isothermal expansion into a vacuum, and these initial and final states are

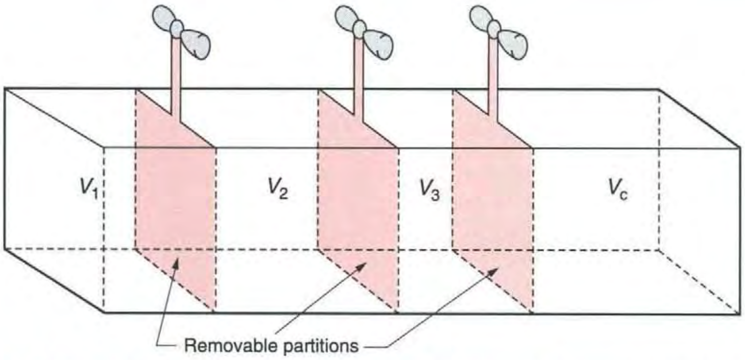

Figure 4.9. A System for Carrying Out the Irreversible Mixing of Gases. The partitions can be removed to that the gases can mix by diffusion.

also the same as those for a reversible isothermal expansion. The entropy change of gas number i is obtained from Eq. (4.3-3):

$$\Delta S_i = n_i R \ln\left(\frac{V}{V_i}\right) \qquad (i = 1, 2, 3, \ldots, s) \tag{4.3-14}$$

where V is the total volume of the container:

$$V = \sum_{i=1}^{c} V_i \tag{4.3-15}$$

The entropy change of the system is

$$\Delta S = \sum_{i=1}^{c} n_i R \ln\left(\frac{V}{V_i}\right) \tag{4.3-16}$$

The **mole fraction** of substance number i is defined by

$$x_i = \frac{n_i}{n} \tag{4.3-17}$$

where n is the total amount of all gases,

$$n = \sum_{j=1}^{c} n_j \tag{4.3-18}$$

From Eqs. (4.3-13), (4.3-15), (4.3-17), and (4.3-18),

$$x_i = \frac{V_i}{V} \tag{4.3-19}$$

so that the entropy change on mixing the ideal gases is

$$\Delta S = -R \sum_{i=1}^{c} n_i \ln(x_i) \tag{4.3-20}$$

All of the mole fractions must be less than or equal to unity, so that the entropy change of mixing is nonnegative. Equation (4.3-20) applies to the mixing of substances in other kinds of systems besides ideal gases if the intermolecular interaction is unimportant. For example, it can be used to calculate the entropy change of mixing of isotopes of a single element, and we will see in a later chapter that it applies to a class of liquid or solid solutions called ideal solutions.

EXAMPLE 4.9

Find the entropy change of mixing of 1.000 mol of dry air. Assume that it is composed of 0.78 mol of nitrogen, 0.21 mol of oxygen, and 0.01 mol of argon.

Solution

$$\begin{aligned}\Delta S &= -(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})[(0.78\ \mathrm{mol})\ln(0.78)\\ &\quad+(0.21\ \mathrm{mol})\ln(0.21)+(0.01\ \mathrm{mol})\ln(0.01)]\\ &=4.72\ \mathrm{J\,K^{-1}}\end{aligned}$$

***Exercise 4.11**

a. Find the entropy change of mixing for 1.000 mol of the normal mixture of Br 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.

4.4 Statistical Entropy

The entropy has been defined as a macroscopic quantity without molecular interpretation. However, a **statistical entropy** was defined by Boltzmann:

$$S_{st}=k_B\ln(\Omega)+S_0 \quad \text{(definition)} \tag{4.4-1}$$

where k_B is Boltzmann's constant and where S_0 is an arbitrary constant that we can take equal to zero. This definition is carved on Boltzmann's tombstone. The **thermodynamic probability** Ω is defined to be the number of mechanical states (microstates) of the system that are compatible with our information about the macroscopic state of the system. The thermodynamic probability is a measure of lack of information about the mechanical state of the system, with larger values corresponding to less information and with a value of unity corresponding to knowledge that the system is in a specific microstate. Since the logarithm is a monotonic function of its argument, the statistical entropy is also a measure of lack of information about the mechanical state of the system. If we know that the system definitely occupies a single mechanical state, the statistical entropy is equal to zero.

In order to show the relationship between the thermodynamic entropy and the statistical entropy, we examine a model system called the **lattice gas**. This system contains a fixed number N of noninteracting point-mass molecules moving freely in a rectangular box of volume V. The molecules are assumed to obey classical mechanics so the states of the molecules are specified by their locations and velocities. We mentally divide the volume of the box into a number M of rectangular cells of equal size arranged in a rectangular array (lattice) as shown schematically in Figure 4.10. We number the cells from 1 to M. Since the cell boundaries are imaginary, the molecules simply pass through them. Instead of giving the values of three coordinates to specify

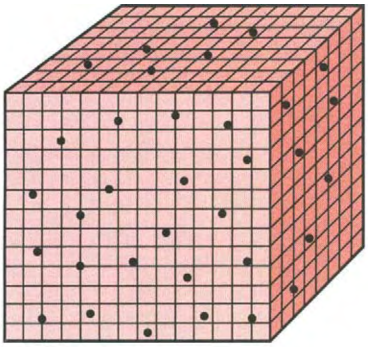

Figure 4.10. The Lattice Gas. This model system is physically no different from a model gas with division of the volume into cells. the planes dividing the system into cells are imaginary and do not affect the motions of the molecules.

the location of one particle we specify which cell it occupies at a given instant. This specification of location is called a **"coarse-grained" description**, and it gives less precise information about the location of the particles than specifying exact coordinate values. We continue to specify the velocity of each particle by specifying the values of three velocity components.

The model system is at thermodynamic equilibrium with known values of T and V and a known number of particles, N. This information suffices to specify the equilibrium macroscopic state, but gives very little information about the mechanical state of the system, since the particles can be arranged with very many positions and velocities. Very many mechanical states could correspond to the known macroscopic state, and Ω has a very large value.

We assume that the probability that a randomly chosen molecule possesses a particular velocity is independent of the probability that the same molecule possesses a particular position. Therefore, any velocity state of all the molecules can be combined with any coordinate state of the molecules. 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. Therefore, the thermodynamic probability is the product of two factors, one for the coordinates and one for the velocities:

$$\Omega = \Omega_{\text{coord}}\Omega_{\text{vel}} \tag{4.4-2}$$

We now seek a formula representing Ω_{coord} for our lattice-gas model. If we have only thermodynamic information, we know nothing about the positions of the molecules except that they are somewhere in the box, and the number of possible coordinate states for a single molecule is equal to the number of cells, M. Since the molecules are mass points they do not interfere with each other, and 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, etc. For a system of N molecules,

$$\Omega_{\text{coord}} = M^N \tag{4.4-3}$$

If the molecules were not mass points this equation would not be valid because a cell could fill up and not be able to accept any more molecules after a certain number were in it.

EXAMPLE 4.10

Calculate the value of Ω_{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

$$V_{\text{cell}} = (0.500 \times 10^{-9}\ \text{m})^3 = 1.25 \times 10^{-28}\ \text{m}^3$$

$$M = \frac{V}{V_{\text{cell}}} = \frac{0.0244\ \text{m}^3}{1.25 \times 10^{-28}\ \text{m}^3} = 1.95 \times 10^{26}$$

$$\Omega_{\text{coord}} = M^N = (1.95 \times 10^{26})^{6.002\times 10^{23}} = 10^{1.58\times 10^{25}}$$

This is such a large number that we are not able to give any significant digits.

*Exercise 4.12

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 with a five on the second die and a five on the first die with 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 and the change in the thermodynamic entropy are equal for isothermal volume changes in our lattice gas. It is shown in Chapter 10 that a model system of independent particles behaves like an ideal gas, and we assume our lattice gas will behave like an ideal gas. Equation (4.3-3) gives the change in the thermodynamic entropy for an isothermal volume change in an ideal gas:

$$\Delta S = nR\ln\left(\frac{V_2}{V_1}\right) \tag{4.4-4}$$

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

The change in the statistical entropy for any process is

$$\Delta S_{\mathrm{st}} = k_{\mathrm{B}}\ln(\Omega_2) - k_{\mathrm{B}}\ln(\Omega_1) = k_{\mathrm{B}}\ln(\Omega_2/\Omega_1) = k_{\mathrm{B}}\ln\left(\frac{\Omega_{\mathrm{coord}(2)}\Omega_{\mathrm{vel}(2)}}{\Omega_{\mathrm{coord}(1)}\Omega_{\mathrm{vel}(1)}}\right) \tag{4.4-5}$$

We assume that the velocity distribution depends only on the temperature. With this assumption, the velocity factor in Ω depends only on the temperature, so that for an isothermal process

$$\Omega_{\mathrm{vel}(2)} = \Omega_{\mathrm{vel}(1)} \tag{4.4-6}$$

The velocity factors in Eq. (4.4-5) cancel, and

$$\Delta S_{\mathrm{st}} = k_{\mathrm{B}}\ln\left(\frac{\Omega_{\mathrm{coord}(2)}}{\Omega_{\mathrm{coord}(1)}}\right) \tag{4.4-7}$$

Using Eq. (4.4-3) and the fact that N is fixed,

$$\Delta S_{\mathrm{st}} = k_{\mathrm{B}}\ln\left(\frac{M_2^N}{M_1^N}\right) = k_{\mathrm{B}}\ln\left(\left(\frac{M_2}{M_1}\right)^N\right) = Nk_{\mathrm{B}}\ln\left(\frac{M_2}{M_1}\right) \tag{4.4-8}$$

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:

$$\frac{M_2}{M_1} = \frac{V_2}{V_1}$$

Therefore,

$$\Delta S_{\mathrm{st}} = Nk_{\mathrm{B}}\ln\left(\frac{V_2}{V_1}\right) \tag{4.4-9}$$

The change in the statistical entropy is identical to the change in thermodynamic entropy given in Eq. (4.4-4) if we let

$$Nk_B = nR$$

which assigns a value to the Boltzmann constant:

$$k_B = \frac{nR}{N} = \frac{R}{N_{Av}} = \frac{8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}}{6.0221 \times 10^{23}\ \mathrm{mol^{-1}}} = 1.3807 \times 10^{-23}\ \mathrm{J\ K^{-1}} \tag{4.4-10}$$

We assert without further discussion that the equivalence between the statistical and thermodynamic entropies in a lattice gas and for isothermal expansions is typical of all systems and all processes and write the general relation

$$S = S_{st} + \text{constant} \tag{4.4-11}$$

where the constant can be taken equal to zero.

EXAMPLE 4.11

Find the value of the coordinate contribution to the statistical entropy for the value of Ω_{coord} in Example 4.10.

Solution

$$S_{st,coord} = k_B \ln\left(10^{1.58\times10^{25}}\right) = (1.38 \times 10^{-23}\ \mathrm{J\ K^{-1}})(3.64 \times 10^{25})$$
$$= 502\ \mathrm{J\ K^{-1}}$$

***Exercise 4.13**

Find the value of Ω for a system if its entropy is equal to 210 J $\mathrm{K^{-1}}$.

Entropy and Randomness

We have established a connection between entropy and 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 way of stating the connection between entropy and lack of information about the mechanical state, because disorder or randomness generally corresponds to lack of information about the mechanical state of the system.

4.5

The Third Law of Thermodynamics and Absolute Entropies

Walter 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, but who also made numerous other contributions, including the Nernst equation of electrochemistry.

Like the first and second laws, the third law of thermodynamics is a summary and generalization of experimental fact. It was first stated by Nernst: *For certain isothermal chemical reactions of solids, the entropy changes approach zero as the thermodynamic temperature approaches zero.* Nernst based this statement on his analysis of experimental data of 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**.

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 crystalline 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 such metastable states. We discuss such systems later in this section.

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, prior to the development of quantum mechanics, proposed that covalent chemical bonds arise from sharing of electrons according to the octet rule.

Sir Franz Eugen 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 proposing the process of adiabatic demagnetization to attain low temperatures.

Exercise 4.14

Show that if the entropies of pure perfect crystalline elements are taken equal to nonzero constants at zero temperature, the 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 4.2 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 4.11, 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 4.2 that irreversible adiabatic processes lead to the high-temperature side of the reversible adiabat, irreversible adiabatic processes cannot lead to lower temperatures than reversible adiabatic processes. Therefore, no adiabatic process can lead to zero temperature.

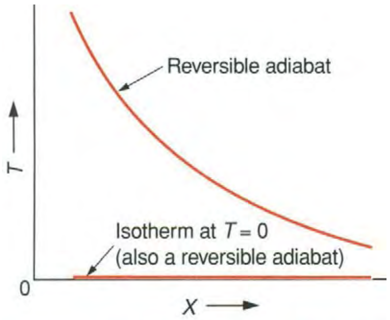

Figure 4.11. Reversible Adiabats Showing the Unattainability of Zero Temperature. The isotherm at $T = 0$ is a reversible adiabat as well as an isotherm. It therefore cannot intersect any reversible adiabat.

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**. This process, invented by Giauque, consists of magnetizing an object isothermally. The

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[4] G. N. Lewis and M. Randall, *Thermodynamics and the Free Energy of Chemical Substances*, McGraw-Hill, New York, 1923, p. 448.

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 microkelvin) 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 nK (nanokelvin).[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 at a temperature of interest is called the **absolute entropy** of that substance at the specified temperature. We write, for 1 mol of any substance,

$$S_{\mathrm{m}}(T_1) = \int_0^{T_1} \frac{dq_{\mathrm{rev}}}{T} \tag{4.5-1}$$

where $S_{\mathrm{m}}(T_1)$ is the absolute molar entropy of the substance at temperature T_1. If there is no phase transition between $T = 0$ and $T = T_1$ (the substance must be in the same crystal structure at temperature T_1 as at 0 K) and if the final and initial states are at the same pressure,

$$S_{\mathrm{m}}(T_1) = \int_0^{T_1} \frac{C_{P,\mathrm{m}}}{T}\, dT \quad \text{(solid substance)} \tag{4.5-2}$$

A similar equation can be written for a constant-volume integration.

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.

Inspection of Eq. (4.5-2) shows that the heat capacity must approach zero as the temperature approaches zero if the integral is not to diverge. 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. An approximate theory of Debye[6] gives the result that for a crystal of a monatomic substance the constant-volume heat capacity at low temperatures has a contribution from vibrational motions that is proportional to the cube of the temperature. An approximate theory for the motion of mobile electrons in metals gives a contribution proportional to the first power of the temperature,[7] so that for sufficiently low temperature

$$C_{V,\mathrm{m}} = aT^3 + bT \quad \text{(valid at low temperature)} \tag{4.5-3}$$

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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).

[6] P. Debye, *Ann. Physik*, **17**(4), 817 (1911). See Section 22.3.

[7] J. S. Blakemore, *Solid State Physics*, 2d ed., W. B. Saunders, Philadelphia, 1974, pp. 176ff.

where a and b are parameters that can be determined from experimental data. For nonconductors the parameter b is equal to zero. Equation (4.5-3) 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. (4.5-3) is usually used for C_P as well as for C_V.

Exercise 4.15

a. Show that if Eq. (4.5-3) 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

$$S_m(T_1) = \frac{aT_1^3}{3} = \frac{C_{V,m}(T_1)}{3} \tag{4.5-4}$$

***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. (4.5-2) must be modified to include the entropy change of the phase transition. If the substance is a liquid at temperature T_1, Eq. (4.5-2) becomes

$$S_m(T_1) = \int_0^{T_f} \frac{C_{P,m}(s)}{T}\,dT + \frac{\Delta_{fus}H_m}{T_f} + \int_{T_f}^{T_1} \frac{C_{P,m}(l)}{T}\,dT \quad \text{(liquid system)} \tag{4.5-5}$$

where T_f is the reversible freezing temperature (melting 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 4.16

Write the equation analogous to Eq. (4.5-5) 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 are included in Table A.8 of Appendix A. These values can be used to calculate entropy changes for chemical reactions. For a reaction beginning with an equilibrium state or a metastable state and ending with an equilibrium state, the change in entropy is equal to the entropy of the products minus the entropy of the reactants. For one mole of an isothermal reaction at temperature T_1 written as in Eq. (3.7-7),

$$\Delta S = \sum_{i=1}^{c} \nu_i S_{m,i}(T_1) \tag{4.5-6}$$

The symbol $S_{m,i}(T_1)$ stands for the absolute molar entropy of substance number i at temperature T_1. Compare this equation with Eq. (3.7-11), which contains enthalpy changes of formation. This equation contains absolute entropies, not entropy changes of formation.

The **standard state for the entropy** is the same as the standard state for the enthalpy. 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 pressure P°. 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 5. For most gases the difference between the real gas and the ideal gas is small, and we can take the standard state as that of the real gas at pressure P° without serious error.

EXAMPLE 4.12

Compute the standard-state entropy change for one mole of the reaction

$$0 = 2CO_2(g) - 2CO(g) - O_2(g)$$

if the product and reactants are at 298.15 K.

Solution

Using values from Table A.8,

$$\begin{aligned}\Delta S^\circ &= (2)(213.64\ \mathrm{J\ K^{-1}\ mol^{-1}}) + (-2)(197.564\ \mathrm{J\ K^{-1}\ mol^{-1}})\\ &\quad + (-1)(205.029\ \mathrm{J\ K^{-1}\ mol^{-1}})\\ &= -172.88\ \mathrm{J\ K^{-1}\ mol^{-1}}\end{aligned}$$

The stoichiometric coefficients are taken as dimensionless, so the units of the entropy change are joules per kelvin per mole.

***Exercise 4.17**

Assuming that the surroundings remain at equilibrium at 298.15 K, calculate the entropy change of the surroundings and of the universe for one mole of the reaction in Example 4.12.

Chapter 3 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. We do not discuss this scheme, but the interested student can read the article by Benson and Buss.[8]

Statistical Entropy and the Third Law of Thermodynamics

There are some substances that originally appeared not to obey the third law of thermodynamics, and these anomalies can be explained using statistical entropy. Carbon monoxide is an example. The absolute entropy of gaseous carbon monoxide determined by an integration such as in Eq. (4.5-1) 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 are nearly symmetrical in shape and have only a small dipole moment, so a carbon monoxide molecule fits into the crystal lattice almost as well with its ends reversed as in the equilibrium position. Metastable crystals can easily form with part of the molecules in the reversed position. (In fact, it is

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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).

difficult to obtain a perfect crystal.) If we assume that the occurrence of reversed molecules is independent of the rest of the state of the crystal, we can write

$$\Omega = \Omega_{\text{orient}}\Omega_{\text{rest}} \tag{4.5-7}$$

where Ω_{orient} is the number of ways of orienting the molecules in ways compatible with our knowledge of the state of the system. The other factor, 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,

$$\lim_{T\to 0} \Omega_{\text{rest}} = 1 \tag{4.5-8}$$

If a metastable crystal exists in which each molecule can occur with equal probability in either the equilibrium state or the reversed state, then

$$\Omega_{\text{orient}} = 2^N \tag{4.5-9}$$

where N is the number of molecules in the crystal. If Ω_{rest} is set equal to unity, the statistical entropy of the metastable crystal near zero temperature is

$$S_{\text{st}}(\text{metastable}) = k_{\text{B}}\ln(2^N) = Nk_{\text{B}}\ln(2) = nR\ln(2) \tag{4.5-10}$$

For 1 mol of carbon monoxide,

$$S_{\text{m,st}}(\text{metastable}) = R\ln(2) = 5.76\ \text{J K}^{-1}\ \text{mol}^{-1} \tag{4.5-11}$$

This value agrees with the amount by which carbon monoxide appeared to deviate from the third law.

***Exercise 4.18**

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. 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 entropy changes of vaporization. It states that for "normal" liquids the molar entropy change of vaporization at the normal boiling temperature (at 1.000 atm) is roughly equal to $10.5R \approx 88\ \text{J K}^{-1}\ \text{mol}^{-1}$. Trouton's rule underestimates the entropy change of vaporization for liquids like 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, so these liquids do not qualify as normal liquids. 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 one atmosphere pressure at the normal boiling temperature. 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]

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[9] D. Hoshino, K. Nagahama, and M. Hirata, *Ind. Eng. Chem. Fundam.*, **22**, 430 (1983).

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's statement of the same law is that heat cannot flow from a cooler to a hotter body if nothing else happens.

The mathematical statement of the second law asserts that S, the entropy, is a state function if we define

$$dS = \frac{dq_{\text{rev}}}{T}$$

It was shown from the second law that in any reversible process the entropy of the universe remains constant, while in any irreversible process the entropy of the universe must increase.

A general procedure for the calculation of an entropy change in a closed system 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

$$S_{\text{st}} = k_B \ln(\Omega) + S_0$$

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 the value of which we take to be zero.

The third law of thermodynamics is that if the entropies of all samples of pure perfect crystalline elements are arbitrarily 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.

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.

PROBLEMS

Problems for Section 4.1

*__4.19.__ **a.** A Carnot engine contains 0.200 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, $V_1 = 0.500$ 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**).

4.20. A Carnot engine contains as working fluid 0.150 mol of neon (assumed 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. State any assumptions.

*__4.21.__ A Carnot engine contains as working fluid 0.150 mol of nitrogen (assumed ideal with $C_{V,m} = 5R/2$). If $T_h = 600.$ K and $T_c = 373$ K, find the values 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. Compare your results with those of Problem 4.20 and explain any differences.

4.22. 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

A decimal point after trailing zeros indicates that the zeros to its left are significant digits.

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.

4.23. **a.** Calculate the coefficient of performance of a Carnot refrigerator with an interior temperature of −18°C and an exterior temperature of 25°C. 1 watt = 1 J s^{-1}.

***b.** Calculate the amount of electrical energy in kilowatt-hours necessary to freeze 1.000 kg of water in the Carnot refrigerator of part (**a**).

4.24. **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. ft^3 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. ft^3 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 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. ft^3 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.

Problems for Section 4.2

***4.25.** Calculate the entropy change for each of the four steps in the Carnot cycle of Problem 4.20, and show that these entropy changes sum to zero.

4.26. A sample of 1.000 mol of helium gas (assumed ideal with $C_{V,\mathrm{m}} = 3R/2$) 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.

***4.27.** A sample of 2.000 mol of nitrogen gas (assumed ideal with $C_{V,\mathrm{m}} = 5R/2$) 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 volumes.

Problems for Section 4.3

4.28. **a.** Find the change in entropy for the vaporization of 1.000 mol of liquid water at 100°C and a constant pressure of 1.000 atm.

b. Find the entropy change for the heating of 1.000 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.

***4.29.** **a.** Calculate the entropy change for the isothermal expansion of 1.000 mol of argon gas (assumed 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 (assumed 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.

4.30. **a.** Calculate the entropy change for the following reversible process: 2.000 mol of neon (assumed ideal with $C_{V,\mathrm{m}} = 3R/2$) 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.

Problems for Section 4.4

***4.31.** Calculate the change in statistical entropy of a deck of 52 cards if it is completely shuffled. That is, it goes from a state in which the order of the cards is known to a completely unknown ordering.

4.32. 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.

4.33. Explain why the thermodynamic entropy of the system changes in each of the following processes, and say whether it increases or decreases. 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 evaporated.

Problems for Section 4.5

4.34. Assign the following nonzero constant values for the standard-state molar entropies at 0 K:

C(s)	$10.00\ \mathrm{J\ K^{-1}\ mol^{-1}}$
O_2(s)	$20.00\ \mathrm{J\ K^{-1}\ mol^{-1}}$
H_2(s)	$30.00\ \mathrm{J\ K^{-1}\ mol^{-1}}$

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.

4.35. Calculate ΔS° 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. $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$
e. $C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(l)$
f. $C_2H_2(g) + 2H_2(g) \rightarrow C_2H_6(g)$

4.36. Using absolute entropy values from Table A.8 and heat-capacity values from Table A.7 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
e. CO_2(g) at 200.0°C
f. H_2O(g) at 200.0°C

4.37. **a.** Using absolute entropy values from the previous problem, calculate $\Delta_{\mathrm{vap}}S_m^\circ$, the standard molar enthalpy of vaporization for H_2O at 100.0°C.

b. Calculate $\Delta_{\mathrm{vap}}S_m^\circ$ for H_2O at 25°C using Eq. (4.3-4).
c. Calculate $\Delta_{\mathrm{vap}}S_m^\circ$ for H_2O at 100.0°C using Eq. (4.3-4).
d. Comment on your values in light of Trouton's rule.

4.38. Using S_m° values from Problem 4.36, calculate ΔS° at 100°C for the reaction

$$0 = 2H_2O(g) - O_2(g) - 2H_2(g)$$

***4.39.** 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 4.12.

4.40. Find the standard-state molar entropy of solid silver at 270.0 K from the following data:

T/K	30.0	50.0	70.0	90.0	110.0
$C_{P,m}^\circ(s)/\mathrm{J\ K^{-1}\ mol^{-1}}$	4.77	11.65	16.33	19.13	20.96
T/K	130.0	150.0	170.0	190.0	210.0
$C_{P,m}^\circ(s)/\mathrm{J\ K^{-1}\ mol^{-1}}$	22.13	22.97	23.61	24.09	214.42
T/K	230.0	250.0	270.0		
$C_{P,m}^\circ(s)/\mathrm{J\ K^{-1}\ mol^{-1}}$	24.73	25.03	25.31		

Assume that the Debye formula can be used from 0 K to 30.0 K. Note that since there is an odd number of data points that are equally spaced, you can use Simpson's rule.

***4.41.** The following are heat capacity data for pyridine.[10]

T/K	13.08	21.26	28.53	35.36	48.14
$C^{\circ}_{P,\mathrm{m}}(\mathrm{s})/\mathrm{J\,K^{-1}\,mol^{-1}}$	4.448	12.083	19.288	25.309	33.723
T/K	64.01	82.91	101.39	132.32	151.57
$C^{\circ}_{P,\mathrm{m}}(\mathrm{s})/\mathrm{J\,K^{-1}\,mol^{-1}}$	40.748	46.413	50.861	58.325	63.434
T/K	167.60	179.44	193.02	201.61	212.16
$C^{\circ}_{P,\mathrm{m}}(\mathrm{s})/\mathrm{J\,K^{-1}\,mol^{-1}}$	68.053	71.756	76.467	79.835	84.446
T/K	223.74	231.49			
$C^{\circ}_{P,\mathrm{m}}(\mathrm{s})/\mathrm{J\,K^{-1}\,mol^{-1}}$	94.328	101.25			
T/K	231.49	239.70	254.41	273.75	293.96
$C^{\circ}_{P,\mathrm{m}}(\mathrm{l})/\mathrm{J\,K^{-1}\,mol^{-1}}$	120.67	122.23	124.54	127.93	131.88
T/K	298.15	307.16			
$C^{\circ}_{P,\mathrm{m}}(\mathrm{l})/\mathrm{J\,K^{-1}\,mol^{-1}}$	132.74	134.55			

A value of 8278.5 J mol^{-1} is reported for the enthalpy change of fusion at 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 either a graphical or a numerical technique to approximate the integrals needed.[11]

General Problems

4.42. 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.

***4.43.** 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.

4.44. 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 of Section 4.3, which consisted 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.

***4.45.** Assume that an automobile engine burns 2,2,4-trimethylpentane (isooctane), forming only $CO_2(g)$ and $H_2O(g)$. The density of isooctane is 0.6909 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 isooctane. 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. kg can be lifted by combustion of 1.000 gallon of isooctane. 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.

4.46. 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.

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[10] F. T. Gucker and R. L. Seifert, *Physical Chemistry*, W. W. Norton, New York, 1966, p. 445.

[11] Robert G. Mortimer, *Mathematics for Physical Chemistry*, 2d ed., Academic Press, San Diego, CA, 1999, pp. 379ff.

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.

4.47. Make an accurate graph of each of the following, stating any assumptions:

a. The molar entropy of a monatomic ideal gas with ($C_{V,\mathrm{m}} = 3R/2 =$ constant) as a function of temperature from 0 K to 300 K. Assume that the molar entropy vanishes at 0 K and assume a constant pressure of 1.000 bar.

b. The molar entropy of an ideal gas as a function of molar volume from 1.000 L to 10.00 L at a constant temperature of 300 K.

c. The molar entropy of water from −50°C to +50°C at a constant pressure of 1.000 atm.

5

The Thermodynamics of Real Systems

OBJECTIVES

After studying this chapter, a student should:

1. be able to use the second law of thermodynamics and formulas derived from it to determine whether a process is spontaneous or not under specific sets of conditions;
2. be able to simplify thermodynamic formulas using appropriate tools;
3. be able to make various kinds of thermodynamic calculations;
4. be familiar with the way in which the Gibbs energy of a system depends on its state;
5. understand the meaning of partial molar quantities and be able to use them in calculations;
6. be able to use Euler's theorem and the Gibbs–Duhem relation in thermodynamic calculations.

PRINCIPAL FACTS AND IDEAS

1. The second law of thermodynamics provides the general criterion for spontaneous processes: the entropy of the universe cannot decrease.
2. This general criterion can be used to derive criteria for spontaneous processes in terms of system properties under specific circumstances.
3. The Gibbs and Helmholtz energies provide information about the maximum amount of work that can be done by a system in a given process.
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.

5.1 Criteria for Spontaneous Processes and for Equilibrium. The Gibbs and Helmholtz Energies

The second law of thermodynamics provides the fundamental criterion that must be obeyed in order for a process to take place: that the entropy of the universe cannot decrease in any real process. We now investigate specific situations and express this fundamental criterion in terms of properties of the system.

Criteria for Spontaneous Processes in Closed Systems

In this section, we examine the behavior of a closed system. If the system is in contact with surroundings, we assume that the surroundings are very large and have a very large thermal conductivity and a very large heat capacity, so that the surroundings can be assumed to remain at equilibrium at a fixed temperature, allowing us to focus on the properties of the system. Consider first a closed system that is not necessarily a simple system. The second law of thermodynamics implies that possible processes must obey the relation of Eq. (4.2-31)

$$dS \geq \frac{dq}{T_{\mathrm{surr}}} = \frac{(dU - dw)}{T_{\mathrm{surr}}} \tag{5.1-1}$$

where T_{surr} is the temperature of the surroundings and where we have used the first law in the form $dq = dU - dw$. This equation is the same as

$$dU - dw - T_{\mathrm{surr}}\, dS \leq 0 \tag{5.1-2}$$

We now consider criteria for possible processes in a closed simple system under various conditions. An **isolated system** is a closed system that cannot exchange either heat or work with anything else: $dq = 0$ and $dw = 0$ so that $dU = 0$ and

$$dS \geq 0 \quad \text{(isolated system)} \tag{5.1-3}$$

We have already obtained this criterion for an adiabatic system.

Next, consider the special case that no work is done and that the entropy of the system is constant. A system known to be in a given mechanical state has constant statistical entropy and can fit this case, but it is otherwise not likely to be encountered. Since $dS = 0$ and $dw = 0$,

$$dU \leq 0 \quad (S \text{ constant},\ dw = 0) \tag{5.1-4}$$

We next consider the important case in which the temperature of the system is constant (and equal to the temperature of the surroundings). Equation (5.1-2) becomes

$$dU - T\, dS - dw \leq 0 \quad (T \text{ constant}) \tag{5.1-5}$$

If our system is simple, $dw = -P_{\mathrm{ext}}\, dV$, and

$$dU - T\, dS + P_{\mathrm{ext}}\, dV \leq 0 \quad (\text{simple system},\ T \text{ constant}) \tag{5.1-6}$$

There are two important cases for isothermal (constant-temperature) processes in closed simple systems. The first case is that of constant volume, so that $dV = 0$:

$$dU - T\, dS \leq 0 \quad (\text{simple system},\ T \text{ and } V \text{ constant}) \tag{5.1-7}$$

The Helmholtz Energy and Processes at Constant *T* and *V*

The **Helmholtz energy** is a convenience variable, named for Hermann Helmholtz, and defined by

$$A = U - TS \quad \text{(definition)} \tag{5.1-8}$$

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

$$dA = dU - T\,dS - S\,dT \tag{5.1-9}$$

so that if T is constant

$$dA = dU - T\,dS \quad \text{(constant } T\text{)} \tag{5.1-10}$$

Equation (5.1-7) is the same as

$$dA \le 0 \quad \text{(simple system, } T \text{ and } V \text{ constant)} \tag{5.1-11}$$

The Gibbs Energy and Processes at Constant *T* and *P*

The second important isothermal case is the case that the pressure of the system is constant (and equal to the external pressure). In this case,

$$dU + P\,dV - T\,dS \le 0 \quad \text{(simple system, } T \text{ and } P \text{ constant)} \tag{5.1-12}$$

When we say that a system is at constant pressure, we mean that the pressure is not only constant, but also equal to the external pressure. The **Gibbs energy** is defined by

$$G = U + PV - TS \quad \text{(definition)} \tag{5.1-13}$$

The Gibbs energy is named for Josiah Willard Gibbs, 1839–1903, an American physicist who made fundamental contributions to thermodynamics and statistical mechanics.

The Gibbs energy has also been called the "free energy," the "Gibbs free energy," the "Gibbs function," and the "free enthalpy."

The Gibbs energy is related to the enthalpy and the Helmholtz energy by the relations

$$G = H - TS = A + PV \tag{5.1-14}$$

From Eq. (5.1-13), the differential of G is

$$dG = dU + P\,dV + V\,dP - T\,dS - S\,dT \tag{5.1-15}$$

If T and P are constant, this equation becomes

$$dG = dU + P\,dV - T\,dS \quad (T \text{ and } P \text{ constant}) \tag{5.1-16}$$

The relation given in Eq. (5.1-12) is the same as

$$dG \le 0 \quad \text{(simple system, } T \text{ and } P \text{ constant)} \tag{5.1-17}$$

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 spontaneous process must obey

$$\Delta G \le 0 \quad \text{(simple system, } T \text{ and } P \text{ constant)} \tag{5.1-18}$$

The relation shown in Eq. (5.1-18) is the most useful criterion for the spontaneity of chemical reactions, since the most common circumstance for chemical reactions is that of constant temperature and pressure. However, thermodynamics does not distinguish between chemical and physical processes, and Eq. (5.1-18) is just as valid for physical processes such as phase transitions as it is 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 nineteenth century, Berthelot incorrectly maintained that all spontaneous reactions must be exothermic ($q < 0$). The incorrectness of Berthelot's conjecture was shown by Duhem, who established Eq. (5.1-17).

From Eq. (5.1-14), Eq. (5.1-18) can be written

$$\Delta H - T\,\Delta S \leq 0 \quad \text{(simple system, } T \text{ and } P \text{ constant)} \tag{5.1-19}$$

In many chemical reactions, the $T\,\Delta S$ term is numerically less important than the ΔH term, and the incorrect criterion of Berthelot gives the correct prediction about the spontaneity of such a reaction. However, in other cases the $T\,\Delta S$ term dominates, and the criterion of Berthelot fails.

The ΔH term dominates at sufficiently low temperature (small values of T give small values of $T\,\Delta S$), but the $T\,\Delta S$ term becomes important and can dominate at sufficiently high temperature. The vaporization of a liquid is a simple nonchemical example. Both ΔH and ΔS are positive. There is some temperature at which the vaporization is a reversible process, and the two phases can coexist. At this temperature, $\Delta G = 0$ 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, the condensation is spontaneous and the equilibrium state is the liquid phase. At a higher temperature the $T\,\Delta S$ term dominates and $\Delta G < 0$. Vaporization is spontaneous and the equilibrium state is the gas phase. Some people say that there are two tendencies: that of the enthalpy or energy of a system to decrease, and that of the entropy of the system to increase. In fact, the lowering of the enthalpy corresponds to an increase in the entropy of the surroundings. There is only one fundamental tendency, that of the entropy of the universe to increase, although we can separately focus on the system or the surroundings.

General Equilibrium Criteria for a Closed System

We now have a set of criteria for possible processes in a closed simple system, given by Eqs. (5.1-3), (5.1-4), (5.1-11), and (5.1-17): *If the system is isolated, the entropy cannot decrease. If S is fixed and no work is done, U cannot increase. If T and V are fixed, A cannot increase. If T and P are fixed, G cannot increase.*

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 for that system at the given pressure and temperature. Figure 5.1 represents the situation. The variable x schematically represents the extent to which a chemical reaction or some other process has occurred. 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 other values of x must correspond to unstable states or metastable states. We nearly always assume that a state variable such as the Gibbs energy is a differentiable function of its independent

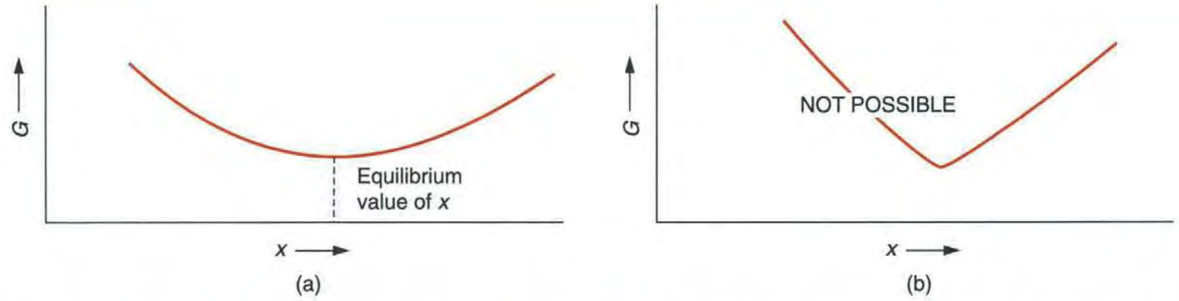

Figure 5.1. The Gibbs Energy as a Function of the Extent of a Process. (a) As it actually is assumed to be (schematic). We assume that the Gibbs energy is a differentiable function of the extent of the process. **(b) As it is assumed not to be (schematic).** This function is not a differentiable function at its minimum.

variables, so that the dependence is as shown in Figure 5.1a, not as shown in Figure 5.1b: there is a smooth minimum at which

$$\left(\frac{\partial G}{\partial x}\right)_{T,P} = 0 \quad \text{(at equilibrium, } P \text{ and } T \text{ constant)} \tag{5.1-20}$$

or

$$dG = 0 \quad \text{(at equilibrium, } P \text{ and } T \text{ constant)} \tag{5.1-21}$$

For a closed simple system at constant temperature and volume, any spontaneous process must lower the value of the Helmholtz energy of the system. Therefore, at equilibrium the Helmholtz energy must be at a minimum, so that

$$\left(\frac{\partial A}{\partial x}\right)_{T,V} = 0 \quad \text{(at equilibrium, } T \text{ and } V \text{ constant)} \tag{5.1-22}$$

or

$$dA = 0 \quad \text{(at equilibrium, } T \text{ and } V \text{ constant)} \tag{5.1-23}$$

If a system is at equilibrium, both G and A are at minimum values at the same time, but with respect to different processes. If a system is at constant temperature and pressure but not yet at equilibrium, a spontaneous process could possibly increase A, but must decrease G. If a system is at constant temperature and volume but is not yet at equilibrium, a spontaneous process could possibly increase the value of G, but must decrease the value of A.

Spontaneity and Equilibrium Criteria for Nonsimple Systems

For a closed system that is not a simple system, we write

$$dw = -P_{\text{ext}}\, dV + dw_{\text{net}} \tag{5.1-24}$$

The term $-P_{\text{ext}}\, dV$ is called "compression work" or "P–V work." The term dw_{net} is called the "net work." It is whatever work can be done in addition to compression work, such as electrical or stress–strain work. Equation (5.1-5) for the case of constant temperature becomes

$$dU - T\,dS + P_{\text{ext}}\,dV - dw_{\text{net}} = dA - dw \le 0 \quad (T \text{ constant}) \tag{5.1-25}$$

which is the same as

$$dA \le dw \quad (T \text{ constant}) \tag{5.1-26}$$

where dw is the total work, including net work (if any). In the case of constant pressure ($P = P_{\text{ext}}$) and constant temperature, Eq. (5.1-25) is

$$dG \le dw_{\text{net}} \quad (T \text{ and } P \text{ constant}) \tag{5.1-27}$$

It is possible to increase the Gibbs energy of a nonsimple system at constant T and P by doing "net" work on the system. An example of this kind of process is electrolysis, in which a chemical reaction is caused to proceed in the nonspontaneous direction by passing an electric current through an electrochemical cell.

The criteria for a nonsimple system to be at equilibrium are also different from those of a simple system: For a nonsimple system to be at equilibrium at constant T and V, the Helmholtz energy is not necessarily at a minimum value. What must be the case is that if a system at equilibrium undergoes an infinitesimal change, instead of $dA = 0$ at constant T and V, as in Eq. (5.1-22),

$$dA = dw_{\text{net}} \quad (\text{at equilibrium, constant } T \text{ and } V) \tag{5.1-28}$$

and in the case of constant T and P, instead of $dG = 0$ as in Eq. (5.1-20),

$$dG = dw_{\text{net}} \quad (\text{equilibrium, constant } T \text{ and } P) \tag{5.1-29}$$

Work and the Helmholtz and Gibbs Energies

The Helmholtz energy and the Gibbs energy have important relationships to the work that can be done on the surroundings in a given process. Since $dw_{\text{surr}} = -dw$, the relation shown in Eq. (5.1-25) is

$$dw_{\text{surr}} \le -dA \quad (T \text{ constant}) \tag{5.1-30}$$

or, for a finite process

$$w_{\text{surr}} \le -\Delta A \quad (T \text{ constant}) \tag{5.1-31}$$

That is, the work that can be done on the surroundings in an isothermal process cannot exceed the negative of the Helmholtz energy change of the system, and only for a reversible process can it be equal to $-\Delta A$. Equation (5.1-31) holds both for a simple system and a nonsimple system. If work is to be done on the surroundings by any kind of a closed system at constant T, a process with negative ΔA must be found.

In the case that $P = P_{\text{ext}} =$ constant and $T = T_{\text{surr}} =$ constant, the relation shown in Eq. (5.1-27) is the same as

$$dw_{\text{surr(net)}} \le -dG \quad (T,\ P \text{ constant}) \tag{5.1-32}$$

For a finite process,

$$w_{\mathrm{surr(net)}} \leq -\Delta G \quad (T,\ P\ \text{constant}) \tag{5.1-33}$$

If the system is simple, Eq. (5.1-33) becomes the same as Eq. (5.1-18).

Just as the total work done on the surroundings at constant temperature is limited by $-\Delta A$, the net work done on the surroundings at constant temperature and pressure is limited by $-\Delta G$. That is, if T and P are constant, only a process corresponding to a negative change in the Gibbs energy can do net work on the surroundings, and the amount of net work done on the surroundings can be no greater than $-\Delta G$. If the process is reversible, the net work done on the surroundings is equal to $-\Delta G$.

***Exercise 5.1**

Write the relation governing the maximum amount of work done on the surroundings in a nonsimple system at constant T and V.

5.2 Fundamental Relations for Closed Simple Systems

For a closed simple system and for reversible processes, the first law is

$$dU = dq - P\,dV \tag{5.2-1}$$

and the second law is

$$dS = \frac{dq_{\mathrm{rev}}}{T} \tag{5.2-2}$$

Combination of these equations gives

$$dU = T\,dS - P\,dV \quad \text{(simple closed system; reversible processes)} \tag{5.2-3}$$

The field of irreversible thermodynamics deals with rates of entropy production and with relations among phenomenological coefficients, which specify the relation between rates of processes and the driving forces. See works in the Additional Reading section.

This equation holds for a closed simple system with any number of phases and any number of substances. The derivation given applies only to reversible changes of state. However, in irreversible thermodynamics, which is a separate branch of thermodynamics, this equation is assumed to be valid for nonequilibrium systems if the deviation from equilibrium is not large. This assumption is an additional hypothesis, and does not follow from our analysis.

Consider a closed system that contains only one phase but can contain any number of substances. Since the state of a simple one-phase closed system at equilibrium is specified by two independent variables (other than the amounts of the substances, which are fixed) we can consider U to be a function of S and V:

$$dU = \left(\frac{\partial U}{\partial S}\right)_{V,n} dS + \left(\frac{\partial U}{\partial V}\right)_{S,n} dV \quad \text{(simple closed system; reversible processes)} \tag{5.2-4}$$

where the single subscript n means that all substances present are at fixed amounts. Comparison of Eqs. (5.2-3) and (5.2-4) gives us two important relations:

$$\left(\frac{\partial U}{\partial S}\right)_{V,n} = T \tag{5.2-5}$$

$$\left(\frac{\partial U}{\partial V}\right)_{S,n} = -P \tag{5.2-6}$$

The Maxwell Relations

From the Euler reciprocity relation shown in Eq. (B-13) of Appendix B,

$$\left(\frac{\partial^2 U}{\partial S\,\partial V}\right)_n = \left(\frac{\partial^2 U}{\partial V\,\partial S}\right)_n \tag{5.2-7}$$

Since the second derivative is the derivative of the first derivative,

$$\left(\frac{\partial^2 U}{\partial V\,\partial S}\right)_n = \left(\frac{\partial T}{\partial V}\right)_{S,n} \tag{5.2-8}$$

$$\left(\frac{\partial^2 U}{\partial S\,\partial V}\right)_n = -\left(\frac{\partial P}{\partial S}\right)_{V,n} \tag{5.2-9}$$

Therefore,

$$\left(\frac{\partial T}{\partial V}\right)_{S,n} = -\left(\frac{\partial P}{\partial S}\right)_{V,n} \quad \text{(a Maxwell relation)} \tag{5.2-10}$$

Equation (5.2-10) is one of a class of equations called **Maxwell relations** after James Clerk Maxwell. Their principal utility is in replacing a hard-to-measure partial derivative 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 5.1

From the relation in Eq. (5.2-10), find an expression for $(\partial P/\partial S)_{V,n}$ for an ideal gas with constant heat capacity.

Solution

Equation (2.4-22) gives

$$T = T_1\left(\frac{V_1}{V}\right)^{nR/C_V}$$

where the subscripts are omitted on the final values of T and V.

$$\left(\frac{\partial P}{\partial S}\right)_{V,n} = -\left(\frac{\partial T}{\partial V}\right)_{S,n} = -T_1(V_1)^{nR/C_V}\left(\frac{nR}{C_V}\right)V^{-1-nR/C_V}$$

*Exercise 5.2

a. Find the value of $(\partial P/\partial S)_{V,n}$ for 1.000 mol of helium gas at 1.000 atm (101,325 Pa) and 298.15 K. Assume that the gas is ideal with $C_V = 3nR/2$.

b. Find the value of $(\partial P/\partial S)_{V,n}$ for 2.000 mol of helium gas at 1.000 atm (101,325 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 gas at 2.000 atm (202,750 Pa) and 298.15 K. Explain the dependence on the pressure.

To obtain the other three principal Maxwell relations we write the differentials dH, dA, and dG:

$$\begin{aligned} dH &= dU + P\,dV + V\,dP = T\,dS - P\,dV + P\,dV + V\,dP \\ &= T\,dS + V\,dP \end{aligned} \tag{5.2-11}$$

Therefore,

$$\left(\frac{\partial H}{\partial S}\right)_{P,n} = T \tag{5.2-12}$$

and

$$\left(\frac{\partial H}{\partial P_{S,n}}\right) = V \tag{5.2-13}$$

By using the Euler reciprocity relation, we obtain a second Maxwell relation from Eqs. (5.2-12) and (5.2-13):

$$\left(\frac{\partial T}{\partial P}\right)_{S,n} = \left(\frac{\partial V}{\partial S}\right)_{P,n} \quad \text{(a Maxwell relation)} \tag{5.2-14}$$

*Exercise 5.3

a. Find an expression for $(\partial V/\partial S)_{P,n}$ for an ideal gas with constant heat capacity.

b. Evaluate $(\partial V/\partial S)_{P,n}$ for 1.000 mol of helium (assumed ideal) at 1.000 atm and 298.15 K. Take the molar heat capacity to be constant and equal to $3R/2$.

c. 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.

The third Maxwell relation comes from the differential of the Helmholtz energy. Equations (5.1-8) and (5.2-3) give

$$dA = -S\,dT - P\,dV \quad \text{(closed system)} \tag{5.2-15}$$

so that

$$\left(\frac{\partial A}{\partial T}\right)_{V,n} = -S \tag{5.2-16}$$

$$\left(\frac{\partial A}{\partial V}\right)_{T,n} = -P \tag{5.2-17}$$

and

$$\left(\frac{\partial S}{\partial V}\right)_{T,n} = \left(\frac{\partial P}{\partial T}\right)_{V,n} \quad \text{(a Maxwell relation)} \tag{5.2-18}$$

Equations (5.1-13) and (5.2-3) give

$$dG = -S\,dT + V\,dP \tag{5.2-19}$$

so that

$$\left(\frac{\partial G}{\partial T}\right)_{P,n} = -S \tag{5.2-20}$$

$$\left(\frac{\partial G}{\partial P}\right)_{T,n} = V \tag{5.2-21}$$

and

$$\left(\frac{\partial S}{\partial P}\right)_{T,n} = -\left(\frac{\partial V}{\partial T}\right)_{P,n} \quad \text{(a Maxwell relation)} \tag{5.2-22}$$

Equations (5.2-10), (5.2-14), (5.2-18), and (5.2-22) are the four principal Maxwell relations.

We can now derive Eq. (4.3-3) in a different way. The entropy change for an isothermal volume change of an ideal gas is equal to

$$\Delta S = \int_{V_1}^{V_2} \left(\frac{\partial S}{\partial V}\right)_{T,n} dV = \int_{V_1}^{V_2} \left(\frac{\partial P}{\partial T}\right)_{V,n} dV = \int_{V_1}^{V_2} \left(\frac{nR}{V}\right) dV = nR \ln\left(\frac{V_2}{V_1}\right) \tag{5.2-23}$$

EXAMPLE 5.2

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 1.000 mol of argon in 25.00 L at 298.15 K. The values of B_2 and dB_2/dT are found in Example 3.7.

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.

Solution

a.

$$\left(\frac{\partial S}{\partial V}\right)_{T,n} = \left(\frac{\partial P}{\partial T}\right)_{V,n} = \left(\frac{\partial[(RT/V_{\mathrm{m}} + RTB_2/V_{\mathrm{m}}^2)]}{\partial T}\right)_{V,n}$$
$$= \frac{R}{V_{\mathrm{m}}} + \frac{R}{V_{\mathrm{m}}^2}\left(B_2 + T\frac{dB_2}{dT}\right)$$

b.

$$\left(\frac{\partial S}{\partial V}\right)_{T,n} = \frac{8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}}}{0.025\ \mathrm{m^3\,mol^{-1}}}$$
$$+ \frac{8.3145\ \mathrm{J^{-1}\,mol^{-1}}}{(0.025\ \mathrm{m^3\,mol^{-1}})^2}[-15.8 \times 10^{-6}\ \mathrm{m^3\,mol^{-1}}$$
$$+ (298.15\ \mathrm{K})(0.25 \times 10^{-6}\ \mathrm{m^3\,mol^{-1}\,K^{-1}})]$$
$$= 332.6\ \mathrm{N\,m^{-2}\,K^{-1}} + 0.78\ \mathrm{N\,m^{-2}\,K^{-1}} = 333.4\ \mathrm{N\,m^{-2}\,K^{-1}}$$
$$= 333.4\ \mathrm{J\,K^{-1}\,m^{-3}}$$

The correction for gas nonideality, $0.78\ \mathrm{J\,K^{-1}\,m^{-3}}$, is numerically almost insignificant. A hard-to-measure quantity, $(\partial S/\partial V)_{T,n}$, has been expressed in terms of more easily measured quantity $(\partial P/\partial T)_{V,n}$.

c. For an isothermal process in a closed system,

$$\Delta S = \int_c dS = \int_{V_1}^{V_2}\left(\frac{\partial S}{\partial V}\right)_{T,n} dV = \int_{V_1}^{V_2}\left[\frac{R}{V_{\mathrm{m}}} + \frac{R}{V_{\mathrm{m}}^2}\left(B_2 + T\frac{dB_2}{dT}\right)\right] dV$$
$$= n\int_{V_1}^{V_2}\frac{R}{V_{\mathrm{m}}}\,dV_{\mathrm{m}} + n\left(B_2 + T\frac{dB_2}{dT}\right)\int_{V_1}^{V_2}\frac{R}{V_{\mathrm{m}}^2}\,dV_{\mathrm{m}}$$
$$= nR\ln\left(\frac{V_{\mathrm{m2}}}{V_{\mathrm{m1}}}\right) - n\left(B_2 + T\frac{dB_2}{dT}\right)\left(\frac{1}{V_{\mathrm{m2}}} - \frac{1}{V_{\mathrm{m1}}}\right)$$

Exercise 5.4

The pressure virial equation of state is shown in Eq. (2.3-4), and in Exercise 2.6 it is shown that $A_2 = B_2$.

a. 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.

b. Evaluate the expression of part (**a**) for 1.000 mol of argon at 1.000 atm and 298.15 K.

c. Derive the expression for the entropy change for an isothermal pressure change of an ideal gas and calculate ΔS for the expansion of 1.000 mol of argon from 10.00 atm to 1.000 atm at 298.15 K. Compare your result with that obtained by assuming argon to be ideal.

5.3 Gibbs Energy Calculations

For a closed simple system at constant temperature, Eq. (5.2-20) is

$$dG = V\,dP \quad \text{(simple system, } T \text{ and } n \text{ constant)} \tag{5.3-1}$$

where constant n (without a subscript) means that the amounts of all substances present are constant. Integration of this formula at constant n and T gives

$$G(T, P_2, n) - G(T, P_1, n) = \int_{P_1}^{P_2} V\,dP \tag{5.3-2}$$

The Gibbs Energy of an Ideal Gas

For an ideal gas, Eq. (5.3-2) becomes

$$\begin{aligned} G(T, P_2, n) &= G(T, P_1, n) + nRT \int_{P_1}^{P_2} \frac{1}{P}\,dP \\ G(T, P_2, n) &= G(T, P_1, n) + nRT \ln\left(\frac{P_2}{P_1}\right) \quad \text{(ideal gas)} \end{aligned} \tag{5.3-3}$$

In terms of the molar Gibbs energy, $G_m = G/n$,

$$G_m(T, P_2) = G_m(T, P_1) + RT \ln\left(\frac{P_2}{P_1}\right) \quad \text{(ideal gas)} \tag{5.3-4}$$

The standard state for the Gibbs energy of an ideal gas is the same as for the entropy: a fixed pressure of P° (exactly 1 bar = 100,000 Pa) and whatever temperature one is interested in. At one time in the past, P° was commonly chosen to be 1 atm. 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. (5.3-4) becomes

$$G_m(T, P) = G_m^\circ(T) + RT \ln\left(\frac{P}{P^\circ}\right) \quad \text{(ideal gas)} \tag{5.3-5}$$

where $G_m^\circ(T)$ is the molar Gibbs energy of the gas in the standard state at temperature T.

EXAMPLE 5.3

Obtain a formula to change from the 1-atm standard state to the 1-bar standard state.

Solution

Call the 1-atm standard-state pressure $P^{\circ\text{atm}}$ with a similar symbol for the 1-atm standard-state molar Gibbs energies. We write

$$\begin{aligned} G_m(T, P) &= G_m^\circ(T) + RT \ln\left(\frac{P}{P^\circ}\right) \\ &= G_m^\circ(T) + RT \ln\left(\frac{P^{\circ\text{atm}}}{P^\circ}\right) + RT \ln\left(\frac{P}{P^{\circ\text{atm}}}\right) \end{aligned}$$

This equation has the correct form if

$$G_{\mathrm{m}}^{\circ\mathrm{atm}} = G_{\mathrm{m}}^{\circ}(T) + RT\ \ln\left(\frac{P^{\circ\mathrm{atm}}}{P^{\circ}}\right) = G_{\mathrm{m}}^{\circ}(T) + RT\ \ln(1.01325)$$

$$= G_{\mathrm{m}}^{\circ}(T) + (0.01316)RT$$

*Exercise 5.5

Find the value of the difference between the two standard-state molar Gibbs energies of an ideal gas at 298.15 K.

The Gibbs Energy of a Real Gas. Fugacity

It is usually an adequate approximation to treat real gases as though they were ideal gases. When corrections for nonideality are necessary, we write a new equation in the same form as Eq. (5.3-5):

$$G_{\mathrm{m}}(T, P) = G_{\mathrm{m}}^{\circ}(T) + RT\ \ln\left(\frac{f}{P^{\circ}}\right) \quad \text{(definition of } f\text{)} \tag{5.3-6}$$

The quantity f is called the **fugacity** of the gas. It has the dimensions of pressure and the fugacity of an ideal gas is equal to its pressure. The fugacity plays the same role for a nonideal gas as does the pressure of an ideal gas in determining the molar Gibbs energy of the gas.

The quantity $G_{\mathrm{m}}^{\circ}(T)$ is the molar Gibbs energy of the gas in its standard state, just as in Eq. (5.3-5) for the ideal gas. However, the standard state of a real gas is not the real gas at pressure P°. It is a "hypothetical" state, defined to be the corresponding ideal gas at pressure P°. That is, the effects of gas nonideality are eliminated from the standard-state quantity.

Since any gas approaches ideal gas behavior as its pressure approaches zero, we can obtain an expression for the difference between the molar Gibbs energy of the real gas at some given pressure P' and the standard-state (ideal-gas) molar Gibbs energy as follows:

$$G_{\mathrm{m,real}}(T, P') - G_{\mathrm{m}}^{\circ}(T) = G_{\mathrm{m,real}}(T, P') - \lim_{P''\to 0}[G_{\mathrm{m,real}}(T, P'') - G_{\mathrm{m,id}}(T, P'')] - G_{\mathrm{m}}^{\circ}(T) \tag{5.3-7}$$

The real gas and the corresponding ideal gas are the same in the limit of low pressure. Therefore, the two terms inside the limit add to zero and can be included without changing the equation. From Eq. (5.3-1), the first two terms on the right-hand side of Eq. (5.3-7) represent the change in Gibbs energy for changing the pressure of the gas from 0 to P' at constant temperature:

$$\text{(first two terms)} = \int_0^{P'} V_{\mathrm{m,real}}\, dP$$

From Eq. (5.3-3), the last two terms in the right-hand-side of Eq. (5.3-7) represent ΔG_{m} for changing the pressure from P° to 0 for an ideal gas:

$$(\text{last two terms}) = \int_{P^{\circ}}^{0} V_{\mathrm{m,id}}\, dP = \int_{P^{\circ}}^{0} \frac{RT}{P}\, dP$$

The formula in Eq. (5.3-7) is therefore 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', the pressure of interest, with the real gas. Since the real gas and the corresponding ideal gas are equivalent at zero pressure, this procedure gives the difference between the real gas at pressure P' and the ideal gas at pressure P°.

The integral to which the last two terms are equal can be broken into two parts, as follows (we have also exchanged the limits and changed the sign):

$$(\text{last two terms}) = -\int_{0}^{P'} \frac{RT}{P}\, dP - \int_{P'}^{P^{\circ}} \frac{RT}{P}\, dP = -\int_{0}^{P'} \frac{RT}{P}\, dP - RT\ \ln(P^{\circ}/P')$$

The left-hand-side of Eq. (5.3-7) 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

$$G_{\mathrm{m,real}}(T, P') - G^{\circ}_{\mathrm{m}}(T) = RT\ \ln\left(\frac{f'}{P^{\circ}}\right) = RT\ \ln\left(\frac{P'}{P^{\circ}}\right) + \int_{0}^{P'} \left(V_{\mathrm{m,real}} - \frac{RT}{P}\right) dP \tag{5.3-8a}$$

or

$$RT\ \ln\left(\frac{f'}{P^{\circ}}\right) + RT\ \ln\left(\frac{P^{\circ}}{P'}\right) = \int_{0}^{P'} \left(V_{\mathrm{m,real}} - \frac{RT}{P}\right) dP \tag{5.3-8b}$$

which is the same as

$$RT\ \ln\left(\frac{f'}{P'}\right) = \int_{0}^{P'} \left(V_{\mathrm{m,real}} - \frac{RT}{P}\right) dP \tag{5.3-9}$$

When the integral is written in this way, the integrand is a function that is generally small.

EXAMPLE 5.4

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 A_2 is a function of temperature. It was shown in Exercise 2.6 that A_2 is equal to B_2, the second virial coefficient.

Solution

$$RT\ \ln(f'/P') = \int_{0}^{P'} \left(\frac{RT}{P} + A_2 - \frac{RT}{P}\right) dP = A_2P'$$

or

$$f' = P' e^{A_2P'/RT}$$

*Exercise 5.6

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 273.15 K, $B_2 = -154\ \mathrm{cm^3\ mol^{-1}}$. Find the value of the fugacity of carbon dioxide gas at 5.000 atm and 273.15 K.

The Gibbs Energy of Solids and Liquids

We now consider the pressure dependence of the Gibbs energy in a condensed phase (solid or liquid). As with the gas, we begin with Eq. (5.3-1). The value of the isothermal compressibility of a typical solid or liquid is near $10^{-9}\ \mathrm{Pa^{-1}}$ so that a change in pressure of 10 atm (roughly 10^6 Pa) produces a change in volume approximately equal to a tenth of a percent. Thus, typical solids and liquids are nearly incompressible under ordinary pressure changes. We assume the volume to be approximately constant in the integrand of Eq. (5.3-2), giving

$$G(T, P_2, n) - G(T, P_1, n) = V(P_2 - P_1) \tag{5.3-10}$$

The standard state of a substance in a condensed phase is chosen to be the actual pure substance at pressure $P°$. For a solid or liquid phase at pressure P,

$$G_{\mathrm{m}}(T, P) = G^{\circ}_{\mathrm{m}}(T) + V_{\mathrm{m}}(P - P^{\circ}) \tag{5.3-11}$$

EXAMPLE 5.5

Calculate $G_{\mathrm{m}} - G^{\circ}_{\mathrm{m}}$ for liquid water at 298.15 K and 10.00 bar.

Solution

$$\begin{aligned} G_{\mathrm{m}} - G^{\circ}_{\mathrm{m}} &= (18.0 \times 10^{-6}\ \mathrm{m^3\ mol^{-1}})(9.00\ \mathrm{bar})\left(\frac{10^5\ \mathrm{N\ m^{-2}}}{1\ \mathrm{bar}}\right) \\ &= 16.2\ \mathrm{J\ mol^{-1}} = 0.0162\ \mathrm{kJ\ mol^{-1}} \end{aligned}$$

This difference can be neglected for most purposes.

*Exercise 5.7

a. Find $G_{\mathrm{m}} - G^{\circ}_{\mathrm{m}}$ for solid copper at 293.15 K and 1.100 bar.

b. Find $G_{\mathrm{m}} - G^{\circ}_{\mathrm{m}}$ for solid copper at 293.15 K and 10.00 bar.

The Temperature Dependence of the Gibbs Energy

From Eq. (5.2-19), if the pressure is constant and the system is closed,

$$dG = -S\,dT \quad \text{(closed system, } P \text{ constant)} \tag{5.3-12}$$

Integration of this equation at constant pressure gives

$$G(T_2, P) - G(T_1, P) = -\int_{T_1}^{T_2} S(T, P)\,dT \quad \text{(closed system)} \tag{5.3-13}$$

The relation in Eq. (5.3-13) is not directly usable, because the actual value of the entropy is not defined. The calculation of "absolute" entropies is a convention, based on an assignment of zero entropy for elements at 0 K. A useful equation that is analogous to that in Eq. (5.3-13) can be written for ΔG of an isothermal process carried out once at temperature T_1 and once at temperature T_2.

We can write Eq. (5.3-13) once for the initial state and once for the final state, using the same values of T_1 and T_2. The difference of these equations gives

$$\Delta G(T_2, P) - \Delta G(T_1, P) = -\int_{T_1}^{T_2} \Delta S(T, P)\, dT \quad \text{(closed system)} \tag{5.3-14}$$

where $\Delta G(T, P)$ is the Gibbs energy change for an isothermal constant-pressure process at temperature T, and where $\Delta S(T, P)$ is the entropy change for the same process. The integration in Eq. (5.3-14) does not mean that we are considering nonisothermal processes. It corresponds to considering isothermal processes at different temperatures.

If ΔS is nearly independent of temperature between T_1 and T_2, Eq. (5.3-14) becomes

$$\Delta G(T_2, P) - \Delta G(T_1, P) \approx -(T_2 - T_1)\,\Delta S \tag{5.3-15}$$

This equation should be a usable approximation if the difference between T_2 and T_1 is not very large. An alternative equation is known as the **Gibbs–Helmholtz equation**:

$$\frac{\Delta G(T_2, P)}{T_2} - \frac{\Delta G(T_1, P)}{T_1} = -\int_{T_1}^{T_2} \frac{\Delta H(T, P)}{T^2}\, dT \tag{5.3-16}$$

If ΔH is nearly constant,

$$\frac{\Delta G(T_2, P)}{T_2} - \frac{\Delta G(T_1, P)}{T_1} = \Delta H\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{5.3-17}$$

Exercise 5.8

***a.** Derive Eq. (5.3-16).

***b.** 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 water at 383.15 K and 1.000 atm, using Eq. (5.3-15). What does the sign of your answer mean?

c. Repeat the calculation of part (**b**) using Eq. (5.3-16). 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**).

Equations (5.3-15) and (5.3-16) apply to any kind of process. Thermodynamics does not distinguish between physical processes such as fusion or vaporization and chemical reactions. We will apply these equations to chemical reactions in Chapter 8.

5.4 The Description of Multicomponent and Open Systems

The equilibrium macroscopic state of a simple closed system is specified by values of only two variables (in addition to the amounts of the substances present, which are fixed). At least one of these two variables must be an extensive variable. In Chapter 1, we asserted as an experimental fact that for a one-phase simple open system the number of variables required to specify the state is $c+2$, where c stands for the number of independent substances, called **components**. The number of components is not necessarily equal to the number of distinct chemical species present. In a one-phase system 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. If chemical reactions can come to equilibrium in the system, all of the substances present are not independent, since some can be produced from others by the chemical reactions. For example, if a gaseous system contains NO_2, it will also contain N_2O_4 at equilibrium, and at equilibrium, the amount of N_2O_4 is not independent of the amount of NO_2. Generally speaking, each chemical reaction that can equilibrate reduces the number of components by one. We will return to the counting of components in a multiphase system in Chapter 6.

The Chemical Potential and Partial Molar Quantities

For a one-phase simple system containing c components, $c+2$ independent variables are required to specify the state. We can make the choice

$$G = G(T, P, n_1, n_2, \ldots, n_c) \tag{5.4-1}$$

where n_i is the amount of substance number i (measured in moles). Equation (5.4-1) corresponds to the differential relation

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n} dP + \sum_{i=1}^{c}\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n'} dn_i \tag{5.4-2}$$

where we use the subscript n to stand for keeping the amounts of all of the components fixed and the subscript n' to stand for keeping the amount of every component fixed except for component number i.

The first two partial derivatives in Eq. (5.4-2) are no different from the partial derivatives in Eqs. (5.2-20) and (5.2-21). In those equations, the amounts of all substances present were held fixed because the system was closed. In Eq. (5.4-2), the amounts of all substances are held fixed because that is how partial derivatives are defined. Therefore, Eq. (5.4-2) is the same as

$$dG = -S\,dT + V\,dP + \sum_{i=1}^{c} \mu_i\,dn_i \tag{5.4-3}$$

where μ_i is defined by

$$\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n'} \tag{5.4-4}$$

The quantity μ_i is called the **chemical potential** of component number i. The relation in Eq. (5.4-3) is called the **Gibbs equation** or the **fundamental relation of chemical thermodynamics**. It is the basis of the thermodynamic description of multicomponent systems.

Other independent variables can be chosen to specify the state of the system. For example,

$$dG = \left(\frac{\partial G}{\partial T}\right)_{V,n} dT + \left(\frac{\partial G}{\partial V}\right)_{T,n} dV + \sum_{i=1}^{c}\left(\frac{\partial G}{\partial n_i}\right)_{T,V,n'} dn_i \qquad (5.4\text{-}5)$$

However, the partial derivatives $(\partial G/\partial T)_{V,n}$ and $(\partial G/\partial V)_{T,n}$ are not equal to any simple thermodynamic variables as are the partial derivatives in Eq. (5.4-2). We therefore say that the **natural independent variables** for the Gibbs energy are $P, T, n_1, n_2, \ldots, n_c$.

Exercise 5.9

Use an analog of Eq. (B-7) of Appendix B to write a relation between $(\partial G/\partial n_i)_{T,V,n'}$ and μ_i.

The internal energy, the enthalpy, and the Helmholtz energy have their own sets of natural independent variables. For example, if

$$H = H(S, P, n_1, n_2, \ldots, n_c) \qquad (5.4\text{-}6)$$

then

$$dH = \left(\frac{\partial H}{\partial S}\right)_{P,n} dS + \left(\frac{\partial H}{\partial P}\right)_{S,n} dP + \sum_{i=1}^{c}\left(\frac{\partial H}{\partial n_i}\right)_{S,P,n'} dn_i \qquad (5.4\text{-}7)$$

Comparison with Eq. (5.2-11) shows that

$$dH = T\,dS + V\,dP + \sum_{i=1}^{c}\left(\frac{\partial H}{\partial n_i}\right)_{S,P,n'} dn_i \qquad (5.4\text{-}8)$$

The definitions of H, A, and G are still as they were, so that from Eq. (5.4-3), Eq. (5.4-8), and the relation $G = H - TS$,

$$dH = dG + T\,dS + S\,dT$$

$$\boxed{dH = T\,dS + V\,dP + \sum_{i=1}^{c}\mu_i\,dn_i} \qquad (5.4\text{-}9)$$

Comparison of Eqs. (5.4-8) and (5.4-9) shows that

$$\mu_i = \left(\frac{\partial H}{\partial n_i}\right)_{S,P,n'} \qquad (5.4\text{-}10)$$

Similarly,

$$\boxed{dU = T\,dS - P\,dV + \sum_{i=1}^{c}\mu_i\,dn_i} \qquad (5.4\text{-}11)$$

and

$$\boxed{dA = -S\,dT - V\,dP + \sum_{i=1}^{c}\mu_i\,dn_i} \qquad (5.4\text{-}12)$$

so that

$$\mu_i = \left(\frac{\partial U}{\partial n_i}\right)_{S,V,n'} \tag{5.4-13}$$

and

$$\mu_i = \left(\frac{\partial A}{\partial n_i}\right)_{T,V,n'} \tag{5.4-14}$$

Exercise 5.10

Carry out the mathematical steps to derive Eqs. (5.4-11) and (5.4-12).

The chemical potential is thus equal to four different partial derivatives. Equation (5.4-4) is the most useful equality.

The chemical potential is an example of a **partial molar quantity** and is called the **partial molar Gibbs energy**. A partial molar quantity is a partial derivative of an extensive quantity with respect to the amount of one substance, keeping pressure, temperature, and the amounts of all other substances fixed. If the letter Y stands for any extensive quantity (U, H, A, G, S, V, etc.), the partial molar quantity for substance number i is denoted the $\bar{Y}_i$ and defined by

$$\bar{Y}_i = \left(\frac{\partial Y}{\partial n_i}\right)_{T,P,n'} \quad \text{(definition)} \tag{5.4-15}$$

All partial molar quantities are intensive quantities. The partial derivatives in Eqs. (5.4-10), (5.4-13), and (5.4-14) are not partial molar quantities, because P and T are not both held fixed in the differentiations.

EXAMPLE 5.6

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 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

$$\mu_i = \bar{H}_i - T\bar{S}_i$$

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:

$$dY = \left(\frac{\partial Y}{\partial T}\right)_{P,n} dT + \left(\frac{\partial Y}{\partial P}\right)_{T,n} dP + \left(\frac{\partial Y}{\partial n}\right)_{T,P} dn \tag{5.4-16}$$

The derivative in the last term is the partial molar Y, since no other substances are present. For a one-component system, the molar Y is given by

$$Y_\mathrm{m} = \frac{Y}{n} \tag{5.4-17}$$

The molar quantity Y_m is an intensive quantity. In a one-component system it cannot depend on n, but depends only on P and T since an intensive quantity cannot depend on an extensive quantity. Therefore

$$\bar{Y} = \left(\frac{\partial Y}{\partial n}\right)_{T,P} = \left(\frac{\partial(nY_\mathrm{m})}{\partial n}\right)_{T,P} = Y_\mathrm{m} \tag{5.4-18}$$

That is, in a one-component system the molar quantity and the partial molar quantity are equal to each other.

Partial Molar Quantities of an Ideal Gas

As with any pure substance, the partial molar volume of a one-component ideal gas is equal to the molar volume:

$$\left(\frac{\partial V}{\partial n}\right)_{T,P} = V_\mathrm{m} = \frac{V}{n} = \frac{RT}{P} \quad \text{(ideal gas)} \tag{5.4-19}$$

The chemical potential of a one-component ideal gas is equal to the molar Gibbs energy. From Eq. (5.3-5),

$$\mu = G_\mathrm{m} = G_\mathrm{m}^\circ(T) + RT\ \ln\left(\frac{P}{P^\circ}\right) \quad \text{(ideal gas)} \tag{5.4-20}$$

The relation of Eq. (5.4-20) is the same as

$$\mu = \mu^\circ + RT\ \ln\left(\frac{P}{P^\circ}\right) \quad \text{(ideal gas)} \tag{5.4-21}$$

where μ° is the chemical potential in the standard state. The standard state for the chemical potential of an ideal gas is the same as the standard state for the other thermodynamic functions: the ideal gas at pressure P° (1 bar).

The partial molar entropy of an ideal gas is obtained by use of Eq. (5.2-21):

$$S_\mathrm{m} = -\left(\frac{\partial G_\mathrm{m}}{\partial T}\right)_P = -\left(\frac{\partial G_\mathrm{m}^\circ}{\partial T}\right)_P + R\ \ln\left(\frac{P}{P^\circ}\right)$$

$$S_\mathrm{m} = S_\mathrm{m}^\circ - R\ \ln\left(\frac{P}{P^\circ}\right) \quad \text{(ideal gas)} \tag{5.4-22}$$

The partial molar enthalpy of a one-component ideal gas is obtained from Eq. (5.1-14):

$$H_{\mathrm{m}} = G_{\mathrm{m}} + TS_{\mathrm{m}} = G_{\mathrm{m}}^{\circ} + RT\ \ln\left(\frac{P}{P^{\circ}}\right) + T\left[S_{\mathrm{m}}^{\circ} - R\ \ln\left(\frac{P}{P^{\circ}}\right)\right]$$

$$H_{\mathrm{m}} = G_{\mathrm{m}}^{\circ} + TS_{\mathrm{m}}^{\circ} = H_{\mathrm{m}}^{\circ} \quad \text{(ideal gas)} \tag{5.4-23}$$

The partial molar enthalpy of an ideal gas does not depend on pressure. We already knew this from Eq. (3.5-18).

Exercise 5.11

a. Find the expression for the partial molar Helmholtz energy of a one-component ideal gas as a function of temperature and pressure.
b. Rewrite the expression of part (**a**) as a function of temperature and molar volume.

According to Dalton's law of partial pressures and also according to our ideal gas model, which we will develop in Chapter 10 and Chapter 21, each gas in a mixture of ideal gases behaves as though it were alone in the container. The chemical potential of a component of a mixture of ideal gases is independent of the presence of the other gases, so that the equations for a one-component ideal gas also apply to any substance in an ideal gas mixture. For example,

$$\mu_i = \mu_i^{\circ} + RT\ \ln\left(\frac{P_i}{P^{\circ}}\right) \quad \text{(ideal gas mixture)} \tag{5.4-24}$$

where μ_i° is the chemical potential of substance i in the standard state, and where P_i is the partial pressure of substance i. All of the other equations for ideal gases apply as well.

***Exercise 5.12**

a. 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.
b. Calculate $\mu_i - \mu_i^{\circ}$ for argon gas at 298.15 K and a partial pressure of 1.000 atm.

In a mixture of gases that cannot be assumed to be ideal, the situation is more complicated. We define f_i, the fugacity of component i, by the relation

$$\mu_i = \mu_i^{\circ} + RT\ \ln\left(\frac{f_i}{P^{\circ}}\right) \quad \text{(definition of } f_i\text{)} \tag{5.4-25}$$

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 f_i in a mixture of nonideal gases. Under most conditions we will consider gases to be ideal.

5.5 Additional Useful Thermodynamic Identities

Our first identity of this section is an expression for $(\partial U/\partial V)_{T,n}$. We convert Eq. (5.2-3) 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:

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = T\left(\frac{\partial S}{\partial V}\right)_{T,n} - P\left(\frac{\partial V}{\partial V}\right)_{T,n}$$

The partial derivative of V with respect to V equals unity. We apply the Maxwell relation of Eq. (5.2-18) to the first term to obtain

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = T\left(\frac{\partial P}{\partial T}\right)_{V,n} - P \tag{5.5-1}$$

The relation shown in Eq. (5.5-1) is called the **thermodynamic equation of state**. It can be used to show that $(\partial U/\partial V)_{T,n} = 0$ for an ideal gas, making it unnecessary to include this property as a separate part of the definition of an ideal gas.

Exercise 5.13

a. Show that $(\partial U/\partial V)_{T,n} = 0$ for an ideal gas, using only the equation of state, $PV = nRT$, and Eq. (5.5-1).

b. Show that P is proportional to T in an ideal gas using Eq. (5.5-1) and the assumption that $(\partial U/\partial V)_{T,n} = 0$.

***c.** For a gas obeying the truncated virial equation of state,

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

show that

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = RT^2\frac{(dB_2/dT)}{V_{\mathrm{m}}^2}$$

Find the value of this derivative for 1.000 mol of argon at 1.000 atm and 298.15 K, using data in Example 3.7.

The partial derivative $(\partial U/\partial V)_{T,n}$ is one measure of the deviation of the 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 (as in the preceding exercise), the energy increases as the volume increases, corresponding to a tendency for the volume to decrease. This indicates that the attractions between the molecules are more important than the repulsions. The internal pressure is considered to be a measure of the net cohesive forces, and can have a large value for liquids, typically equal to several thousand bar.

An equation for $(\partial H/\partial P)_{T,n}$ that is analogous to Eq. (5.5-1) can be derived in a similar way. We convert Eq. (5.2-11) to a derivative equation:

$$\left(\frac{\partial H}{\partial P}\right)_{T,n} = T\left(\frac{\partial S}{\partial P}\right)_{T,n} + V\left(\frac{\partial P}{\partial P}\right)_{T,n}$$

Using the Maxwell relation of Eq. (5.2-22), we obtain

$$\left(\frac{\partial H}{\partial P}\right)_{T,n} = -T\left(\frac{\partial V}{\partial T}\right)_{P,n} + V \tag{5.5-2}$$

Exercise 5.14

a. Show that for an ideal gas $(\partial H/\partial P)_{T,n} = 0$, using only the equation of state, $PV = nRT$, and Eq. (5.5-2).

b. Show that V is proportional to $1/T$ for an ideal gas using Eq. (5.5-2) and the assumption that $(\partial H/\partial P)_{T,n} = 0$. Using the result of Exercise 5.13b, complete the derivation of the ideal gas equation of state by asserting that at constant T, and P, V must be proportional to n.

***c.** 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 $A_2 = B_2$, the second virial coefficient. Evaluate $(\partial H/\partial P)_{T,n}$ for 1.000 mol of argon at 1.000 atm and 298.15 K.

We can substitute the relation of Eq. (5.5-1) into Eq. (3.5-11) to obtain a relation between C_P and C_V:

$$C_P = C_V + \left[T\left(\frac{\partial P}{\partial T}\right)_{V,n} + P - P\right]\left(\frac{\partial V}{\partial T}\right)_{P,n} = C_V + T\left(\frac{\partial P}{\partial T}\right)_{V,n}\left(\frac{\partial V}{\partial T}\right)_{P,n}$$

We apply the cycle rule in the form:

$$\left(\frac{\partial P}{\partial T}\right)_{V,n}\left(\frac{\partial T}{\partial V}\right)_{P,n}\left(\frac{\partial V}{\partial P}\right)_{T,n} = -1$$

to obtain

$$C_P = C_V - T\left(\frac{\partial P}{\partial V}\right)_{T,n}\left[\left(\frac{\partial V}{\partial T}\right)_{P,n}\right]^2 \tag{5.5-3}$$

Using the definition of the isothermal compressibility, Eq. (2.1-8), and the coefficient of thermal expansion, Eq. (2.1-9):

$$C_P = C_V + \frac{TV\alpha^2}{\kappa_T} \tag{5.5-4}$$

Since the coefficient of thermal expansion (which is occasionally negative) is squared and since the compressibility is always positive, C_P is never smaller than C_V.

EXAMPLE 5.7

Calculate the constant-volume molar heat capacity of liquid water at 0.00°C and 1.000 atm. The constant-pressure heat capacity is equal to 75.983 J K^{-1} mol^{-1}. The coefficient of thermal expansion is equal to -68.14×10^{-6} K^{-1} (this is one of the few cases in which this quantity is negative). The compressibility is equal to 50.98×10^{-6} bar^{-1}. The molar volume is equal to 18.012 cm^3 mol^{-1}.

Solution

$$\begin{aligned} C_{P,\mathrm{m}} - C_{V,\mathrm{m}} &= \frac{(273.15\ \mathrm{K})(18.012 \times 10^{-6}\ \mathrm{m^3})(-68.14 \times 10^{-6}\ \mathrm{K^{-1}})^2}{(50.98 \times 10^{-6}\ \mathrm{bar^{-1}})(1\ \mathrm{bar}/10^5\ \mathrm{N\ m^{-2}})} \\ &= 0.04481\ \mathrm{J\ K^{-1}\ mol^{-1}} \end{aligned}$$

$$C_{V,\mathrm{m}} = 75.983\ \mathrm{J\ K^{-1}\ mol^{-1}} - 0.04481\ \mathrm{J\ K^{-1}\ mol^{-1}} = 75.938\ \mathrm{J\ K^{-1}\ mol^{-1}}$$

Exercise 5.15

***a.** Find the value of $C_{V,\mathrm{m}}$ for liquid water at 25.00°C and 1.000 atm. The coefficient of thermal expansion is equal to 49.60×10^{-6} K^{-1}, the molar volume is equal to 18.0687 cm^3 mol^{-1}, and the compressibility is equal to 45.24×10^{-6} bar^{-1}. $C_{P,\mathrm{m}}$ is equal to 75.297 J K^{-1} mol^{-1}.

***b.** At 3.98°C liquid water has maximum density and the coefficient of thermal expansion vanishes. What is the value of $C_{P,\mathrm{m}} - C_{V,\mathrm{m}}$ at this temperature?

c. Show that Eq. (5.5-4) leads to the expression for an ideal gas obtained in Chapter 3:

$$C_{P,\mathrm{m}} - C_{V,\mathrm{m}} = R \quad \text{(ideal gas)}$$

***d.** Calculate the value of the ratio $\gamma = C_{P,\mathrm{m}}/C_{V,\mathrm{m}}$ for liquid water at 25.000°C and 1.000 atm and compare it to the value of the same ratio for argon gas at the same temperature and pressure.

This example and this exercise illustrate that fact that the difference $C_{P,\mathrm{m}} - C_{V,\mathrm{m}}$ is generally small for condensed phases. There are a number of organic liquids that have fairly large coefficients of thermal expansion. Even in these cases the difference between $C_{V,\mathrm{m}}$ and $C_{P,\mathrm{m}}$ is much smaller than with a gas. For almost all solids the difference between $C_{P,\mathrm{m}}$ and $C_{V,\mathrm{m}}$ is very small.

*Exercise 5.16

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. (3.5-8) and (3.4-8),

$$C_P = \left(\frac{\partial H}{\partial T}\right)_{P,n}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,n}$$

We take Eq. (5.2-11) for a closed system and convert it to a derivative relation, specifying that P is fixed:

$$\left(\frac{\partial H}{\partial T}\right)_{P,n}=T\left(\frac{\partial S}{\partial T}\right)_{P,n}+V\left(\frac{\partial P}{\partial T}\right)_{P,n}$$

The derivative of P with respect to anything at constant P is equal to zero, so that

$$C_P=\left(\frac{\partial H}{\partial T}\right)_{P,n}=T\left(\frac{\partial S}{\partial T}\right)_{P,n} \tag{5.5-5}$$

Similarly,

$$C_V=\left(\frac{\partial U}{\partial T}\right)_{V,n}=T\left(\frac{\partial S}{\partial T}\right)_{V,n} \tag{5.5-6}$$

Exercise 5.17

Use Eqs. (5.5-5) and (5.5-6) and the cycle rule to show that

$$\frac{C_P}{C_V}=\frac{\kappa_T}{\kappa_S} \tag{5.5-7}$$

where κ_S is the adiabatic compressibility,

$$\kappa_S=-\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_{S,n} \tag{5.5-8}$$

We now obtain some equations similar to the Maxwell relations that can be used for multicomponent open systems. We begin with the Gibbs equation, Eq. (5.4-3):

$$dG=-S\,dT+V\,dP+\sum_{i=1}^{c}\mu_i\,dn_i \tag{5.5-9}$$

Using the Euler reciprocity relation, Eq. (B-13) of Appendix B,

$$-\left(\frac{\partial S}{\partial n_i}\right)_{T,P,n'}=\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n}$$

which is the same as

$$-\bar{S}_i=\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n} \tag{5.5-10}$$

A second use of the Euler reciprocity relation gives

$$\left(\frac{\partial V}{\partial n_i}\right)_{T,P,n'}=\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n}$$

which is the same as

$$\bar{V}_i=\left(\frac{\partial \mu_i}{\partial P}\right)_{T,n} \tag{5.5-11}$$

5.6 Euler's Theorem and the Gibbs–Duhem Relation

Euler's theorem is a mathematical theorem that applies to homogeneous functions. A proof of this theorem is found in Appendix E. 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

$$f(n_1, n_2, \ldots, n_c) = n_1^k g(n_2/n_1, n_3/n_1, \ldots, n_c/n_1) \qquad (5.6\text{-}1)$$

where g is some function of $c - 1$ variables, and where k is an integer (it can equal zero). Equation (5.6-1) is the same as

$$f(an_1, an_2, an_3, \ldots, an_c) = a^k f(n_1, n_2, n_3, \ldots, n_c) \qquad (5.6\text{-}2)$$

where a is a positive constant. For example, if each 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, Euler's theorem states that

$$kf = \sum_{i=1}^{c} n_i \left(\frac{\partial f}{\partial n_i}\right)_{n'} \qquad (5.6\text{-}3)$$

where we use the subscript n' to stand for holding all of the n's constant except for n_i. 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 implies:

$$Y = \sum_{i=1}^{c} n_i \bar{Y}_i \qquad (5.6\text{-}4)$$

where $\bar{Y}_i$ is the partial molar quantity for substance i. Of course, both sides of the equation must refer to the same state of the system. Two examples of Eq. (5.6-4) are

$$G = \sum_{i=1}^{c} n_i \mu_i \qquad (5.6\text{-}5)$$

and

$$V = \sum_{i=1}^{c} n_i \bar{V}_i \qquad (5.6\text{-}6)$$

Equation (5.6-4) contains 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.

$$Y_{\mathrm{m}} = \frac{1}{n}\sum_{i=1}^{c} n_i \bar{Y}_i = \sum_{i=1}^{c} x_i \bar{Y}_i \tag{5.6-7}$$

EXAMPLE 5.8

In a solution of acetone (component 1) and chloroform (component 2), $x_1 = 0.531$ and $\bar{V}_1 = 74.2\ \mathrm{cm^3\ mol^{-1}}$. If V_{m}, the mean molar volume, is equal to $77.0\ \mathrm{cm^3\ mol^{-1}}$ at this composition, find $\bar{V}_2$ at this composition.

Solution

From Euler's theorem,

$$\bar{V}_2 = \frac{V_{\mathrm{m}} - x_1\bar{V}_1}{x_2} = \frac{77.0\ \mathrm{cm^3\ mol^{-1}} - (0.531)(74.2\ \mathrm{cm^3\ mol^{-1}})}{0.469}$$
$$= 80.2\ \mathrm{cm^3\ mol^{-1}}$$

The Gibbs–Duhem Relation

From Euler's theorem, Eq. (5.6-4), we write an expression for dY, the differential of some extensive quantity:

$$dY = \sum_{i=1}^{c} n_i\, d\bar{Y}_i + \sum_{i=1}^{c} \bar{Y}_i\, dn_i \tag{5.6-8}$$

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 an amount of one of the substances. Considering Y to be a function of T, P, and the n's, we write another expression for dY:

$$dY = \left(\frac{\partial Y}{\partial T}\right)_{P,n} dT + \left(\frac{\partial Y}{\partial P}\right)_{T,n} dP + \sum_{i=1}^{c} \bar{Y}_i\, dn_i \tag{5.6-9}$$

Equation (5.6-8) and Eq. (5.6-9) both represent an infinitesimal change in Y produced by the same infinitesimal change in state, so we can equate the right-hand sides of the two equations:

$$\sum_{i=1}^{c} n_i\, d\bar{Y}_i = \left(\frac{\partial Y}{\partial T}\right)_{P,n} dT + \left(\frac{\partial Y}{\partial P}\right)_{T,n} dP \tag{5.6-10}$$

where we have canceled equal sums on the two sides of the equation.

Equation (5.6-10) 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:

$$\sum_{i=1}^{c} n_i\, d\mu_i = 0 \quad (\text{constant } T \text{ and } P) \tag{5.6-11}$$

This result is as remarkable as Euler's theorem. In a two-component mixture, it 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:

$$d\mu_1 = -\frac{x_2}{x_1}\,d\mu_2 \quad \text{(constant } T \text{ and } P\text{)} \tag{5.6-12}$$

EXAMPLE 5.9

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. (5.4-24), is compatible with Eq. (5.6-12).

Solution

$$d\mu_1 = \left(\frac{\partial\mu_1}{\partial P_1}\right)_T dP_1 = \frac{RT}{P_1}\,dP_1$$

$$d\mu_2 = \left(\frac{\partial\mu_2}{\partial P_2}\right)_T dP_2 = \frac{RT}{P_2}\,dP_2$$

Since $P_1 + P_2 = P = \text{constant}$, $dP_2 = -dP_1$.

$$d\mu_2 = -\frac{RT}{P_2}\,dP_1$$

$$-\frac{x_2}{x_1}\,d\mu_2 = \frac{x_2RT}{x_1P_2}\,dP_1$$

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,

$$x_1\left(\frac{\partial\mu_1}{\partial x_1}\right)_{T,P} + x_2\left(\frac{\partial\mu_2}{\partial x_1}\right)_{T,P} = 0 \tag{5.6-13}$$

Both derivatives must be with respect to the same mole fraction. For a system with more than two components, the equation is

$$\sum_{i=1}^{c} x_i\left(\frac{\partial\mu_i}{\partial x_k}\right)_{T,P} = 0 \tag{5.6-14}$$

where the index k must be the same in every term. Equation (5.6-14) is valid for any kind of changes in the mole fractions if T and P are fixed.

The Experimental Determination of Partial Molar Quantities

The partial molar volume is probably the most easily measured partial molar quantity and we discuss it as an example. The most direct way to determine the partial molar volume is to 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 other functional form, 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 means.[1]

Exercise 5.18

At constant temperature and pressure, the volume of a solution made from component 1 and component 2 is represented by the polynomial

$$V = b_1 n_1 + b_2 n_2 + b_{12} n_1 n_2 + b_{11} n_1^2 + b_{22} n_2^2$$

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 the partial molar volume of component 2 as a function of n_1 and n_2.

The Method of Intercepts

This is a graphical method for the determination of partial molar quantities in a two-component system. In this method, the mean molar quantity is graphed as a function of one of the mole fractions for a fixed value of T and a fixed value of P. Figure 5.2 shows V_m, the mean molar volume of a solution of ethanol (component 1) and water (component 2), as a function of x_1, the mole fraction of ethanol. From Euler's theorem, Eq. (5.6-4),

$$Y_m = x_1 \bar{Y}_1 + x_2 \bar{Y}_2 \tag{5.6-15}$$

where Y stands for any extensive variable. Since $x_2 = 1 - x_1$ in a two-component system, this equation can be written as a function of x_1:

$$Y_m = (\bar{Y}_1 - \bar{Y}_2)x_1 + \bar{Y}_2 \tag{5.6-16}$$

Let x_1' be a particular value of x_1 for which we desire the values of the partial molar quantities $\bar{Y}_1$ and $\bar{Y}_2$. At $x_1 = x_1'$, we draw a tangent line to the curve, 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 E.

In order to gain better accuracy, it is better to graph a quantity of smaller magnitude than the mean molar quantity, and there is a modified method of intercepts that exploits this fact. We define the change in the mean molar quantity on mixing:

$$\Delta Y_{m,mix} = Y_m - (x_1 Y_{m,1}^* + x_2 Y_{m,2}^*) \quad \text{(definition)} \tag{5.6-17}$$

where $Y_{m,1}^*$ is the molar quantity of pure substance 1 and similarly for substance 2. Since $x_2 = 1 - x_1$, we can write

$$\Delta Y_{m,mix} = Y_m - [Y_{m,2}^* + x_1(Y_{m,1}^* - Y_{m,2}^*)] \tag{5.6-18}$$

To carry out the method, one plots experimental values of $\Delta Y_{m,mix}$ as a function of x_1, as in Figure 5.3, which shows a graph made from data for ethanol and water. The

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[1] 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*, 2d ed., Academic Press, San Diego, CA, 1999, pp. 327ff.

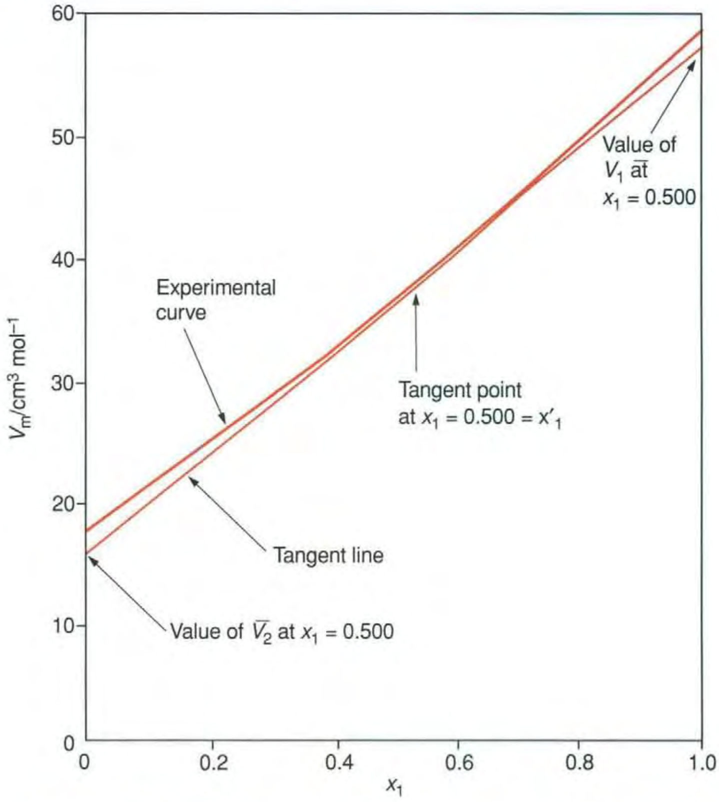

Figure 5.2. The Mean Molar Volume of an Ethanol–Water Solution as a Function of Mole Fraction of Ethanol. This diagram is used to carry out the method of intercepts graphically.

intercepts of the line tangent to the curve at $x_1 = x'_1$ give the partial molar quantities evaluated at $x_1 = x'_1$:

$$\text{left intercept} = \bar{Y}_1(x'_1) - Y^*_{\text{m},1} \tag{5.6-19}$$

$$\text{right intercept} = \bar{Y}_2(x'_1) - Y^*_{\text{m},2} \tag{5.6-20}$$

EXAMPLE 5.10

From the intercepts in Figure 5.3, 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 $V^*_{\text{m},1} = 58.4\,\text{cm}^3\,\text{mol}^{-1}$, $V^*_{\text{m},2} = 18.02\,\text{cm}^3\,\text{mol}^{-1}$.

Solution

The tangent line is drawn in the figure.

$$\text{right intercept} = \bar{V}_1 - V^*_{\text{m},1} = -0.83\ \text{cm}^3\ \text{mol}^{-1}$$

$$\text{left intercept} = \bar{V}_2 - V^*_{\text{m},2} = -1.31\ \text{cm}^3\ \text{mol}^{-1}$$

$$\bar{V}_1 = 58.4\ \text{cm}^3\ \text{mol}^{-1} - 0.83\ \text{cm}^3\ \text{mol}^{-1} = 57.6\ \text{cm}^3\ \text{mol}^{-1}$$

$$\bar{V}_2 = 18.02\ \text{cm}^3\ \text{mol}^{-1} - 1.31\ \text{cm}^3\ \text{mol}^{-1} = 16.7\ \text{cm}^3\ \text{mol}^{-1}$$

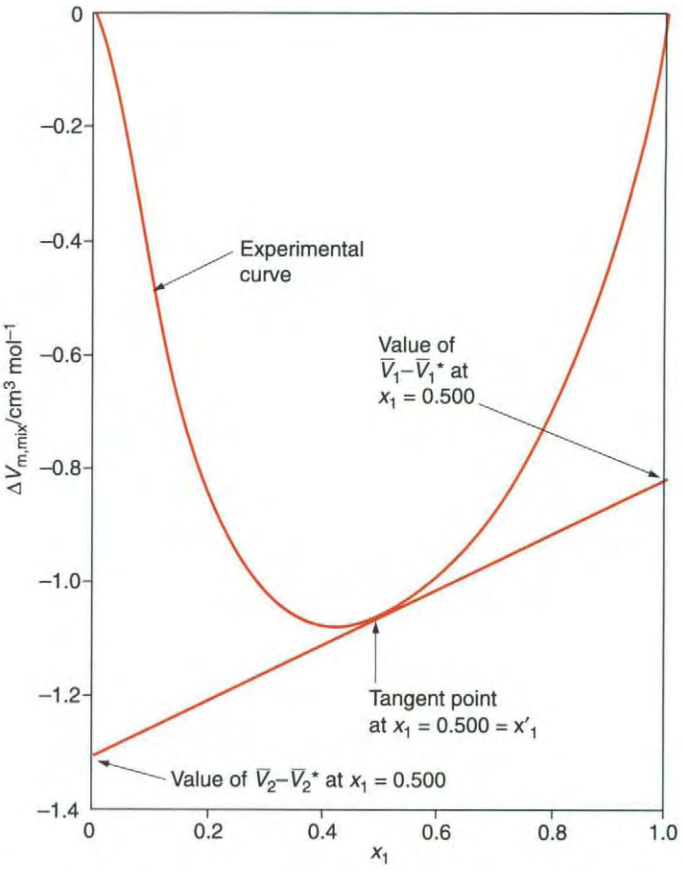

Figure 5.3. The Change in the Mean Molar Volume on Mixing for an Ethanol–Water Solution as a Function of Mole Fraction of Ethanol. This diagram is used to carry out a modified version of the method of intercepts that gives greater accuracy.

Summary of the Chapter

In this chapter we have obtained two types thermodynamic tools for the application of thermodynamics to real systems: criteria for spontaneous processes and useful formulas. These are obtained from the fundamental laws of thermodynamics. The second law of thermodynamics provides the general criterion for possible 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 simple closed systems. The first relations were for the differentials of the different energy-related state variables for closed simple systems. For example,

$$dG = -S\,dT + V\,dP$$

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 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 is based on the Gibbs equation,

$$dG = -T\ dS + V\ dP + \sum_{i=1}^{c} \mu_i\ dn_i$$

where μ_i is the chemical potential of component i. A number of useful thermodynamic relations were obtained from this relationship. The "thermodynamic equation of state" is

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

For an extensive quantity, represented by Y, Euler's theorem is

$$Y = \sum_{i=1}^{c} n_i \bar{Y}_i$$

The generalized Gibbs–Duhem relation is

$$\sum_{i=1}^{c} n_i\ d\bar{Y}_i = \left(\frac{\partial Y}{\partial T}\right)_{P,n} dT + \left(\frac{\partial Y}{\partial P}\right)_{T,n} dP$$

PROBLEMS

Problems for Section 5.1

5.19. If a simple system is somehow maintained at constant S and P, show that its enthalpy cannot increase.

5.20. Consider the reaction

$$2\mathrm{H_2(g)} + \mathrm{O_2(g)} \rightarrow 2\mathrm{H_2O(l)}$$

a. Calculate the values of ΔH°, ΔU°, ΔG°, and ΔA° for this reaction. 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 3).

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 $P\ dV$ 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**).

Problems for Section 5.2

***5.21.** The **fundamental equation** or **fundamental relation** of thermodynamics for a particular system is a formula giving

$$S = S(U, V, n) \qquad \text{or} \qquad U = U(S, V, n)$$

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,[2]

$$S = \frac{nS_0}{n_0} + nR \ln\left[\left(\frac{U}{U_0}\right)^{3/2}\left(\frac{V}{V_0}\right)\left(\frac{n}{n_0}\right)^{-5/2}\right]$$

---

[2] H. B. Callen, *Thermodynamics*, Wiley, New York, 1960, pp. 26ff, 53ff.

where S_0, n_0, and V_0 are constants.

a. Solve this equation for $U = U(S, V, n)$.

b. Use Eq. (5.2-5) to obtain an expression for T.

c. Use Eq. (5.2-6) to obtain an expression for P.

5.22. **a.** Find an expression for $(\partial S/\partial P)_{T,n}$ for a gas obeying the truncated pressure virial equation of state

$$PV_{\mathrm{m}} = RT + A_2P + A_3P^2$$

b. Write an expression for $G(T, P_2, n) - G(T, P_1, n)$ for a gas obeying this equation of state.

c. Find the value ΔG for pressurizing 2.500 mol of argon gas from 1.000 atm to 25.00 atm at 298.15 K. Assume that $A_3 \approx 0$.

5.23. **a.** If a gas is represented by the truncated virial equation of state

$$\frac{PV_{\mathrm{m}}}{RT} = 1 + \frac{B_2}{V_{\mathrm{m}}} + \frac{B_3}{V_{\mathrm{m}}^2}$$

where the virial coefficients depend on T, 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 1.000 mol of argon from 5.000 L to 10.00 L at a constant temperature of 298.15 K. Assume that $B_3 \approx 0$.

5.24. **a.** Find an expression for $(\partial S/\partial V)_{T,n}$ for a gas obeying the van der Waals equation of state.

b. Find the value of 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 van der Waals equation of state. Compare with the value for the same change in state assuming argon to be ideal.

5.25. **a.** Find an expression for $(\partial S/\partial V)_{T,n}$ for a gas obeying the Redlich–Kwong equation of state.

***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.

Problems for Section 5.3

5.26. **a.** Find the value of ΔG for 1.000 mol of 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 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.

***5.27.** **a.** Find the value of ΔG if 1.000 mol of liquid water is pressurized at 0.00°C from 1.000 atm to 20.000 atm. State any assumptions.

b. Find the value of ΔG if 1.000 mol of solid water is pressurized at 0.00°C from 1.000 atm to 20.000 atm. State any assumptions.

c. Find the value of ΔG if 1.000 mol of solid water 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 20.000 atm. What does the sign of your answer indicate?

5.28. **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. (5.3-15). What does the sign of your answer mean?

b. Repeat the calculation of part (**a**) using Eq. (5.3-17). Comment on the comparison between your values for parts (**a**) and (**b**).

***5.29.** **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 5.26. Explain the relationship of these values to the values of ΔG for the same processes.

5.30. **a.** Find the value of $G_{\mathrm{m}} - G_{\mathrm{m}}^{\circ}$ for argon gas at 298.15 K and 1.000 atm, assuming the truncated pressure virial equation of state

$$PV_{\mathrm{m}} = RT + A_2P$$

with $A_2 = -15.8\ \mathrm{cm}^3\ \mathrm{mol}^{-1}$.

b. Repeat the calculation for 298.15 K and 10.00 atm.

5.31. **a.** Write an expression for ΔA for the isothermal expansion from volume V_1 to volume V_2 for n moles of a gas obeying the truncated virial equation of state

$$\frac{PV_{\mathrm{m}}}{RT} = 1 + \frac{B_2}{V_{\mathrm{m}}} + \frac{B_3}{V_{\mathrm{m}}^2}$$

***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.

5.32. **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 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 5.31.

Problems for Section 5.4

5.33. 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.

Percentage 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

5.34. 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 prime on 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:

$$y_i = \frac{w_i}{w_{\text{total}}}$$

for every substance. Using the data of Problem 5.33, find the partial specific volume of ethanol in the mixture with mass fraction 0.500.

Problems for Section 5.5

***5.35.** **a.** Find an expression for $(\partial U/\partial V)_{T,n}$ (the internal pressure) for a gas obeying the van der Waals equation of state. Explain why this is an intensive quantity.

b. Find the value of $(\partial U/\partial V)_{T,n}$ for argon at a molar volume of 0.0244 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 molar volume and a temperature of 298.15 K.

c. Find the value of $(\partial U/\partial V)_{T,n}$ for argon at a molar volume of 5.0×10^{-5} m^3 (a liquidlike value). Compare the internal pressure with the pressure of the gas at this molar volume and a temperature of 298.15 K.

d. Find the value of $(\partial U/\partial V)_{T,n}$ for argon at a molar volume of 0.0244 m^3 mol^{-1}, using the truncated virial equation of state as in Exercise 5.13. Compare your answer with that of part (**b**).

5.36. **a.** Show that

$$C_P = VT\alpha\left(\frac{\partial P}{\partial T}\right)_{S,n}$$

where α is the coefficient of thermal expansion.

b. Show that

$$C_P - C_V = (P + P_{\text{int}})\alpha V$$

where P_{int} is the internal pressure, equal to $(\partial u/\partial V)_{T,n}$.

5.37. **a.** It is shown in the theory of hydrodynamics[3] 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 defined in Eq. (5.5-8), V_m is the molar volume, and M is the molar mass. 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 0.029 kg mol^{-1} and $C_{V,m} = 5R/2$.

***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. (17.3-6).

5.38. Derive the following equation:

$$\left(\frac{\partial U}{\partial V}\right)_{T,n} = -P + \left[\left(\frac{\partial H}{\partial P}\right)_{T,n} - V\right]\left(\frac{\partial P}{\partial V}\right)_{T,n}$$

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[3] H. Lamb, *Hydrodynamics*, 6th ed., Cambridge University Press, New York, 1932, pp. 477 ff.

5.39. **a.** Find an expression for μ_{JT}, the Joule–Thomson coefficient, for a gas that obeys the truncated virial equation of state

$$PV_m = RT + A_2P + A_3P^2$$

where the virial coefficients depend on temperature.

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 3.7 and the fact that $A_2 = B_2$ (from Exercise 2.6).

5.40. **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 $A_3 = B_3 - B_2^2$ (Exercise 2.6). Obtain the value of B_2 and B_3 as in Problem 2.44 from the van der Waals parameters.

b. Repeat the calculation for 15.00 bar and the same temperature.

***5.41.** **a.** Find the change in enthalpy if 1.000 mol of liquid water is pressurized at 0.00°C from 1.000 atm to 20.000 atm. State any assumptions.

b. Find the change in enthalpy if 1.000 mol of solid water is pressurized at 0.00°C from 1.000 atm to 20.000 atm. State any assumptions.

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 20.00 atm.

5.42. 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.

Problems for Section 5.6

***5.43.** 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. $f(x, y, z) = ax^2 + b\ \cos(x^2y^{-2}) + cz^2$
d. $f(x, y, z) = az^3 + bx^3\ \cos(x^4y^{-4}) + c\ \exp(yz^{-1})$
e. $(x, y, z) = ax^4 + bx^2yz\ \sin(x/y) + cy^3z\ \ln(z^2y^{-2})$

5.44. **a.** From the data of Problem 5.33, make a graph of $\Delta V_{m,mix}$ 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 5.33.

General Problems

***5.45.** 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.

5.46. **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 5.37:

$$v_s^2 = \frac{V_m C_P}{M\kappa_T C_V} = \frac{V_m \gamma}{M\kappa_T}$$

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**).

*5.47. 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.

5.48. A nonideal gas is described equally well by two truncated virial equations of state:

$$\frac{PV_{\mathrm{m}}}{RT} = 1 + \frac{B_2}{RT} \qquad \text{and} \qquad PV_{\mathrm{m}} = RT + A_2 P$$

where A_2 and B_2, the second virial coefficients, are functions of T and can be shown to equal each other (see Exercise 2.6).

a. Find expressions for the following:

1. $G_{\mathrm{m}}(T, P') - G^{\circ}_{\mathrm{m}}(T)$
2. $S_{\mathrm{m}}(T, P') - S^{\circ}_{\mathrm{m}}(T)$
3. $H_{\mathrm{m}}(T, P') - H^{\circ}_{\mathrm{m}}(T)$
4. $A_{\mathrm{m}}(T, P') - A^{\circ}_{\mathrm{m}}(T)$
5. $U_{\mathrm{m}}(T, P') - U^{\circ}_{\mathrm{m}}(T)$

where P' is some pressure not necessarily equal to P°.

b. Evaluate each of the quantities in part (**a**) for carbon dioxide at 0°C, using data in Table A.2.

5.49. 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?

6

Phase Equilibrium

OBJECTIVES

After studying this chapter, a student should:

1. understand how the laws of thermodynamics determine the equilibrium of a multiphase system;
2. understand the role of the chemical potential in phase equilibria, and be able to solve problems involving phase equilibria;
3. be able to apply the phase rule to the interpretation of phase equilibria;
4. be able to solve problems involving the Clapeyron and Clausius–Clapeyron equations;
5. understand the relationship of the Gibbs energy to phase equilibria;
6. understand the modifications to ordinary thermodynamics required by the inclusion of surface energy;
7. be able to solve problems involving surface tension.

PRINCIPAL FACTS AND IDEAS

1. The laws of thermodynamics determine equilibrium behavior in multiphase systems.
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 the 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.

6.1

A **phase** is a region of a 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**.

Numerous elements such as carbon exhibit **allotropy** in the solid phase. That is, there is more than one kind of solid phase of a single substance. Many compounds exhibit the same phenomenon, which is then called **polymorphism**. Most pure substances exhibit only one liquid phase, but helium is a special case, exhibiting allotropy in liquid phases. Pure ^{4}He (the most abundant isotope) exists in two different liquid forms, while pure ^{3}He exists in three different liquid forms. A pure substance can exhibit only one gas phase.

In a mixture at equilibrium there can often be several solid phases or several liquid phases present. For example, if one equilibrates mercury, a mineral oil, a methylsilicone oil, water, benzyl alcohol, and a perfluoro compound such as perfluoro-(N-ethylpiperidine) at room temperature, one can obtain six coexisting liquid phases.[1] Each phase in this mixture contains a large concentration of one substance and small concentrations of the other substances. Under ordinary conditions, only a single gas phase can exist in a single system. 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

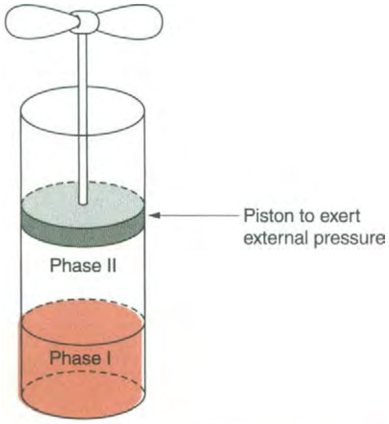

Figure 6.1. A Two-Phase Simple System. This system is closed to the surroundings, but each phase is open to the other.

A two-phase simple closed system at a given temperature and a given pressure is depicted in Figure 6.1. If the contribution of the surface area between the phases is negligible, the Gibbs energy of the system is the sum of the Gibbs energies of the two phases:

$$G = G^{(\mathrm{I})} + G^{(\mathrm{II})} \tag{6.1-1}$$

where we denote the two phases by the superscripts (I) and (II). The system contains several substances. The substances whose amounts can be independently varied are called components. We number the components from 1 to c. We assume that the system is closed, so that any substance moving out of one phase must move into the other phase:

$$dn_i^{(\mathrm{I})} = -dn_i^{(\mathrm{II})} \qquad (i = 1, 2, \ldots, c) \tag{6.1-2}$$

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[1] J. Kochansky, *J. Chem. Educ.*, **68**, 653 (1991).

For an infinitesimal transfer of matter, the change in the Gibbs energy is given by

$$\begin{aligned} dG &= dG^{(\mathrm{I})} + dG^{(\mathrm{II})} \\ &= -S^{(\mathrm{I})}\,dT + V^{(\mathrm{I})}\,dP + \sum_{i=1}^{c} \mu_i^{(\mathrm{I})}\,dn_i^{(\mathrm{I})} \\ &\quad + \left(-S^{(\mathrm{II})}\,dT + V^{(\mathrm{II})}\,dP + \sum_{i=1}^{c} \mu_i^{(\mathrm{II})}\,dn_i^{(\mathrm{II})}\right) \end{aligned} \tag{6.1-3}$$

Let us maintain the system at equilibrium at constant T and P, so that dP and dT vanish, and carry out an infinitesimal transfer of matter between the phases. From our criteria for equilibrium in Chapter 5, dG must vanish for an equilibrium change at constant T and P. From Eqs. (6.1-2) and (6.1-3)

$$dG = \sum_{i=1}^{c} \mu_i^{(\mathrm{I})}\,dn_i^{(\mathrm{I})} + \sum_{i=1}^{c} \mu_i^{(\mathrm{II})} dn_i^{\mathrm{II}} = \sum_{i=1}^{c} [\mu_i^{(\mathrm{I})} - \mu_i^{(\mathrm{II})}]\,dn_i^{(\mathrm{I})} = 0 \tag{6.1-4}$$

It is possible, without violating the second law, to find a semipermeable membrane that will selectively allow any one of the components to pass, but not the others. Therefore, each term of the sum in the right-hand side of Eq. (6.1-4) must vanish since all of the *dn*'s but one can be made to vanish. Since dn_i is not necessarily equal to zero, the other factors must vanish, and

$$\mu_i^{(\mathrm{I})} = \mu_i^{(\mathrm{II})} \quad \text{(system at equilibrium)} \tag{6.1-5a}$$

This analysis does not depend on whether a suitable semipermeable membrane can be found in the real world. The important thing is that nothing in thermodynamics forbids the existence of such membranes. One can reach the same conclusion without membranes by arguing mathematically that each term must separately vanish because the *dn*'s are linearly independent. Equation (6.1-5a) is not restricted to a system with just two phases. If more than two phases are present at equilibrium, we can consider any pair of phases, and conclude that the chemical potential of any substance has the same value in every phase into which it can pass. We write a second version of the equation

$$\mu_i^{(\alpha)} = \mu_i^{(\beta)} \quad \text{(system at equilibrium)} \tag{6.1-5b}$$

where the superscripts (α) and (β) designate any two phases of a multiphase system.

The properties of any equilibrium system are no different than they would be if the system arrived at its equilibrium state under some other conditions than the actual conditions. Therefore, Eq. (6.1-5) is also valid for an open system and for a system that approached equilibrium without being at constant temperature and pressure. It is the **fundamental fact of phase equilibrium**: *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 maintained at constant temperature and pressure, but in a metastable state that is not yet at equilibrium. The Gibbs energy of the system is still given by Eq. (6.1-1). The criterion for possible processes is given by the inequality in Eq. (5.1-17):

$$dG < 0 \quad (T \text{ and } P \text{ constant}) \tag{6.1-6}$$

Since dT and dP vanish and since the system as a whole is closed,

$$dG = \sum_{i=1}^{c} \mu_i^{(\mathrm{I})}\, dn_i^{(\mathrm{I})} + \sum_{i=1}^{c} \mu_i^{(\mathrm{II})}\, dn_i^{(\mathrm{II})} = \sum_{i=1}^{c} [\mu_i^{(\mathrm{I})} - \mu_i^{(\mathrm{II})}]\, dn_i^{(\mathrm{I})} < 0 \qquad (6.1\text{-}7)$$

Each term separately must be negative since the introduction of semipermeable membranes would not violate the second law of thermodynamics. The two factors in each term of the sum in Eq. (6.1-7) must be of opposite signs:

$$\mu_i^{(\mathrm{I})} > \mu_i^{(\mathrm{II})} \quad \text{implies that } dn_i^{(\mathrm{I})} < 0 \qquad (6.1\text{-}8)$$

$$\mu_i^{(\mathrm{I})} < \mu_i^{(\mathrm{II})} \quad \text{implies that } dn_i^{(\mathrm{I})} > 0 \qquad (6.1\text{-}9)$$

Therefore, *any substances moves spontaneously from a phase of higher values of its chemical potential to a phase of lower value of its chemical potential.* The name "chemical potential" was chosen by analogy with the tendency of a mechanical system to move toward states of lower potential energy.

The spontaneous transfer of a substance from a phase of higher chemical potential to a phase of lower chemical potential is not restricted to systems at constant pressure.

Exercise 6.1

Argue that a substance will move spontaneously from any phase of higher value of its chemical potential to any other phase of lower value of its chemical potential in a system with each phase at constant V and with both phases at the same constant T.

Transport of Matter in a Nonuniform Phase

Assume that a one-phase system is at the same temperature and pressure throughout but is of nonuniform composion. Imagine dividing the system into small regions (subsystems), each one of which is small enough that the composition is almost uniform within one subsystem. We treat each subsystem in the same way as one phase was treated in obtaining Eqs. (6.1-8) and (6.1-9) so that any substance will move from a subsystem of higher values of its chemical potential to another subsystem with a lower value. The analogue of the fundamental fact of phase equilibrium for nonuniform systems is obtained: *In a system with uniform temperature and pressure, any substance tends to move from a region of larger value of its chemical potential to a region of smaller value of its chemical potential.* A nonuniformity of the chemical potential is the driving force for diffusion, which will be discussed in Chapter 11.

6.2 The Gibbs Phase Rule

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 (both extensive and intensive) are dependent variables. The **intensive state** is the state of the system so far as only intensive variables are concerned. Intensive variables cannot depend on extensive variables. The number of variables required to specify the intensive state is smaller by one than the number to specify the full equilibrium state: the equilibrium intensive state of a one-phase simple system is specified by the values of $c + 1$ variables, all of which are intensive. A convenient set of independent variables to specify the intensive state of a one-phase simple system consists of T, P, and $c - 1$ mole fractions. The mole fractions automatically obey the relation

$$\sum_{i=1}^{c} x_i = 1 \tag{6.2-1}$$

so that if all of the mole fractions but one are known, the last one can be calculated from this relation. Therefore, no more than $c - 1$ of them can be used as independent variables.

Now consider a multiphase system with a number of phases equal to p and a number of components equal to c. In counting phases, we count only regions that are different in their intensive properties from other regions. For example, crushed ice and liquid water are a two-phase system, just like a system of liquid water and a single ice cube.

Counting the Number of Components in a System

A component of a system is a substance whose amount can be varied independently of the other substances. The number of components is equal to the number of substances present minus the number of relations that constrain the amounts of the substances. There are three principal types of relations: relations due to chemical equilibrium, relations due to a requirement of electrical neutrality, and relations due to the way the system was prepared (such as a specification that two substances are in their stoichiometric ratio). For each chemical reaction that comes to equilibrium, the number of components is reduced by unity. If charged particles are present, electrical neutrality reduces the number of components by unity.

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, due to the slowness of the reaction. We treat the metastable mixture as we would if no reaction were possible and say that there are three components. However, if a platinum catalyst is introduced into the system chemical equilibrium is rapidly established, reducing the number of components to two (besides 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 two moles to one, then the system has only one component. The fact that there is one component can be seen from the fact that the system could be produced from water vapor in the presence of the catalyst.

EXAMPLE 6.1

Determine the number of components in:

a. An aqueous solution containing Na^+, Cl^-, Br^-.

b. An aqueous solution containing Na^+, K^+, 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 charge 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 6.2

Determine the number of components in:

a. An aqueous solution containing 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 with each other.

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, all of which was produced by the combustion of a stoichiometric mixture of methane and oxygen (assume that the residual methane and oxygen are negligible in amount). Explain any difference from part (e).

g. A system containing solid $Na_2SO_4 \cdot 10H_2O$ and an aqueous phase containing Na^+ and SO_4^{2-} ions, which was produced by dissolving some of the sodium sulfate decahydrate.

Derivation of the Gibbs Phase Rule

If the p phases in a multiphase simple system of c components are separated from each other, there are a total of $p(c+1)$ independent intensive variables to specify the equilibrium intensive states of all phases ($c+1$ variables for each phase). Let the phases be placed in contact with each other, opened to each other, and allowed to equilibrate. 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 constraint (or equality) that did not exist when the phases were separated 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, etc., so that $p-1$ equalities suffice for one variable and p phases. The number of variables that have equal values in all phases is $c+2$ (P, T, and the chemical potentials of c components), for a total of $(p-1)(c+2)$ constraints. This means that f, the **number of independent intensive variables** after equilibrium of all phases, is equal to

$$f = p(c+1) - (p-1)(c+2) = pc + p - pc + c - 2p + 2$$

$$f = c - p + 2 \tag{6.2-2}$$

This equation is the **phase rule** of Gibbs. The number of independent intensive variables is also called the **number of degrees of freedom** or the **variance**.

For a one-component, one-phase system, the number of independent intensive variables at equilibrium is

$$f = 1 - 1 + 2 = 2 \quad \text{(one component, one phase)}$$

In a phase diagram such as that of Figure 2.3, an open area represents a single phase. Since there are two independent intensive variables, T and P 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

$$f = 1 - 2 + 2 = 1 \quad \text{(one component, two phases)}$$

If we choose to fix the temperature, then every other variable is a dependent variable with a value determined by the nature of the system and that value of the temperature. Only one value of the pressure is possible, only one value for the density of each phase is possible, etc. For example,

$$P = P(T) \qquad (c = 1, p = 2) \tag{6.2-3}$$

Such a function is represented by a curve in a phase diagram such as in Figure 2.3. The equilibrium pressure when a liquid and a vapor phase are equilibrated is called the **vapor pressure**. The vapor pressure of water at 100.00°C is equal to 1.000 atm (760.00 torr), and at 25.00°C is equal to 23.756 torr. Figure 6.2 shows the equilibrium vapor pressure of water as a function of temperature.

If one component and three phases are present, the number of independent intensive variables is zero. There is no choice about the temperature, pressure, density of each phase, or any other intensive variable, and the system is said to be at a **triple point**. The solid–liquid–vapor triple point of water occurs at temperature of 273.16 K (this value defines the size of the kelvin) and a pressure of 4.562 torr.

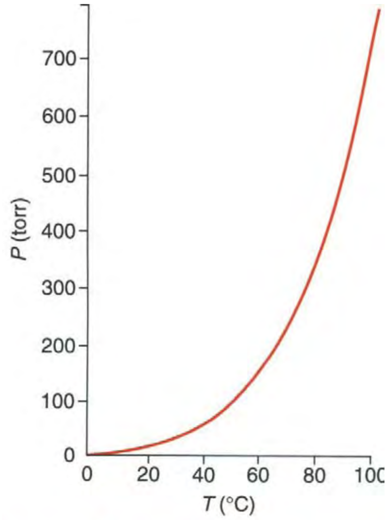

Figure 6.2. The Equilibrium Vapor Pressure of Water as a Function of Temperature. If both the liquid and the vapor phase are present, the equilibrium pressure is a function only of temperature. (Data from R. C. Weast, *Handbook of Chemistry and Physics*, 64th ed., CRC Press, Boca Raton, FL, 1983–84, p. D192.)

One-Component Phase Diagrams

Figure 6.3 shows the phase diagram of water. This kind of phase diagram is a plot of curves representing functional relationships as shown in Eq. (6.2-3). The pressure scale in this diagram is so compressed that the liquid–vapor curve of Figure 6.2 is too close to the horizontal axis to be visible. Water exhibits **polymorphism**, the existence of different crystalline forms for the same substance. Eight different crystalline forms of water are shown, denoted by Roman numerals. There is no ice IV, since a metastable phase was mistaken for an equilibrium phase and given this number. When this error was discovered the other forms were not renumbered.

In the novel *Cat's Cradle*[2] 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 water on the earth freezes to this form of ice, destroying life as we know it. In the late 1960s, it was thought for a time that there might be a second liquid phase of water, which was named "polywater" since it seemed to consist of polymers of water molecules.[3] This phase seemed to have a lower chemical potential than ordinary liquid water at the same

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[2] Kurt Vonnegut, *Cat's Cradle*, Delacorte Press, New York, 1963.

[3] E. R. Lippincott, *et al.*, *Science*, **164**, 1482 (1969); A. Cherkin, *Nature*, **224**, 1293 (1969).

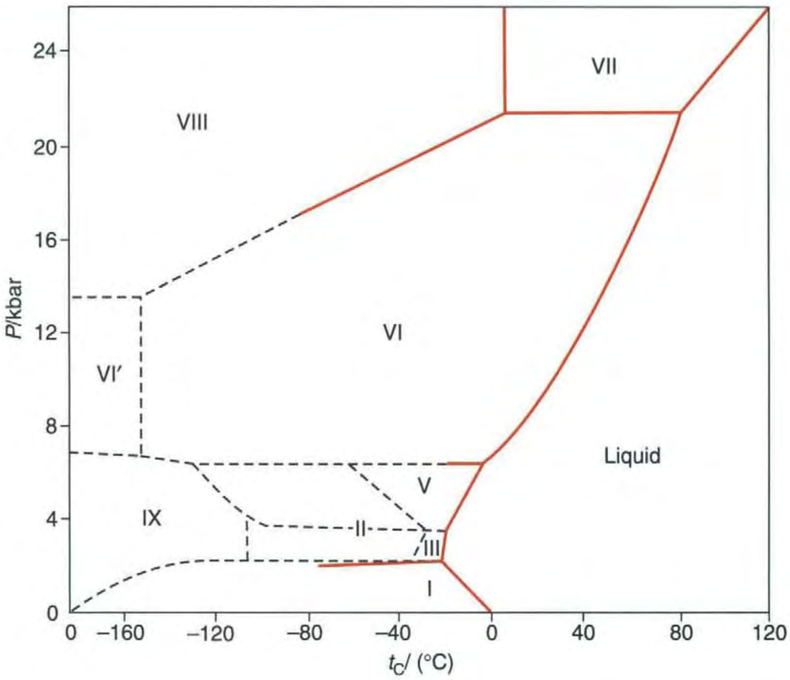

Figure 6.3 The Phase Diagram of Water. The liquid–vapor coexistence curve is too close to the horizontal axis to be seen. Of the solid phases that can equilibrate with the liquid, only ice (I) is less dense than the liquid. From B. Kamb, in E. Whalley, S. Jones, and L. Gold (eds.), *Physics and Chemistry of Ice*, University of Toronto Press, Toronto, 1973.)

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 some properties that it does not share with any other substance. It is apparently the only substance that exhibits different allotropic liquid phases. It also has qualitatively different phase diagrams for different isotopes. Figure 6.4 shows the low-temperature phase diagrams of ^{4}He and ^{3}He. The diagram for ^{4}He shows two triple points, for 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 triple points, since there are three different allotropic liquid phases. Neither isotope exhibits coexistence between the solid and the vapor, and the solid phases of both isotopes can exist only at pressures somewhat larger than 1 atm. Helium seems to be the only substance that cannot freeze at a pressure of 1 atm.

6.3 Phase Equilibrium in a One-Component System

A one-component equilibrium system can consist of one phase, two phases, or three phases. If more than one phase occurs, the phases have equal values of the temperature, the pressure, and the chemical potential of the single component. In a one-component

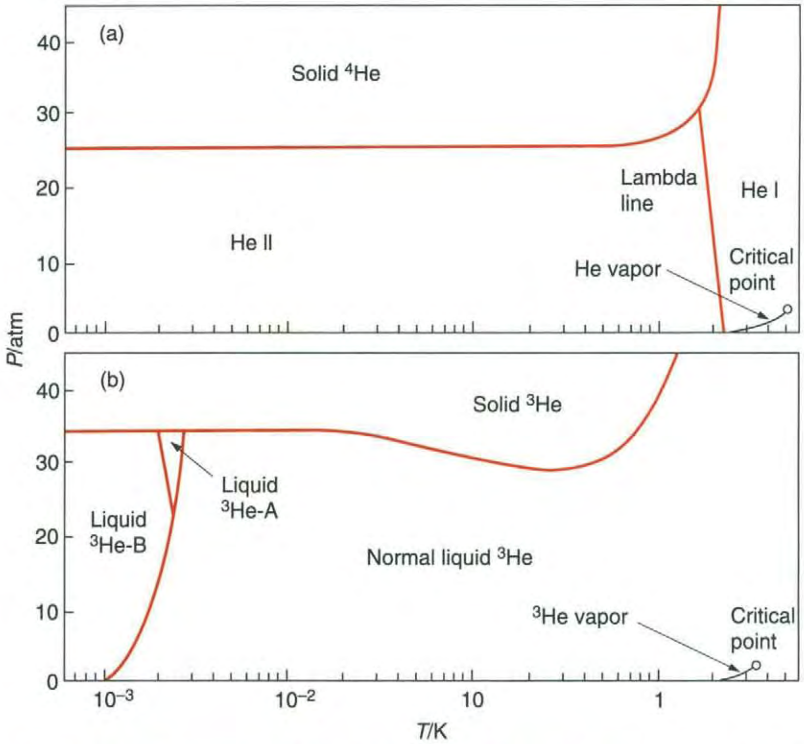

Figure 6.4. The Low-Temperature Phase Diagrams of ^{3}He and ^{4}He. (From P. V. E. McClintock, D. J. Meridth, and J. K. Wigmore, *Matter at Low Temperatures*, Wiley, New York, 1984, p. 18.)

system the chemical potential is equal to the molar Gibbs energy, so that for phases α and β,

$$G_{\mathrm{m}}^{(\alpha)} = G_{\mathrm{m}}^{(\beta)} \tag{6.3-1}$$

The equality of the chemical potential in the different phases imposes conditions as specified by the Gibbs phase rule.

The Clapeyron Equation

The Clapeyron equation governs the dependence of P on T as shown in Eq. (6.2-3). To derive the equation, 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, $G_{\mathrm{m}}^{(\mathrm{II})}$ and $G_{\mathrm{m}}^{(\mathrm{II})}$, will undergo changes that are given in terms of dP and dT by Eq. (5.2-19):

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.

$$dG_{\mathrm{m}}^{(\mathrm{I})} = -S_{\mathrm{m}}^{(\mathrm{I})}\,dT + V_{\mathrm{m}}^{(\mathrm{I})}\,dP \tag{6.3-2}$$

$$dG_{\mathrm{m}}^{(\mathrm{II})} = -S_{\mathrm{m}}^{(\mathrm{II})}\,dT + V_{\mathrm{m}}^{(\mathrm{II})}\,dP \tag{6.3-3}$$

The molar Gibbs energies remain equal to each other during the change, so that $dG_{\mathrm{m}}^{(\mathrm{I})} = dG_{\mathrm{m}}^{(\mathrm{II})}$, and

$$-S_{\mathrm{m}}^{(\mathrm{I})}\,dT + V_{\mathrm{m}}^{(\mathrm{I})}\,dP = -S_{\mathrm{m}}^{(\mathrm{II})}\,dT + V_{\mathrm{m}}^{(\mathrm{II})}\,dP \tag{6.3-4}$$

Nonrigorously "dividing" this equation by dT, we obtain the differential equation

$$\frac{dP}{dT} = \frac{\Delta S_{\mathrm{m}}}{\Delta V_{\mathrm{m}}} \tag{6.3-5}$$

where $\Delta S_{\mathrm{m}} = S_{\mathrm{m}}^{(\mathrm{II})} - S_{\mathrm{m}}^{(\mathrm{I})}$ and $\Delta V_{\mathrm{m}} = V_{\mathrm{m}}^{(\mathrm{II})} - V_{\mathrm{m}}^{(\mathrm{I})}$. The relation of Eq. (6.3-5) is the **Clapeyron equation.**

For a reversible phase change, Eq. (4.3-4) gives

$$\Delta S_{\mathrm{m}} = \frac{\Delta H_{\mathrm{m}}}{T} \tag{6.3-6}$$

so that the Clapeyron equation can be written

$$\frac{dP}{dT} = \frac{\Delta H_{\mathrm{m}}}{T\,\Delta V_{\mathrm{m}}} \tag{6.3-7}$$

Using the Clapeyron equation, we can interpret the curves in a phase diagram.

EXAMPLE 6.2

Interpret the vertical and horizontal line segments in the phase diagram of water, Figure 6.3

Solution

A horizontal line corresponds to zero value of dP/dT, implying zero value of ΔH_{m} and of ΔS_{m} for the phase transition. For example, between ice VI and ice VII there appears to be zero change in enthalpy and in entropy. The value of ΔV_{m} is presumably nonzero. A vertical line corresponds to an undefined value for dP/dT, implying zero value for ΔV_{m}. For example, ice VII and ice VIII appears to have the same density.

Exercise 6.3

For most substances a solid–liquid coexistence curve has a positive slope. 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 water.

In order to have a representation for the function $P = P(T)$, we integrate the Clapeyron equation. We write Eq. (6.3-5) in the form

$$dP = \frac{\Delta S_{\mathrm{m}}}{\Delta V_{\mathrm{m}}}\,dT \tag{6.3-8}$$

Consider first a solid–liquid or a solid–solid phase transition. We apply our calculation practice, that solids and liquids have nearly constant volume so that ΔV_{m}

is nearly equal to a constant. Over a sufficiently small range of temperature, ΔS_m is nearly constant and we can write

$$P_2 - P_1 \approx \frac{\Delta S_m}{\Delta V_m}(T_2 - T_1) \qquad (T_2 - T_1 \text{ small}) \qquad (6.3\text{-}9a)$$

$$\approx \frac{\Delta H_m}{T\,\Delta V_m}(T_2 - T_1) \qquad (T_2 - T_1 \text{ small}) \qquad (6.3\text{-}9b)$$

where P_1 is the pressure corresponding to temperature T_1 and P_2 is the pressure corresponding to temperature T_2. In Eq. (6.3-9b), T is a value of the temperature such that $T_1 < T < T_2$.

EXAMPLE 6.3

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

$$\Delta V_m = (18.01\text{ g mol}^{-1})\left(\frac{1}{1.00\text{ g cm}^{-3}} - \frac{1}{0.917\text{ g cm}^{-3}}\right)\frac{1\text{ m}^3}{10^6\text{ cm}^3}$$

$$= -1.63 \times 10^{-6}\text{ m}^3\text{ mol}^{-1}$$

$$P_2 - P_1 \approx \frac{6008\text{ J mol}^{-1}}{(273.15\text{ K})(-1.63 \times 10^{-6}\text{ m}^3\text{ mol}^{-1})}(-0.100\text{ K})$$

$$\approx 1.35 \times 10^6\text{ J m}^{-3} = 1.35 \times 10^6\text{ N m}^{-2} = 1.35 \times 10^6\text{ Pa} = 13.3\text{ atm}$$

$$P_2 \approx 14.3\text{ atm}$$

Equation (6.3-9) implies that the curve in the phase diagram should be linear. 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. However, some of the solid–liquid curves are noticeably curved and a different approximation is needed. If instead of assuming that the quotient $\Delta S_m/\Delta V_m$ is approximately constant, one assumes that the quotient $\Delta H_m/\Delta V_m$ is approximately constant, one can integrate

$$dP = \frac{1}{\Delta V_m}\frac{\Delta H_m}{T}\,dT$$

to obtain

$$P_2 - P_1 \approx \frac{\Delta H_m}{\Delta V_m}\ln\left(\frac{T_2}{T_1}\right) \qquad (\Delta H_m \text{ constant}) \qquad (6.3\text{-}10)$$

The relation of Eq. (6.3-10) is probably better than that of Eq. (6.3-9) for large differences between T_2 and T_1, since ΔH is likely to be more nearly independent of T than is ΔS.

*Exercise 6.4

Estimate the pressure of the system of Example 6.3, using Eq. (6.3-10) instead of Eq. (6.3-9). Compare the answer with that of Example 6.3 to see whether the assumption of constant ΔH gives different results from the assumption of constant ΔS.

The Clausius–Clapeyron Equation

If one of the two phases involved is a gas, we can write a useful modification of the Clapeyron equation by making two approximations: (1) that the vapor phase is an ideal gas, and (2) that the molar volume of the condensed phase (solid or liquid) is negligible compared with that of the vapor (gas) phase. These are both good approximations. Most gases obey the ideal gas equation to about one percent under ordinary conditions, and the molar volumes of vapor phases are typically several hundred times as large as the molar volumes of condensed phases. For a vaporization (liquid–vapor transition):

$$\Delta V_{\mathrm{m}} = V_{\mathrm{m}}^{(\mathrm{g})} - V_{\mathrm{m}}^{(\mathrm{l})} \approx V_{\mathrm{m}}^{(\mathrm{g})} \approx \frac{RT}{P} \qquad (6.3\text{-}11)$$

From Eqs. (6.3-7) and (6.3-11) we obtain the derivative form of the Clausius–Clapeyron equation:

$$\frac{dP}{dT} = \frac{P\,\Delta_{\mathrm{vap}}H_{\mathrm{m}}}{RT^2} \qquad (6.3\text{-}12)$$

where $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ is the molar enthalpy change of vaporization. For a sublimation (solid–vapor transition), Eq. (6.3-12) applies except that $\Delta_{\mathrm{vap}}H_{\mathrm{m}}$ 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 multiply Eq. (6.3-12) by dT and divide by P:

$$\frac{1}{P}\frac{dP}{dT}\,dT = \frac{\Delta H_{\mathrm{m}}}{RT^2}\,dT \qquad (6.3\text{-}13)$$

Integration of Eq. (6.3-13) with the assumption that ΔH_{m} is constant gives the integral form of the Clausius–Clapeyron equation:

$$\ln\left(\frac{P_2}{P_1}\right) = -\frac{\Delta H_{\mathrm{m}}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (6.3\text{-}14)$$

If the enthalpy change of vaporization or sublimation depends on temperature, then ΔH_{m} in this formula represents an average enthalpy change over the interval from T_1 to T_2.

Exercise 6.5

Carry out the steps to obtain Eq. (6.3-14).

EXAMPLE 6.4

Using the vapor pressure values for water given in Section 6.2, find the average enthalpy change of vaporization of water between 25°C and 100°C.

Solution

$$\Delta_{\text{vap}}H_{\text{m}} = \frac{-RT_2T_1}{T_1 - T_2}\ln\left(\frac{P_2}{P_1}\right)$$

$$= \frac{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})(373.15\ \text{K})}{75.00\ \text{K}}\ln\left(\frac{760.0\ \text{torr}}{23.756\ \text{torr}}\right)$$

$$= 4.274 \times 10^4\ \text{J mol}^{-1} = 42.74\ \text{kJ mol}^{-1}$$

***Exercise 6.6**

The normal boiling temperature of ethanol is equal to 78.5°C and the molar enthalpy change of vaporization is equal to $40.5\ \text{kJ mol}^{-1}$. Estimate the vapor pressure of ethanol at 100°C. State any assumptions or approximations.

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 4.5) can be used as an approximation.

***Exercise 6.7**

The normal boiling temperature of chloroform is 61.7°C. Estimate the vapor pressure of chloroform at 50.0°C, using Trouton's rule.

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. The presence of other substances in the gas phase can make a difference. The principal effect that the other gases have is to change the pressure on the condensed phase, since the amounts of other substances that dissolve in the condensed phase are negligible. We denote the total pressure by P' and the vapor pressure (the partial pressure of the substance that occurs in the liquid phase) by P. From the fundamental fact of phase equilibrium,

$$G_{\text{m}}^{(\text{l})} = G_{\text{m}}^{(\text{g})} \qquad (6.3\text{-}15)$$

When the total pressure is changed from one value P'_1 to another value P'_2, the change in the molar Gibbs energies of the two phases must be equal. Assuming the vapor phase to be ideal and using Eqs. (5.3-10) and (5.3-4)

$$V_{\text{m}}(\text{liq})(P'_2 - P'_1) = RT\ \ln(P_2/P_1) \qquad (6.3\text{-}16)$$

Equation (6.3-16) can be solved for P_2:

$$P_2 = P_1 \exp\left(\frac{V_{\text{m}}(\text{liq})(P'_2 - P'_1)}{RT}\right) \qquad (6.3\text{-}17)$$

EXAMPLE 6.5

At 298.15 K, the vapor pressure of water is equal to 23.756 torr if the total pressure is equal to the vapor pressure. Calculate the vapor pressure of water if enough air is present in the vapor phase to give a total pressure of 1.000 atm.

Solution

The molar volume of water at this temperature is 18.05 cm^3 mol^{-1}.

$$\frac{V_{\mathrm{m}}(\mathrm{liq})(P_2' - P_1')}{RT} = \frac{(18.05\times 10^{-6}\ \mathrm{m}^3\ \mathrm{mol}^{-1})(760\ \mathrm{torr} - 24\ \mathrm{torr})}{(8.3145\ \mathrm{J\ K}^{-1}\ \mathrm{mol}^{-1})(298.15\ \mathrm{K})}\ \frac{101{,}325\ \mathrm{Pa}}{760\ \mathrm{torr}}$$
$$= 7.14\times 10^{-4}$$
$$P = (23.756\ \mathrm{torr})e^{7.14\times 10^{-4}} = 23.772\ \mathrm{torr}$$

For most purposes, this change in the vapor pressure is negligible.

***Exercise 6.8**

Find the total pressure necessary to change the vapor pressure of water by 1.00 torr at 100.0°C.

6.4

The Gibbs Energy and Phase Transitions

In this section, we investigate such questions as: Why is equilibrium water a liquid at 1.000 atm and 373.14 K, but a vapor at 1.000 atm and 373.16 K? Why should such a small change in temperature make such a large change in structure? The thermodynamic answer to this question involves the fact that at equilibrium at constant T and P, the Gibbs energy of the system is at a minimum.

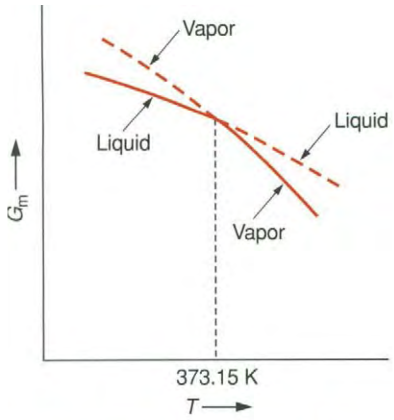

Figure 6..5. The Molar Gibbs Energy of Water as a Function of Temperature Near the Liquid–Vapor Phase Transition (Schematic). This diagram, which applies at constant pressure, shows how the minimization of the Gibbs energy determines the stable phase at any temperature.

Figure 6.5 shows schematically the molar Gibbs energy (chemical potential) of liquid and gaseous water as a function of temperature at 1 atm pressure. If one phase has a more negative value of the molar Gibbs energy than the other phase, the system can lower its Gibbs energy by making the transition to the phase of lower molar Gibbs energy.

In order to construct Figure 6.5, we have written Eq. (4.2-21) for molar quantities:

$$\left(\frac{\partial G_{\mathrm{m}}}{\partial T}\right)_P = -S_{\mathrm{m}} \tag{6.4-1}$$

The molar entropy of the water vapor is greater than the molar entropy of the liquid water, so that the vapor curve in Figure 6.5 has a more negative slope than the liquid curve. The temperature at which the curves cross is the temperature of phase coexistence, since this is the temperature at which the values of the chemical potential in the two phases are equal. Above this temperature, the vapor curve lies lower, so that the vapor is the stable phase, and the liquid must be metastable if it occurs (indicated by a broken curve). Below the normal boiling temperature, the liquid is stable and the vapor is metastable if it occurs.

We can also reach the same conclusion as follows: the molar Gibbs energy is given by

$$G_{\mathrm{m}} = H_{\mathrm{m}} - TS_{\mathrm{m}} \tag{6.4-2}$$

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, but the phase of lower molar enthalpy is the more stable phase at low temperature. The temperature of coexistence is the temperature at which these two tendencies balance each other.

Figure 6.6 shows schematically the molar Gibbs energy of liquid and gaseous water as a function of pressure. The slope of the tangent to the curve is given by Eq. (5.2-21):

$$\left(\frac{\partial G_m}{\partial P}\right)_T = V_m \qquad (6.4\text{-}3)$$

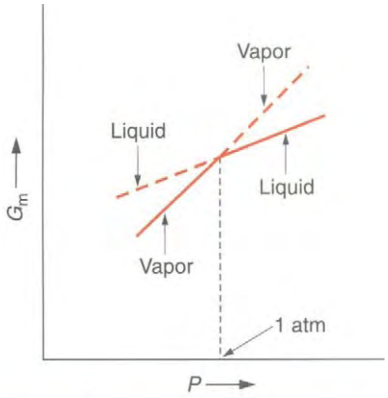

Figure 6.6. The Molar Gibbs Energy of Water as a Function of Pressure Near the Liquid–Vapor Phase Transition (Schematic). This diagram, which applies at a constant temperature of 373.15 K, shows how the minimization of the Gibbs energy determines the stable phase at any pressure.

The molar volume of the vapor is greater than that of the liquid phase, so that the vapor curve has a more positive slope than the liquid curve. At a pressure greater than 1 atm at 373.15 K the liquid is the stable phase, but at a pressure less than 1 atm the vapor is the stable phase.

Exercise 6.9

Sketch the 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.

The Maxwell Equal-Area Construction

For a fluid described by a particular equation of state, we can locate the pressure of liquid–vapor coexistence. Figure 6.7a shows the pressure as a function of molar volume at a fixed subcritical temperature as described by an equation of state such as the van der Waals equation. Instead of the tie line that actually describes the behavior of the fluid, there is an S-shaped curve (a "loop"). If we exchange the roles of the variables in this figure, we obtain Figure 6.7b. Two points, labeled a and e, correspond to equal values of the chemical potential in the two phases, and we want to find the location of these points. There are two regions, from a to b and from d to e, which can represent metastable phases. There is one region, from b to d, which corresponds to a negative compressibility. A real compressibility cannot be negative, so that this portion of the curve cannot represent even a metastable system.

Since the curve corresponds to fixed temperature,

$$d\mu = dG_m = V_m\,dP \quad \text{(constant temperature)} \qquad (6.4\text{-}4)$$

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. This integral is written in the following way, since the curve does not represent a single-valued function:

$$G_m(e) - G_m(a) = \int_{P_a}^{P_b} V_m\,dP + \int_{P_b}^{P_c} V_m\,dP + \int_{P_c}^{P_d} V_m\,dP + \int_{P_d}^{P_e} V_m\,dP \qquad (6.4\text{-}5)$$

The area to the right of the vertical line segment between points a and e is called area 1 and is equal to

$$\text{area } 1 = \int_{P_a}^{P_b} V_m\,dP - \int_{P_c}^{P_b} V_m\,dP = \int_{P_a}^{P_b} V_m\,dP + \int_{P_b}^{P_c} V_m\,dP \qquad (6.4\text{-}6)$$

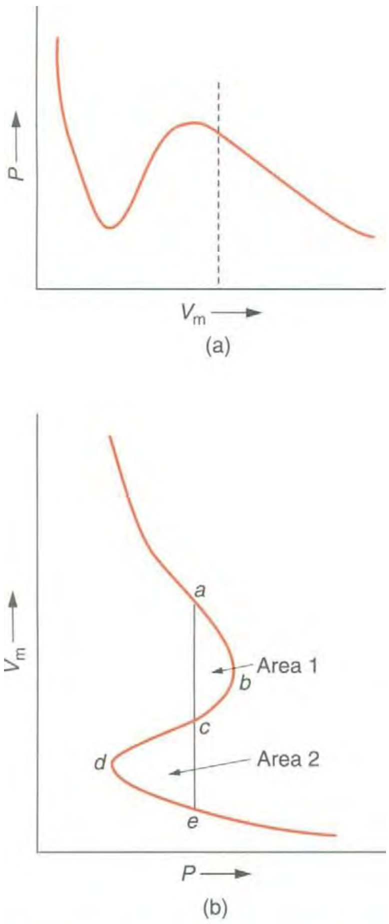

Figure 6.7. The Pressure and the Molar Volume for a Fluid Obeying an Equation of State Such as the van der Waals Equation (Schematic). (a) **The pressure as a function of molar volume.** The region of positive slope cannot describe any real system, because it corresponds to negative compressibility. (b) **The molar volume as a function of pressure.** This diagram is used to determine the liquid state and the vapor state that have the same molar Gibbs energy, using the Maxwell construction.

and the area to the left of this line segment, labeled area 2 in the figure, is given by

$$\text{area } 2 = \int_{P_d}^{P_c} V_\mathrm{m}\, dP - \int_{P_d}^{P_e} V_\mathrm{m}\, dP = -\int_{P_c}^{P_d} V_\mathrm{m}\, dP - \int_{P_d}^{P_e} V_\mathrm{m}\, dP \tag{6.4-7}$$

Comparison of Eq. (6.4-5) with Eqs. (6.4-6) and (6.4-7) shows that when $G_\mathrm{m}(e) - G_\mathrm{m}(a) = 0$, area 1 and area 2 are equal. The adjustment of the locations of points a and e to make these areas equal is known as the **equal-area construction** and is due to Maxwell, and locates the liquid and vapor states of equal chemical potential.

The van der Waals equation of state provides only 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 with their modification of the Redlich–Kwong equation of state (see Table 2.1).

Classification of Phase Transitions

A **first-order phase transition** is one in which at least one of the first derivatives of the molar Gibbs energy is discontinuous at the phase transition. Either the molar volume or the molar entropy (or both) is discontinuous. Usually both qualities are discontinuous, but in some first-order phase transitions, such as the transition between ice VI and ice VII, only one of these quantities will be discontinuous. Ordinary phase transitions such as vaporizations, freezings, etc., are first-order transitions. In a first-order transition, the Gibbs energy has a cusp in at least one of the graphs like those of Figure 6.5 or Figure 6.6. Figure 6.8 shows schematically the molar volume of solid and liquid water as a function of pressure, and Figure 6.9 shows the molar entropy as a function of temperature for a typical first-order transition.

Second derivatives of the Gibbs energy are also used in characterizing phase transitions. Equations (4.2-21), (4.2-22), (1.3-9), and (4.5-5) give

$$\left(\frac{\partial^2 G_\mathrm{m}}{\partial T^2}\right)_P = -\left(\frac{\partial S_\mathrm{m}}{\partial T}\right)_P = -\frac{C_{P,\mathrm{m}}}{T} \tag{6.4-8}$$

$$\left(\frac{\partial^2 G_\mathrm{m}}{\partial P^2}\right)_T = \left(\frac{\partial V_\mathrm{m}}{\partial P}\right)_T = -V_\mathrm{m}\kappa_T \tag{6.4-9}$$

where $C_{P,\mathrm{m}}$ is the molar heat capacity at constant pressure and κ_T is the isothermal compressibility.

If the molar volume or the molar entropy has a discontinuity, the heat capacity or the compressibility must have a singularity (a point at which it becomes infinite). Figure 6.10 shows the constant-pressure heat capacity as a function of temperature in the vicinity of a first-order phase transition, and Figure 6.11 shows the compressibility as a function of pressure in the vicinity of a first-order phase transition. 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, and 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.

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 6.12 schematically shows the heat capacity in the vicinity of a second-order phase transition and Figure 6.13 shows the compressibility in the vicinty of a second-order phase transition. In a second-order transition, neither the compressibility nor the heat capacity becomes infinite. Therefore, 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.

There are several types of phase transitions that are not first-order transitions. These include normal–superconducting transitions in some metals and ceramics, paramagnetic–ferromagnetic transitions in some magnetic materials, and a type of transition that occurs in certain solid metal alloys, called an **order–disorder transition**. For example, β-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 state in which the atoms are randomly mixed in the same crystal lattice.

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 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. A phase transition that was once said to be second-order is the transition between normal liquid helium and liquid helium II. (See Figure 6.4 for the phase diagram.) Later experiments indicated that the heat capacity of liquid helium does appear to approach infinity at the transition, so that the transition is not second-order. However, 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 6.14, and the transition is called a **lambda transition**. The order–disorder transition in β-brass is also a lambda transition. A lambda transition is generally considered not to be either first-order or second-order.

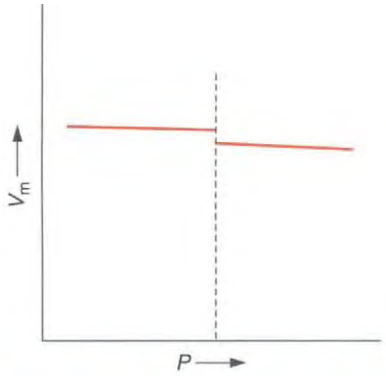

Figure 6.8. The Molar Volume as a Function of Pressure at a First-Order Phase Transition. There is a discontinuity in the molar volume at the phase transition.

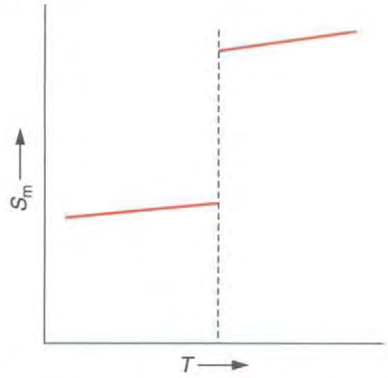

Figure 6.9. The Molar Entropy as a Function of Temperature at a First-Order Phase Transition. There is a discontinuity in the molar entropy at the phase transition.

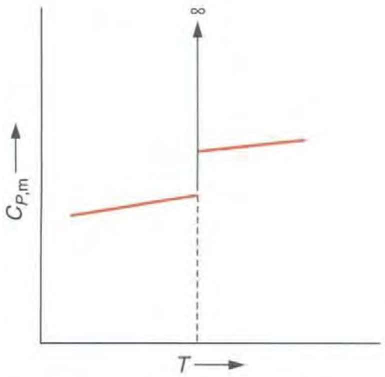

Figure 6.10. The Constant-Pressure Heat Capacity as a Function of Temperature at a First-Order Phase Transition. Because of the discontinuity in the entropy as a function of temperature, there is an infinite spike in the heat capacity at the phase transition.

The Critical Point of a Liquid–Vapor Transition

The liquid–vapor critical point, which was introduced in Section 2.6, is the point beyond which the liquid–vapor phase transition does not occur. As can be seen in Figure 2.4, the molar volumes of the liquid and the vapor become more and more nearly equal to each other as the temperature is increased toward the cricial temperature. The discontinuities in Figures 6.8 and 6.9 gradually shrink to zero while two curves in Figure 6.6 approach each other more and more closely, until there is only one curve at the critical temperature, with a vertical tangent at the critical point. Figure 6.15 shows schemically the molar volume as a function of pressure at the crucial temperature.

Many properties of the system in states near the critical point are abnormal. In the vicinity of the critical point, the fluid scatters light strongly, a phenomenon called **critical opalescence**. Furthermore, as shown in Figure 2.5, if the system is near the critical state the meniscus between the liquid and vapor phases is diffuse, instead of appearing to be sharp like a mathematical plane. Quantities such as the compressibility and the heat capacity, which become infinite at the crucial point, do not suddenly jump to infinite values as they do away from the critical point, but rise smoothly (and steeply) toward infinite values. The behavior is described in terms of **critical exponents**. For example, the temperature dependence of the constant-volume heat capacity for fixed

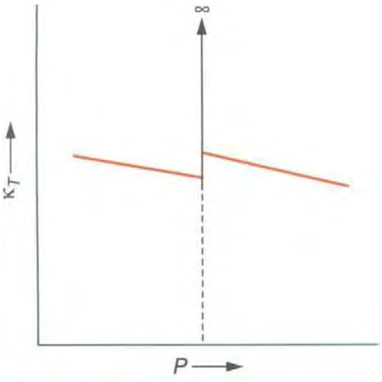

Figure 6.11. The Isothermal Compressibility as a Function of Pressure at a First-Order Phase Transition (Schematic). Because of the discontinuity in the molar volume as a function of pressure, there is an infinite spike in the compressibility at the phase transition.

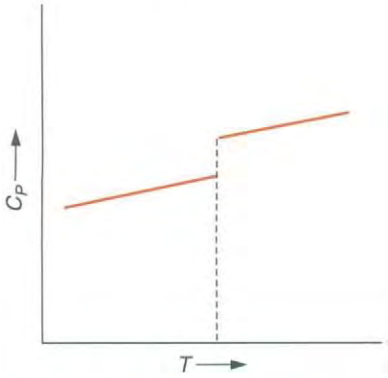

Figure 6.12. The Constant-Pressure Heat Capacity as a Function of Temperature at a Second-Order Phase Transition. In a second-order phase transition, there is no discontinuity in the molar entropy as a function of temperature, but there is a discontinuity in the heat capacity at the phase transition.

density equal to the critical density can be represented in the immediate vicinity of the critical point by the expression

$$C_V \propto (T - T_c)^{-\alpha} \qquad (\text{for } T > T_c) \qquad (6.4\text{-}10)$$

$$C_V \propto (T_c - T)^{-\alpha'} \qquad (\text{for } T > T_c) \qquad (6.4\text{-}11)$$

The exponents α and α' are the critical exponents for the heat capacity.

Similarly, the densities of the coexisting liquid and gas phases just below the critical point are represented by

$$\rho(\mathrm{l}) - \rho(\mathrm{g}) \propto (T_c - T)^{\beta} \qquad (6.4\text{-}12)$$

The temperature dependence of the compressibility for fixed density equal to the critical density is represented by

$$\kappa_T \propto (T - T_c)^{-\gamma} \qquad (\text{for } T > T_c) \qquad (6.4\text{-}13)$$

$$\kappa T \propto (T_c - T)^{-\gamma'} \qquad (\text{for } T < T_c) \qquad (6.4\text{-}14)$$

The dependence of the pressure on the density at constant temperature equal to the critical temperature is described by

$$P - P_c \propto |\rho - \rho_c|^{\delta - 1}(\rho - \rho_c) \qquad (6.4\text{-}15)$$

Equation (6.4-16) has this form to ensure that the correct sign is produced for the left-hand side of the equation for any value of δ.

It appears that many fluids are well described by nearly equal values of the critical exponents, as would be expected from the law of corresponding states. Following are some experimental values, along with the values that are predicted by the van der Waals equation of state. We do not discuss the analysis that provides these predictions.[4]

	α'	β	γ'	δ	α	γ
CO_2	0.1	0.34	1.0	4.2	0.1	1.35
Xe	<0.2	0.35	1.2	4.4	—	1.3
van der Waals	0	0.5	1	3	0	1

Exercise 6.10

Draw rough graphs representing the behavior described by Eqs. (6.4-10) through (6.4-15) for a van der Waals gas.

6.5 Surface Structure and Thermodynamics

Some thermodynamic equations are valid only in the case that surface tension can be neglected. For example, we assumed that the thermodynamic energy of a one-component fluid system depended on three variables, such as T, V, and n, but not on the surface area. Although this is ordinarily an excellent approximation, the energy actually depends on the surface area.

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[4] H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena*, Oxford University Press, New York, 1971, pp. 74ff.

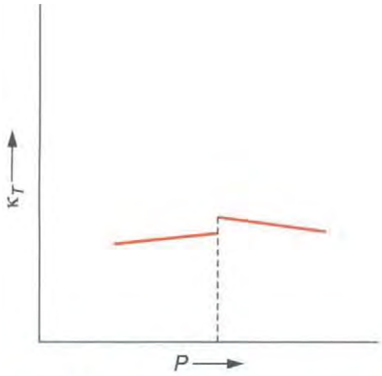

Figure 6.13. The Isothermal Compressibility as a Function of Pressure at a Second-Order Phase Transition. In a second-order phase transition, there is no discontinuity in the molar volume as a function of pressure, but there is a discontinuity in the compressibility at the phase transition.

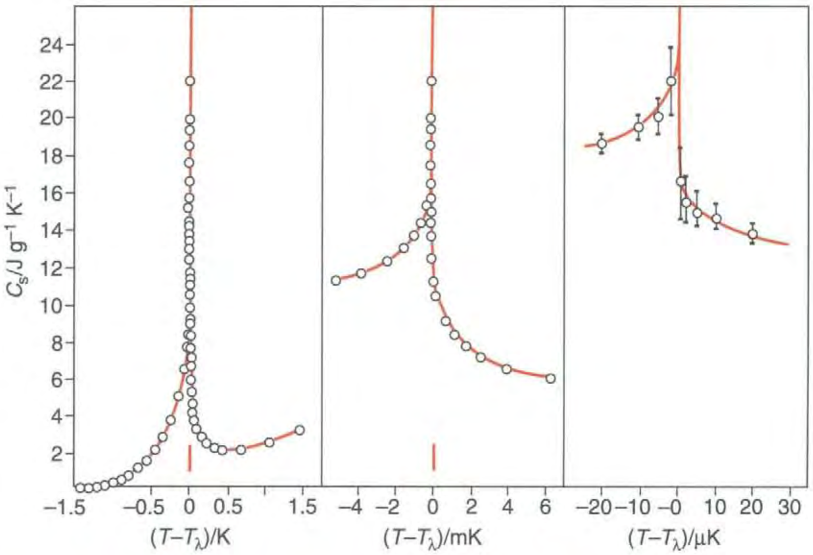

Figure 6.14. The Heat Capacity of Helium near the Lambda Transition. The heat capacity appears to become infinite, as in a first-order phase transition, but it rises smoothly instead of showing a spike at one point as does a first-order phase transition.

The Energy Attributed to a Surface

The surface energy is primarily potential energy of molecular interaction. Since molecules at the surface of the liquid have fewer nearest neighbors than molecules in the bulk of the liquid, they have a different average potential energy than molecules in the bulk. However, the values of surface energies indicate that the surface energy is numerically unimportant unless a system has a very large surface area or a small amount of substance.

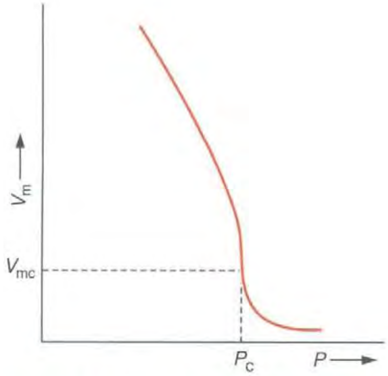

Figure 6.15. The Molar Volume near a Liquid–Vapor Critical Point. On the critical-temperature isotherm, the compressibility has an infinite value at the critical point, where the derivative $(\partial V/\partial P)_T$ is undefined.

EXAMPLE 6.6

For liquid carbon tetrachloride in contact with its vapor, estimate the surface energy per unit area, using the heat of vaporization to estimate the net attractive energy of the molecules.

Solution

In a solid lattice, carbon tetrachloride molecules can pack together like spherical molecules and are surrounded by 12 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 about 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 about seven nearest neighbors.

To estimate the surface energy, we first estimate the difference between the average attractive energy of a molecule and its neighbors in the bulk liquid and at the surface. 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

$$\frac{31330\ \mathrm{J\ mol^{-1}}}{6.022 \times 10^{23}\ \mathrm{mol^{-1}}} = 5.203 \times 10^{-20}\ \mathrm{J}$$

When a molecule is brought to the surface, it gains energy equal to 30% of this value, since it loses three of ten nearest neighbors instead of losing all ten as in vaporization. The surface energy per molecule is thus

$$(\text{surface energy per molecule}) = (6.203 \times 10^{-20}\ \mathrm{J})(0.30) = 1.6 \times 10^{-20}\ \mathrm{J}$$

We now estimate the surface area per molecule. The density of CCl_4 at 20°C is equal to $1.594\ \mathrm{g\,cm^{-3}}$, and its molar mass is $153.82\ \mathrm{g\,mol^{-1}}$. This gives a molar volume of $96.5\ \mathrm{cm^3\ mol^{-1}}$, and a volume per molecule of

$$(\text{volume per molecule}) = \frac{96.5 \times 10^{-6}\ \mathrm{m^3\ mol^{-1}}}{6.022 \times 10^{23}\ \mathrm{mol^{-1}}} = 1.60 \times 10^{-28}\ \mathrm{m^3}$$

A sphere with this volume has radius equal to 3.4×10^{-10} m, so we take this as the radius of the molecule

$$\text{area per molecule} = \pi r^2 = \pi(3.4 \times 10^{-10}\ \mathrm{m})^2 = 3.6 \times 10^{-19}\ \mathrm{m^2}$$

The surface energy per square meter is

$$\gamma \approx \frac{1.56 \times 10^{-20}\ \mathrm{J}}{3.6 \times 10^{-19}\ \mathrm{m^2}} = 0.043\ \mathrm{J\ m^{-2}}$$

This value agrees only roughly with the experimental value, $0.02695\ \mathrm{J\,m^{-2}}$ at 20°C. This analysis is mostly a web of assumptions. It is an important skill to be able to decide what assumptions are reasonable.

Exercise 6.11

***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 $20\ \mathrm{kJ\,mol^{-1}}$ 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, $0.072\ \mathrm{J\,m^{-2}}$.

***b.** For 1.00 mol of 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.

There can be several different kinds of surfaces. 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, one surface between the upper liquid phase and the vapor phase, and 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. If a system has only one component and one kind of surface the Gibbs energy G is a function of T, P, $\mathscr{A}$ (the surface area), and the amount of the substance, n:

$$dG = -S\,dT + V\,dP + \gamma\,d\mathscr{A} + \mu\,dn \tag{6.5-1}$$

where

$$\gamma = \left(\frac{\partial G}{\partial \mathscr{A}}\right)_{T,P,n} \tag{6.5-2}$$

and where the other partial derivatives are now defined to be taken at constant area in addition to whatever was previously held constant. The quantity γ is the Gibbs energy per unit area.

Since $U = G - PV + TS$, we can also write

$$dU = dG - d(PV) + d(TS) = T\,dS - P\,dV + \gamma\,d\mathscr{A} + \mu\,dn \tag{6.5-3}$$

so that γ can be interpreted as the internal energy per unit area or as the Gibbs energy per unit area. It is equal to the reversible work per unit area required to produce new surface and can be interpreted as a force per unit length. In SI units γ has the unit joules per square meter or newtons per meter.

Surface Energy as Surface Tension

Consider a liquid system such as depicted in Figure 6.16, which has a wire frame that protrudes from the surface of a sample of liquid. There is a film of liquid within the area of the frame, which has a length equal to L, and the system is at equilibrium with a gas phase at constant temperature. Let the frame be moved reversibly upward by a distance dx, increasing the area by an amount $L\,dx$ and the energy by

$$dU = T\,ds + \gamma\,d\mathscr{A} \tag{6.5-4}$$

Since there are two sides to the liquid layer, the area increases by $2L\,dx$, and

$$dU = T\,dS + \gamma 2L\,dx \tag{6.5-5}$$

By comparison with Eq. (3.1-5),

$$dw_{\text{rev}} = F_{\text{rev}}\,dx = \gamma\,d\mathscr{A} = 2L\gamma\,dx \tag{6.5-6}$$

and γ is recognized as the force per unit length exerted by the surface. It is therefore usually called the **surface tension**. The unit of surface tension is usually quoted as newtons per meter instead of joules per square meter. Table A.10 in Appendix A gives

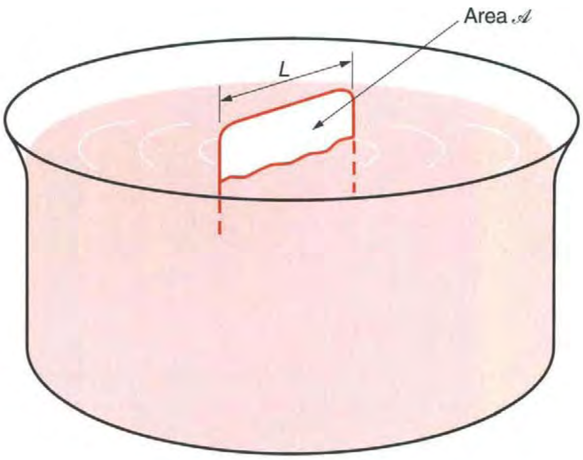

Figure 6.16. A Wire Frame of Adjustable Size to Illustrate Surface Tension. As the wire frame is raised, a thin film of liquid fills the area within the frame.

values of the surface tension for several pure substances in contact with the vapor of the same substance.

The surface of a liquid in contact with a vapor phase acts somewhat like a stretched elastic film that has a tendency to pull the surface toward the bulk of the phase. This produces a force that can have some noticeable effects. For example, a liquid can be attracted into or repelled from a tube of small diameter (or other small passages). Water molecules are attracted to the polar and ionic groups on a glass surface, and water is drawn into a vertical glass tube as shown in Figure 6.17a. The liquid surface is tangent to the glass surface and approximates a hemisphere. Figure 6.17b shows another case, in which the liquid does not completely wet the surface of the solid. 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 equal to zero.

The liquid rises into the tube because the surface tension force 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. The height of the column is thus

$$h = \frac{2\gamma}{\rho g r} \quad \text{(zero contact angle)} \qquad (6.5\text{-}7)$$

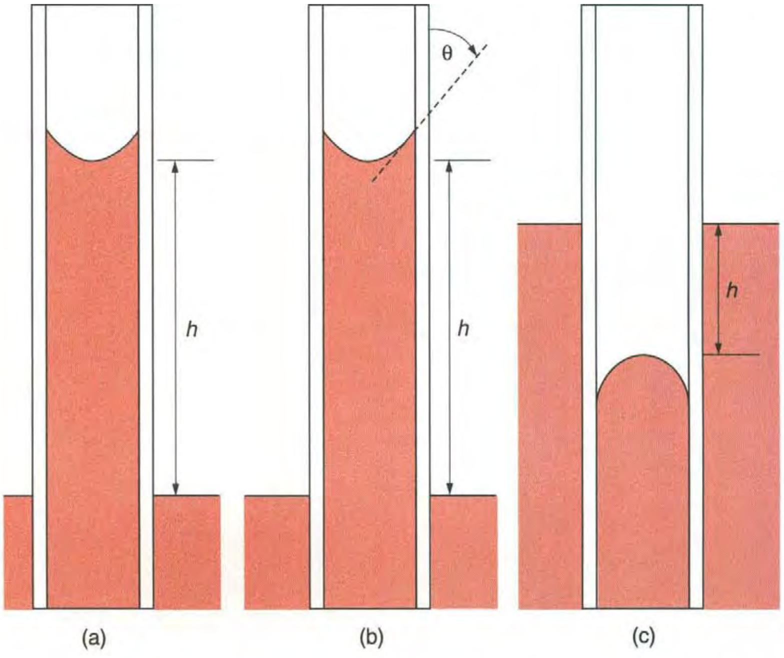

Figure 6.17. Capillary Rise or Depression of a Liquid in a Tube. (a) **A liquid that wets the solid surface.** The liquid surface (the meniscus) is tangent to the inner surface of the tube. This surface approximates a hemisphere. (b) **A liquid that partially wets the solid surface.** The contract angle, θ, is larger than 0, so that the liquid surface is not tangent to the inner surface of the tube. The liquid surface approximates a portion of a hemisphere. (c) **Capillary depression of mercury in a glass capillary.** Since the liquid does not wet the glass surface, the contact angle is greater than 90°, and the meniscus is depressed below the surface of the bulk liquid.

*Exercise 6.12

a. Find the height to which water at 20°C will rise in a capillary tube of diameter 0.60 mm.

b. Find the height to which the surface of water will rise in a tube with a diameter equal to 6.0 cm.

If the contact angle is not equal to zero, the surface tension force is not vertical, but 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

$$h = \frac{2\gamma\cos(\theta)}{\rho g h} \tag{6.5-8}$$

Mercury is attracted so weakly to glass that it forms a contact angle 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 6.17c.

*Exercise 6.13

Assuming a contact angle of 180°, calculate the distance to which the mercury meniscus is depressed in a glass capillary tube of radius 0.500 mm.

Since the surface of a liquid acts like a stretched film, in an isolated sample of liquid there is a difference between the pressure inside and outside the droplet. The system depicted in Figure 6.18 consists of a cylinder with a movable piston and containing a small droplet of liquid suspended in a vapor phase. The piston is displaced reversibly so that the volume of the system changes. The work done is

$$dw_{\text{rev}} = -P(\text{gas})\,dV = -P(\text{gas})(dV(\text{gas}) + dV(\text{liq})) \qquad (6.5\text{-}9))$$

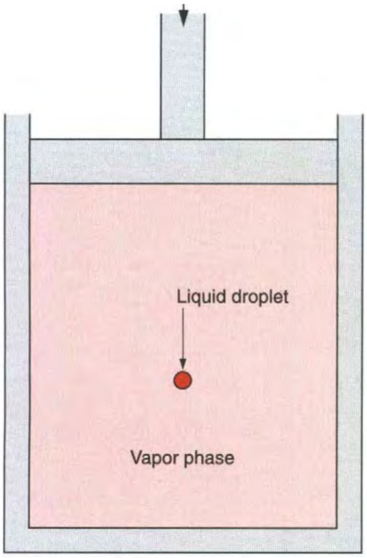

Figure 6.18. System to Illustrate the Pressure Difference in a Spherical Droplet. The droplet is assumed to be surrounded by the vapor phase, and is assumed to be small enough that it does not immediately settle to the bottom of the vessel.

where P(gas) is the pressure of the gas phase, P(liq) is the pressure of the liquid phase, V(gas) is the volume of the glass phase, and V(liq) is the volume of the liquid phase. Only the pressure of the gas phase 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 $\gamma\ d\mathcal{A}$ term of Eq. (6.5-6) is added to the usual expression for dw_{rev} for the liquid phase. No such term is added for the vapor phase, which has negigible surface tension:

$$dw_{\text{rev}} = -P(\text{gas})\,dV(\text{gas}) - P(\text{liq})\,dV(\text{liq}) + \gamma\,d\mathcal{A} \tag{6.5-10}$$

Equating the two expressions for dw_{rev} and canceling the term $P(\text{gas})\,dV(\text{gas})$ from both sides, we obtain

$$(P(\text{liq}) - P(\text{gas}))\,dV(\text{liq}) = \gamma\,d\mathcal{A} \tag{6.5-11}$$

The droplet is assumed to be spherical, so

$$dV(\text{liq}) = d(\tfrac{4}{3}\pi r^3) = 4\pi r^2\,dr \tag{6.5-12a}$$

$$d\mathcal{A} = d(4\pi r^2) = 8\pi r\,dr \tag{6.5-12b}$$

Substituting these relations into Eq. (6.5-11) and canceling the common factor dr, we obtain

$$P(\text{liq}) - P(\text{gas}) = \frac{2\gamma}{r} \tag{6.5-13}$$

Equation (6.5-13) is known as the **Laplace equation**. If the radius of the droplet becomes large, the difference in pressure between the inside and outside of the droplet approaches zero, as we would expect.

EXAMPLE 6.7

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 $0.07197\,\text{N m}^{-1}$.

$$P(\text{liq}) - P(\text{gas}) = \frac{(2)(0.07197\ \text{N m}^{-1})}{1.00 \times 10^{-6}\,\text{m}} = 1.44 \times 10^5\ \text{N m}^{-2} = 1.41\ \text{atm}$$

If the pressure on a sample of liquid is increased, its vapor pressure increases (see Eq. (6.3-17)), so the vapor pressure of a small droplet of a liquid increases as the size of the droplet decreases. For a planar surface the relation of Eq. (6.5-1) is

$$dG = -S\,dT + V\,dP + \gamma\,d\mathscr{A} + \mu^{(\text{p})}\,dn \tag{6.5-14}$$

where the superscript (p) means that the value pertains to a planar surface.

Let our system consist of a small spherical liquid droplet and the vapor that is at equilibrium with the droplet. If the volume of the droplet is changed by an amount dV at constant T, constant P, and constant composition, then

$$dV = V_{\text{m}}\,dn \tag{6.5-15}$$

where V_{m} is the molar volume of the liquid. From Eq. (6.5-12),

$$d\mathscr{A} = \frac{2}{r}\,dV = \frac{2V_{\text{m}}}{r}\,dn \tag{6.5-16}$$

The relation of Eq. (6.5-14) can now be written

$$dG = -S\,dT + V\,dP + \left(\mu^{(\text{p})} + \frac{2V_{\text{m}}\gamma}{r}\right) dn \tag{6.5-17}$$

The effective chemical potential is therefore

$$\mu = \mu^{(\text{p})} + \frac{2V_{\text{m}}\gamma}{r} \tag{6.5-18}$$

If the vapor can be assumed ideal, the chemical potential and the partial vapor pressure are related by Eq. (4.4-24):

$$\mu_i = \mu_i^{\circ} + RT\,\ln\!\left(\frac{P_i}{P^{\circ}}\right) \tag{6.5-19}$$

When this equation is combined with Eq. (6.5-18), we obtain

$$\ln\!\left(\frac{P_i}{P_i^{(\text{p})}}\right) = \frac{2V_{\text{m}}\gamma}{rRT} \tag{6.5-20}$$

where $P_i^{(\text{p})}$ is the partial vapor pressure for substance i at a planar surface.

EXAMPLE 6.8

The vapor pressure of a planar surface of water is 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 $0.07197\ \mathrm{N\,m^{-1}}$.

Solution

$$r = \frac{2(1.806\times 10^{-5}\ \mathrm{m^3\,mol^{-1}})(0.07197\ \mathrm{N\,m^{-1}})}{(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})(298.15\ \mathrm{K})\ \ln\left(\dfrac{24.756\ \mathrm{torr}}{23.756\ \mathrm{torr}}\right)}$$

$$= 2.544\times 10^{-8}\ \mathrm{m} = 2.544\times 10^{-5}\ \mathrm{mm}$$

Since small droplets of a liquid have a larger vapor pressure than large droplets, small droplets disappear while large droplets grow. This is the mechanism by which raindrops grow large enough to fall. The initial formation of a small droplet from the vapor is called **nucleation** and often requires a partial pressure of the liquid that is considerably larger than the equilibrium vapor pressure at a planar surface. Most raindrops apparently nucleate on specks of solid material, and seeding of supersaturated air with small crystals of silver iodide is sometimes used in efforts to produce rain. **Homogeneous nucleation** (without a solid speck) requires the spontaneous collection of a cluster of molecules, which is quite improbable unless the partial pressure of the substance greatly exceeds the equilibrium vapor pressure at a planar surface. Silver iodide is used for "cloud seeding" because it can be made into very small particles. It is possible to make 10^{15} particles of solid silver iodide from a single gram by spraying a solution of silver iodide in acetone through a suitable nozzle.

The surface of a cavity inside a liquid produces a greater pressure inside the cavity (often carelessly called a "bubble"). The vapor phase is inside a cavity, and the vapor pressure inside the cavity is therefore decreased below that of a planar surface.

Exercise 6.14

a. Show that the vapor pressure inside a spherical cavity is given by

$$\ln\left(\frac{P_i}{P_i^{(\mathrm{p})}}\right) = -\frac{2V_\mathrm{m}\gamma}{rRT} \qquad (6.5\text{-}21)$$

***b.** 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 inside 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 heated well above its normal boiling temperature if its container is smooth and there are no dust particles in the liquid at which cavities can begin to form. In such a case, the superheated liquid can suddenly boil ("bump") when the metastable superheated liquid finally begins to form cavities.

6.6 Surfaces in Multicomponent Systems

In Example 6.6 we calculated the energy as though one layer of molecules had the normal liquid on one side and the normal vapor on the other. A solid surface might

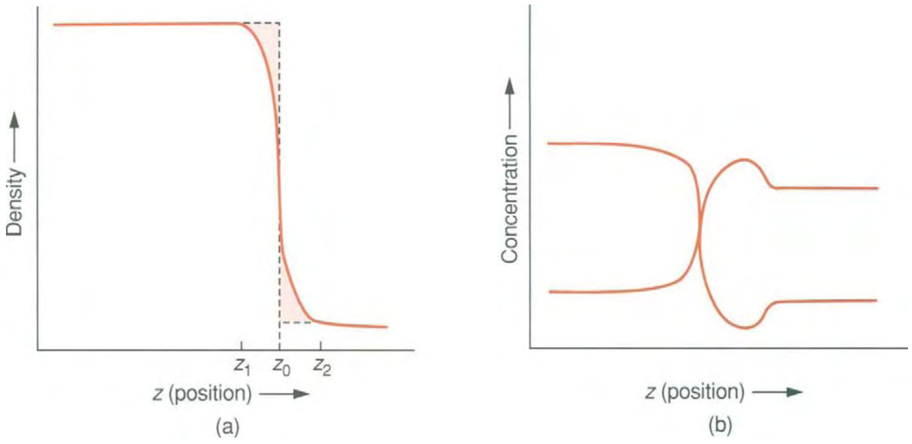

Figure 6.19. A Typical Density Profile through a Surface Region (Schematic). (a) **A one-component system.** The thickness of the surface region is several times as large as a molecular diameter. The density profile shown in the diagram is an average profile. (b) **A two-component system.** The density profiles of the two substances are not required to have any simple relation to each other, since either or both of the substances can accumulate at the interface.

nearly be like this crude model, but a liquid surface is more diffuse and it is perhaps appropriate to call it a surface region or a surface phase. Figure 6.19a shows schematically an average density profile through a single-component liquid–vapor surface at equilibrium. The thickness of a liquid–vapor interfacial region is typically equal to several molecular diameters, perhaps near 1 nm. We assume that the surface is planar and perpendicular to the z coordinate. A dividing plane is placed at z_0 inside the surface region, which extends from z_1 to z_2. The volume of each phase is assigned to be the volume that extends up to the dividing plane. The volume of the system is then exactly equal to the sum of the volumes of the two phases, and 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 6.19a. 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 6.19a represents the amount of substance that is present but not accounted for in phase II by this convention. The shaded area to the left of the surface plane represents the amount of substance that is included in phase I by the convention, but is actually not present. For a one-component system it is possible to place the plane in the interfacial region so that these two amounts of substance cancel, which would make the two shaded areas equal in size and make it unnecessary to ascribe any amount of the substance to the surface.

In a multicomponent system, this cancelation cannot be achieved for every substance. Figure 6.19b shows a schematic concentration profile for a two-component system, and it is apparent that no placement of the plane will produce equal areas for both substances. However, the plane can be placed so that the cancelation occurs for one substance (usually the solvent). The extrapolation is carried out for each substance, 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 for substance number i

$$n_i^{(\sigma)} = n_i - n_i^{(\mathrm{I})} - n_i^{(\mathrm{II})} \quad \text{(definition)} \tag{6.6-1}$$

where n_i is the total amount of substance number i and $n_i^{(\sigma)}$ is the amount of substance i attributed to the surface, called the **surface excess**. The surface excess of one substance (usually the solvent) can be made to vanish by the appropriate placement of the plane, but the surface excess will then not generally vanish for the other substances. 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 values of the thermodynamic variables for each phase are equilibrium values for the volume assigned by the convention, as though this volume were an interior portion of a very large system (and thus with no surface contributions). They obey all of the equations of thermodynamics without surface contributions. For phase I,

$$dG^{(\mathrm{I})} = -S^{(\mathrm{I})}\,dT + V^{(\mathrm{I})}\,dP + \sum_{i=1}^{c} \mu_i\,dn_i^{\mathrm{I}} \tag{6.6-2}$$

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. (6.6-2) and its analogue for phase II from the version of Eq. (6.5-1) that applies to a multicomponent system:

$$\begin{aligned} d[G - G^{(\mathrm{I})} - G^{(\mathrm{II})}] = {} & -[S - S^{(\mathrm{I})} - S^{(\mathrm{II})}]\,dT + [V - V^{(\mathrm{I})} - V^{(\mathrm{II})}]\,dP \\ & + \gamma\,d\mathscr{A} + \sum_{i=1}^{c} d[n_i - n_i^{(\mathrm{I})} - n_i^{(\mathrm{II})}] \end{aligned} \tag{6.6-3a}$$

which we rewrite as

$$dG^{(\sigma)} = -S^{(\sigma)}\,dT + \gamma\,d\mathscr{A} + \sum_{i=1}^{c} \mu_i\,dn_i^{(\sigma)} \tag{6.6-3b}$$

where $G^{(\sigma)}$ is called the **surface Gibbs energy**:

$$G^{(\sigma)} = G - G^{(\mathrm{I})} - G^{(\mathrm{II})} \tag{6.6-3c}$$

In Eq. (6.6-3b), we have used the fact that $V^{(\mathrm{I})} + V^{(\mathrm{II})} = V$, so that the dP term vanishes. The surface Gibbs energy is the Gibbs energy that is assigned to the surface by our definition of the Gibbs energies of the phases. It depends on the location of the plane with which we divide the phases from each other. There are definitions for $S^{(\sigma)}$ and other thermodynamic variables that are analogous to that of $G^{(\sigma)}$ in Eq. (6.6-3).

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. (5.6-5), is

$$G = \gamma\mathscr{A} + \sum_{i=1}^{c} \mu_i n_i \tag{6.6-4}$$

Each phase obeys Euler's theorem without a surface term, so that

$$G^{(\mathrm{I})} = \sum_{i=1}^{c} \mu_i n_i^{(\mathrm{I})} \tag{6.6-5}$$

with an analogous equation for phase II. When Eq. (6.6-5) and its analogue for phase II are subtracted from Eq. (6.6-4), we obtain

$$G^{(\sigma)} = \gamma\mathscr{A} + \sum_{i=1}^{c} \mu_i n_i^{(\sigma)} \tag{6.6-6}$$

We can write an expression for $dG^{(\sigma)}$ from Eq. (6.6-6):

$$dG^{(\sigma)} = \gamma \, d\mathscr{A} + \mathscr{A} \, d\gamma + \sum_{i=1}^{c} n_i^{(\sigma)} \, d\mu_i + \sum_{i=1}^{c} \mu_i \, dn_i^{(\sigma)} \tag{6.6-7}$$

Equating Eq. (6.6-3b) and Eq. (6.6-7) and dividing by $\mathscr{A}$, we obtain a surface version of the Gibbs–Duhem equation:

$$0 = \frac{S^{(\sigma)}}{\mathscr{A}} \, dT + d\gamma + \sum_{i=1}^{c} \Gamma_i^{(\sigma)} \, d\mu_i \tag{6.6-8}$$

The surface excess per unit area, $\Gamma_i^{(\sigma)}$, is called the **surface concentration**:

$$\Gamma_i^{(\sigma)} = \frac{n_i^{(\sigma)}}{\mathscr{A}} \quad \text{(definition)} \tag{6.6-9}$$

If the temperature is constant,

$$d\gamma = -\sum_{i=1}^{c} \Gamma_i^{(\sigma)} \, d\mu_i \quad \text{(constant temperature)} \tag{6.6-10}$$

This equation can be interpreted as follows: if adding substance i (raising its chemical potential) 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 is called a **surfactant**, and accumulates at the surface. 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 7 that for a solute in a dilute solution we can write to an adequate approximation

$$\mu_i = \mu_i^\circ + RT \, \ln\left(\frac{c_i}{c^\circ}\right) \tag{6.6-11}$$

where μ_i° is a constant at constant T and P, and where c_i is the molar concentration of substance i expressed in mol L^{-1}, and c° is defined to equal 1 mol L^{-1} (exactly). For a two-component solution, the surface dividiing the phases can be positioned so that Γ_1, the surface concentration of the solvent, is zero. It can be shown that

$$\Gamma_2 = -\frac{1}{RT}\left(\frac{\partial \gamma}{\partial \ln(c_2)}\right)_{T,P,c_i} \tag{6.6-12a}$$

and

$$\Gamma_2 = -\frac{c_2}{RT}\left(\frac{\partial \gamma}{\partial c_2}\right)_{T,P,c_i} \tag{6.6-12b}$$

Exercise 6.15

Show that both versions of Eq. (6.6-12) follow from Eqs. (6.6-10) and (6.6-11).

There are many kinds of systems with interfacial effects that are of intrinsic and 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. A number of solids act as **heterogeneous catalysts**, which allow adsorbed reactants to react on their surfaces. We discuss adsorption and catalysis in Chapter 13. **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. Surface effects, including surface charges, dominate in determining the behavior of such systems.

Summary of the Chapter

The fundamental fact of phase equilibrium is that

$$\mu_i^{\alpha} = \mu_i^{\beta}$$

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 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 integrated Clausius–Clapeyron equation is

$$\ln(P) = \frac{-\Delta H_{\mathrm{m}}}{RT} + \text{constant}$$

Inclusion of surface effects lead to the expression for dU,

$$dU = T\,dS - P\,dV + \gamma\,d\mathscr{A} + \mu\,dn$$

where γ is called 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.

PROBLEMS

Problems for Section 6.1

6.16. For water at equilibrium at 1.000 atm and 273.15 K, find the values of $G_{\mathrm{m}}^{(\mathrm{l})} - G_{\mathrm{m}}^{(\mathrm{s})}$, $A_{\mathrm{m}}^{(\mathrm{l})} - A_{\mathrm{m}}^{(\mathrm{s})}$, $H_{\mathrm{m}}^{(\mathrm{l})} - H_{\mathrm{m}}^{(\mathrm{s})}$, $U_{\mathrm{m}}^{(\mathrm{l})} - U_{\mathrm{m}}^{(\mathrm{s})}$, and $S_{\mathrm{m}}^{(\mathrm{l})} - S_{\mathrm{m}}^{(\mathrm{s})}$.

***6.17.** For water at equilibrium at 1.000 atm and 373.15 K, find the values of $G_{\mathrm{m}}^{(\mathrm{g})} - G_{\mathrm{m}}^{(\mathrm{l})}$, $A_{\mathrm{m}}^{(\mathrm{g})} - A_{\mathrm{m}}^{(\mathrm{l})}$, $H_{\mathrm{m}}^{(\mathrm{g})} - H_{\mathrm{m}}^{(\mathrm{l})}$, $U_{\mathrm{m}}^{(\mathrm{g})} - U_{\mathrm{m}}^{(\mathrm{l})}$, and $S_{\mathrm{m}}^{(\mathrm{g})} - S_{\mathrm{m}}^{(\mathrm{l})}$. State any assumptions.

6.18. For water at equilibrium at 23.756 torr and 298.15 K, find the values of $G_{\mathrm{m}}^{(\mathrm{g})} - G_{\mathrm{m}}^{(\mathrm{l})}$, $A_{\mathrm{m}}^{(\mathrm{g})} - A_{\mathrm{m}}^{(\mathrm{l})}$, $H_{\mathrm{m}}^{(\mathrm{g})} - H_{\mathrm{m}}^{(\mathrm{l})}$, $U_{\mathrm{m}}^{(\mathrm{g})} - U_{\mathrm{m}}^{(\mathrm{l})}$, and $S_{\mathrm{m}}^{(\mathrm{g})} - S_{\mathrm{m}}^{(\mathrm{l})}$. State any assumptions.

Problems for Section 6.2

***6.19.** Give the number of independent 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 CO_2 only.

6.20. 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

$$N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$$

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.

*6.21. A researcher exhibits a photograph showing four phases, which he claims are ice I, ice II, liquid water, and water vapor. What is your comment?

Problems for Section 6.3

6.22. Find 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 Gibbs energy change of formation of diamond is $2.90\ \mathrm{kJ\,mol^{-1}}$ at 298.15 K. State any assumptions.

*6.23. The triple point of ammonia is at 196.2 K and 49.42 torr. The molar enthalpy change of vaporization is equal to $24.65\ \mathrm{kJ\,mol^{-1}}$ at this temperature.

a. Find the normal boiling temperature of ammonia. State any assumptions.

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.

6.24. **a.** The vapor pressure of ice 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. State any assumptions.

c. Find the enthalpy change of fusion of water. State any assumptions.

*6.25. **a.** Find the pressure needed in an autoclave 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 psi.

b. Calculate the freezing temperature of water at a pressure equal to the pressure of part (a).

6.26. The enthalpy change of vaporization of ethanol at its normal boiling temperature of 78.5°C is $40.48\ \mathrm{kJ\,mol^{-1}}$.

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). State any assumptions or approximations.

*6.27. Calculate 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.

6.28. At −78.5°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.

6.29. 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.

6.30. 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 graphical method or a linear least-square procedure, find the enthalpy change of vaporization of aluminum.

6.31. **a.** Derive a modified version of the Clausius–Clapeyron equation using the relation

$$\Delta H_{\mathrm{m}}(T) = \Delta H_{\mathrm{m}}(T_1) + \Delta C_{P,\mathrm{m}}(T - T_1)$$

where $\Delta C_{P,\mathrm{m}}$ is assumed to be constant.

*b. Using data from Table A.8 and the value of water's vapor pressure at 25.0°C, 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. (6.3-14). Compare both results with the experimental value, 92.5 torr.

Problems for Section 6.4

6.32. **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.

6.33. 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 1.00 atm, using data in Tables A.7 and A.8 of the appendix. Assume that the heat capacities are constant.

6.34. 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 273.15 K equal zero. State any assumptions.

***6.35.** Find difference in the slopes of the two tangent lines at the cusp in each of the following graphs:

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.

Problems for Section 6.5

6.36. 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) droplets with diameter 10.0 μm and (b) a "drop" containing 1.00 mol.

6.37. Explain why interfacial tensions between two liquid phases are generally smaller in magnitude than surface tensions between liquid and vapor phases.

6.38. Estimate the surface tension of ethanol as was done for carbon tetrachloride in Example 6.6. 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.

***6.39.** Calculate the capillary rise of pure water in a glass capillary of radius 0.300 mm at 298.15 K. Assume zero contact angle.

6.40. Give an alternate derivation of the capillary rise formula for zero contact angle beginning with the Laplace equation, Eq. (6.5-13), and assuming that the meniscus is a hemisphere.

***6.41.** 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 15 mm in diameter. Remember that there is a surface on both the inner and outer diameter of the ring.

6.42. Calculate the vapor pressure of a droplet of ethanol with a radius of 0.00500 mm at 19°C. The vapor pressure at a planar surface is equal to 40.0 torr at this temperature.

6.43. Give an alternate derivation of the expression for the vapor pressure of a spherical droplet, Eq. (6.5-20), using the Laplace equation, Eq. (6.5-13) and the relation between pressure on the liquid phase and the vapor pressure, Eq. (6.3-17).

Problems for Section 6.6

6.44. The following data on the surface tension of aqueous sodium chloride solutions at 25.0°C were taken by a student in a physical chemistry laboratory:

c/mol L^{-1}	0.00	1.00	2.00	3.00	4.00
γ/N m^{-1}	0.0720	0.0809	0.0821	0.0841	0.0904

Using Eq. (6.6-12b), find the surface concentration of sodium chloride at 1.00 mol L^{-1} and at 2.00 mol L^{-1}. What does the sign of this quantity tell you?

***6.45.** The following data on the surface tension of aqueous 1-butanol solutions at 25.0°C were taken by a student in a physical chemistry laboratory:

c/mol L^{-1}	0.00	0.110	0.140	0.190	0.250	0.450	0.600
γ/N m^{-1}	0.0720	0.0595	0.0574	0.0515	0.0475	0.0412	0.0354

Using Eq. (6.6-12a), find the surface concentration of 1-butanol at 0.100 mol L^{-1} and at 0.200 mol^{-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.

General Problems

6.46. **a.** 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. Use the Clausius–Clapeyron equation to estimate the vapor pressure of water at 100°C. Compare your result with an actual value, 760.0 torr.

b. Use the modified Clausius–Clapeyron equation derived in Problem 6.31 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 $\Delta_{\text{vap}}H_{\text{m}}$ 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 6.31 to estimate the vapor pressure of water at 647.4 K. Comment on your result.

f. As the critical temperature is approached from below, all distinctions between the liquid phase and the vapor phase gradually disappear. Among other things, $\Delta_{\text{vap}}H_{\text{m}}$ must vanish at the critical point. 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 $\Delta_{\text{vap}}H_{\text{m}}$ that this assumption predicts at 647.4 K. Find the temperature at which $\Delta_{\text{vap}}H_{\text{m}}$ vanishes according to this assumption, and compare your value with the actual critical temperature.

***6.47.** 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.

7

Multicomponent Systems

OBJECTIVES

After studying this chapter, the student should:

1. be able to solve problems involving ideal solutions and dilute solutions;
2. be able to solve problems involving activities and activity coefficients in nonideal solutions;
3. understand the principles governing phase diagrams and be able to interpret phase diagrams for various kinds of systems;
4. be able to solve problems involving colligative properties.

PRINCIPAL FACTS AND IDEAS

1. Ideal solutions are defined such that 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, R is the ideal gas constant, T is the absolute temperature, and x_i is the mole fraction of the substance in the solution, which can be a liquid solution or a solid solution.

2. Every component in an ideal solution at equilibrium with an ideal vapor phase obeys Raoult's law at all compositions:

$$P_i = P_i^* x_i$$

where P_i is the partial pressure of gaseous substance i at equilibrium with the solution and P_i^* is the partial pressure of gaseous substance i at equilibrium with pure liquid or solid substance i.

3. Solutes in dilute solutions at equilibrium with an ideal phase 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.

4. Activities and activity coefficients describe deviations from ideal or dilute behavior.
5. The activities of strong electrolyte solutes require special treatment.
6. Phase diagrams can be used to show the phase equilibria of multicomponent systems, and can be understood through the phase rule of Gibbs.
7. Colligative properties depend on concentrations of solutes, but not on their identities.

7.1 Ideal Solutions

A homogeneous liquid or solid mixture is often called a solution. If in a given solution one component is present in a larger amount than the others, it is called the **solvent**. The other substances are called **solutes**. An **ideal solution** is defined as one in which the chemical potential of each component is given for all compositions by the formula

$$\mu_i(T, P) = \mu_i^*(T, P) + RT\ \ln(x_i) \quad \text{(definition of an ideal solution)} \tag{7.1-1}$$

where $\mu_i^*(T, P)$ is the chemical potential of the pure substance i when it is at the temperature T, and pressure, P, of the solution, and where x_i is the mole fraction of substance i in the solution. Like the ideal gas, the ideal solution is a model system. It closely resembles some real solutions. However, any dilute gas approximates ideal gas behavior, while there are solutions that do not approximate ideal solution behavior under any circumstances.

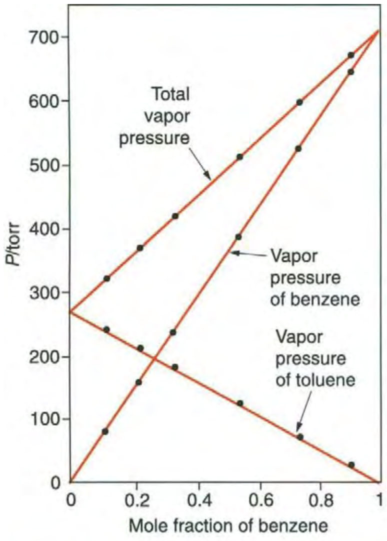

Figure 7.1. The Partial Vapor Pressures of Benzene and Toluene in a Solution at 80°C. These substances form a very nearly ideal solution, as shown by conformity to Raoult's law. Drawn from data of M. A. Rosanoff, C. W. Bacon, and F. W. Schulze, *J. Am. Chem. Soc.*, **36**, 1993 (1914).

Raoult's law is named for Francois Marie Raoult, 1830–1901, a French chemist who was one of the founders of physical chemistry.

Raoult's Law

Ideal solutions exhibit two important properties that follow from Eq. (7.1-1). The first property is: *The equilibrium partial vapor pressure of each component of an ideal solution very nearly obeys Raoult's law for all compositions of the solution.* We state Raoult's law as

$$P_i = P_i^* x_i \quad \text{(Raoult's law)} \tag{7.1-2}$$

where P_i is the **partial vapor pressure** of substance i, the partial pressure of the substance in the vapor phase that is equilibrated with the solution. P_i^* is the equilibrium vapor pressure of the pure substance i at the temperature and pressure of the solution, and x_i is the mole fraction of substance i in the solution (not in the vapor phase). Figure 7.1 illustrates Raoult's law in the case of toluene and benzene, which form a very nearly ideal solution. It 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 version of Raoult's law shown in Eq. (7.1-2) corresponds to the assumption that the vapor phase at equilibrium with the solution is an ideal gas mixture. If the vapor phase is not ideal, the partial vapor pressure of the substance in the gas phase must be replaced by the fugacity of the gas, defined in Eq. (5.3-6). We will assume that the vapor phase is ideal.

Raoult's law is a consequence of the relation shown in Eq. (7.1-1) if the ideal solution is at equilibrium with an ideal vapor phase. The chemical potential of component i in the vapor phase is given by Eq. (5.4-24),

$$\mu_i = \mu_i^{\circ(\text{gas})} + RT\ \ln\left(\frac{P_i}{P^\circ}\right) \tag{7.1-3}$$

where P° is the standard-state pressure (1 bar), $\mu_i^{\circ(\text{gas})}$ is the chemical potential of the gas in its standard state, and P_i is the partial pressure of component i in the vapor phase.

From the fundamental fact of phase equilibrium, the chemical potential of component i has the same value in the solution and in the vapor:

$$\mu_i^*(T, P) + RT\ \ln(x_i) = \mu_i^{\circ(\text{gas})} + RT\ \ln\left(\frac{P_i}{P^\circ}\right) \tag{7.1-4}$$

where P stands for the actual pressure exerted on the solution. With this equation, we are using the vapor phase as a probe to study the solution.

Since P is not necessarily equal to P° or to the equilibrium vapor pressure of the pure substance, we can write from Eq. (6.4-4)

$$\mu_i^*(T, P_i^*) - \mu_i^*(T, P) = V_\text{m}^*(i, \text{liq})(P_i^* - P) \approx 0 \tag{7.1-5}$$

where $V_\text{m}^*(i, \text{liq})$ is the molar volume of the pure liquid substance i. We will assume that this quantity is negligible (See Exercise 7.1.)

The chemical potential of pure liquid component i is equal to the chemical potential of gaseous component i at pressure P_i^* by the fundamental fact of phase equilibrium, so that

$$\mu_i^{(\text{gas})}(T, P_i^*) = \mu_i^{\circ(\text{gas})} + RT\ \ln\left(\frac{P_i^*}{P^\circ}\right) \tag{7.1-6}$$

When Eqs. (7.1-4), (7.1-6), and (7.1-5) are combined, we obtain

$$RT\ \ln\left(\frac{P_i^* x_i}{P^\circ}\right) = RT\ \ln\left(\frac{P_i}{P^\circ}\right) \tag{7.1-7}$$

We take antilogarithms and obtain

$$P_i = P_i^* x_i \tag{7.1-8}$$

which is Raoult's law, Eq. (7.1-2). An ideal solution obeys Raoult's law except for a small pressure correction (shown in Eq. (7.1-5)), which we neglect. There is an also small correction for nonideality of the vapor, which we also neglect.

*Exercise 7.1

The density of ethanol is equal to $0.7885\ \text{g cm}^{-3}$ at 19.0°C. Its equilibrium vapor pressure at 19.0°C is equal to 40.0 torr. Find the value of the quantity shown in Eq. (7.1-5) at 19.0°C for ethanol at $P = 1.000\ \text{atm}$ and compare the value of this term with the value of $RT\ \ln(P_i^*/P^\circ)$, assuming a mole fraction of 0.500.

An ideal solution is sometimes defined as a solution that obeys Raoult's law for all compositions. If this definition is taken, it can be shown that Eq. (7.1-1) follows as a consequence.

Exercise 7.2

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 Eq. (7.1-1). State any assumptions.

The Thermodynamic Variables of an Ideal Solution

The thermodynamic properties of any kind of a system are specified with reference to a standard state. We have already defined the standard state of a gas to be the ideal gas at a pressure of exactly 1 bar (denoted by P°), and that of pure liquids and solids to be the substance at pressure P°. There does not seem to be universal agreement about the standard state for a component of an ideal solution. Some authors take the pure substance i at the pressure of the solution as the standard state of substance i in the solution, so that $\mu_i^*(T, P) = \mu_i^\circ$. The pressure on the solution can take any value, although if the solution is open to the atmosphere, the pressure on it will be equal to the barometric pressure. In this case the pressure is not necessarily equal to the vapor pressure of the solution, because air is also present in the gas mixture at equilibrium with the solution.

We will use the other (more common) practice of defining the standard state of a component of an ideal liquid solution to be the pure liquid at a pressure of 1 bar (exactly), and the standard state of a component of an ideal solid solution to be the pure solid at a pressure of 1 bar. This will have the advantage that all of our standard states are at the same pressure, exactly 1 bar (100,000 Pa or 0.98692 atm). If the solution is not under an extremely high pressure, it makes no significant numerical difference whether the standard state is at 1 bar or at some other pressure, as the correction would be like the correction term of Eq. (7.1-5), evaluated in Exercise 7.2. To adequate accuracy, we will write a modified version of Eq. (7.1-1):

$$\mu_i(T, P) = \mu_i^\circ(T) + RT \ln(x_i) \tag{7.1-9}$$

where $\mu_i^\circ(T)$ is the chemical potential of the pure substance i in its standard state at pressure 1 bar. The standard state does not specify any particular temperature, so we include its dependence on T.

The thermodynamic variables of a solution are usually expressed in terms of the quantities of mixing. These quantities are *defined* as the change in the variable for formation of the solution from the unmixed components at the same temperature and pressure. For example, the **Gibbs energy change of mixing** is

$$\Delta G_{\text{mix}} = G(\text{solution}) - G(\text{unmixed}) = \sum_{i=1}^{c} n_i\mu_i - \sum_{i=1}^{c} n_i\mu_i^* \tag{7.1-10}$$

where we have used Euler's theorem, Eq. (5.6-4), to express G(solution) and have used the fact that the Gibbs energy of the unmixed components is a sum of contributions, one for each component.

The second important property of an ideal solution is: *The Gibbs energy change of mixing and the entropy change of mixing of an ideal solution are given by the same formulas as for a mixture of ideal gases.* From Eq. (7.1-1) and from Euler's theorem,

$$G(\text{solution}) = \sum_{i=1}^{c} n_i[\mu_i^* + RT \ln(x_i)] \tag{7.1-11}$$

The Gibbs energy change of mixing is now

$$\Delta G_{\text{mix}} = G(\text{solution}) - G(\text{unmixed}) = RT \sum_{i=1}^{c} n_i \ln(x_i) \tag{7.1-12}$$

This is the same formula as for the Gibbs energy change of mixing for a mixture of ideal gases.

Exercise 7.3

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. (7.1-12).

Once an expression for one thermodynamic quantity is obtained, we can obtain an expression for other thermodynamic quantities by the use of thermodynamic identities. For example, we can obtain the entropy change of mixing for an ideal solution by use of Eq. (5.2-20).

$$-S(\text{solution}) = \left(\frac{\partial G(\text{solution})}{\partial T}\right)_{P,n} \tag{7.1-13}$$

Using Eq. (7.1-11), this equation becomes

$$-S(\text{solution}) = \sum_{i=1}^{c} n_i\left[\left(\frac{\partial \mu_i^*}{\partial T}\right)_P + R\ \ln(x_i)\right] \tag{7.1-14}$$

For the unmixed components,

$$-S(\text{unmixed}) = \sum_{i=1}^{c} n_i\left(\frac{\partial \mu_i^*}{\partial T}\right)_P \tag{7.1-15}$$

so that

$$\Delta S_{\text{mix}} = -R\sum_{i=1}^{c} n_i\ \ln(x_i) \quad \text{(ideal solution)} \tag{7.1-16}$$

which is the same as the formula for an ideal gas mixture, Eq. (4.3-20).

The enthalpy change of mixing for a solution is defined as the change in enthalpy to form the solution from the unmixed components at the same temperature and pressure. For an isothermal mixing process, we apply Eq. (5.1-14) to both the solution and the unmixed substances, and obtain

$$\Delta H_{\text{mix}} = \Delta G_{\text{mix}} + T\ \Delta S_{\text{mix}} \tag{7.1-17}$$

from which we can write

$$\Delta H_{\text{mix}} = RT\sum_{i=1}^{c} n_i[\ln(x_i) - \ln(x_i)] = 0 \quad \text{(ideal solution)} \tag{7.1-18}$$

As with ΔS_{mix} and ΔG_{mix}, this is the same formula as for ΔH_{mix} for an ideal gas mixture. We can obtain a formula for the volume change of mixing from the relation of Eq. (5.2-21), writing this equation for the solution and for the unmixed components. The result is

$$\Delta V_{\text{mix}} = 0 \quad \text{(ideal solution)} \tag{7.1-19}$$

Exercise 7.4

Show that Eq. (7.1-19) is correct.

EXAMPLE 7.1

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.

Solution

We assume the solution to be ideal:

$$\Delta G_{\text{mix}} = RT[1.200\ \text{mol})\ \ln(0.4800) + (1.300\ \text{mol})\ \ln(0.5200)] = -4219\ \text{J}$$

$$\Delta S_{\text{mix}} = -R[(1.200\ \text{mol}\ \ln(0.4800) + (1.300\ \text{mol})\ \ln(0.5200)] = 14.39\ \text{J K}^{-1}$$

$$\Delta H_{\text{mix}} = 0$$

$$\Delta V_{\text{mix}} = 0$$

We can also obtain expressions for other partial molar quantities from the expression for the chemical potential. For example, to obtain the expression for the partial molar entropy, we use Eq. (5.5-10):

$$\bar{S}_i = -\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n} \tag{7.1-20}$$

Application of this equation to Eq. (7.1-1) gives

$$\bar{S}_i = -\left(\frac{\partial \mu_i^*}{\partial T}\right)_{P,n} - R\ \ln(x_i)$$

$$\boxed{\bar{S}_i = S^*_{\text{m},i} - R\ \ln(x_i) \quad \text{(ideal solution)}} \tag{7.1-21}$$

where $S^*_{\text{m},i}$ is the molar entropy of pure substance i.

Exercise 7.5

In the same way that Eq. (7.1-21) was derived, obtain the relations for an ideal solution:

$$\boxed{\bar{V}_i = V^*_{\text{m},i} \quad \text{(ideal solution)}} \tag{7.1-22}$$

$$\boxed{\bar{H}_i = H^*_{\text{m},i} \quad \text{(ideal solution)}} \tag{7.1-23}$$

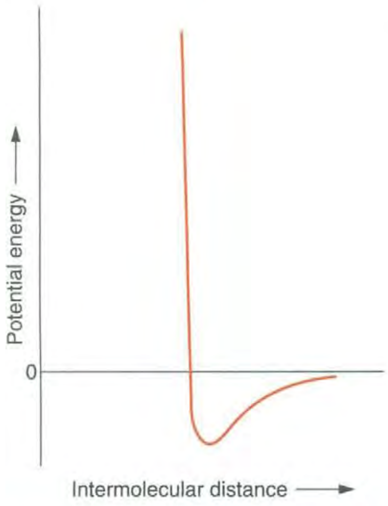

Figure 7.2. The Potential Energy of a Pair of Molecules (Schematic). This potential energy leads to attractions at moderate intermolecular distances and repulsions at small intermolecular distances.

Although the entropy change of mixing, the Gibbs energy change of mixing, and the enthalpy change of mixing for an ideal solution are given by the same formulas as the corresponding quantities for a mixture of ideal gases, this does not imply that an ideal solution resembles a mixture of ideal gases in its molecular structure. The ideal gas is a model system in which the molecules do not interact with each other. In a liquid or solid solution there is a large intermolecular attraction that holds the system together and a large intermolecular repulsion that keeps the system from collapsing to a smaller volume. The intermolecular attraction and repulsion of a pair of molecules correspond to a potential energy that depends on intermolecular distance as shown in Figure 7.2, which depicts the potential energy of a pair of spherical molecules as a function of the distance between their centers. Since any potential energy $\mathcal{V}$ corresponds to a force pointing in the direction in which $\mathcal{V}$ decreases, there is an attraction at moderate distances and a repulsion at smaller distances. For nonspherical molecules there is also a dependence of the potential energy on the relative orientations of the molecules.

It is found experimentally that Raoult's law applies most nearly to mixtures of substances in which the substances have molecules of similar size, shape, and polarity. For example, benzene and toluene form a nearly ideal solution. The explanation for this fact is that two molecules of similar substances interact with each other in much the same way as with molecules of their own kind. The potential energy curve analogous to that of Figure 7.2 that applies to one benzene molecule and one molecule of toluene must be nearly the same as the curve that applies to two benzene molecules or the curve that applies to two toluene molecules. If a molecule of toluene is substituted for a molecule of benzene in the solution, the energy, the enthalpy, and the volume of the solution are therefore almost unchanged. The similarity between the molecules also allows them to mix randomly in a solution just as noninteracting molecules mix randomly in an ideal gas mixture, so that the formulas for the entropy changes of mixing are the same for an ideal solution and for an ideal gas mixture.

***Exercise 7.6**

From the following list, pick pairs of substances that you think will probably form nearly ideal liquid solutions:

o-xylene
p-xylene
ethylbenzene
2-propanol
anthracene
3-methylpentane
3-pentanone
propanol
m-xylene
toluene
1-propanol
naphthalane
phenanthrene
2-methylpentane
2-pentanone
propanone

Phase Diagrams of Two-Component Ideal Solutions

Phase diagrams are graphs that show the regions in a state space that corresponds to various numbers of phases. In a phase diagram for one component, as in Figure 6.3 or Figure 6.4, the plane of the diagram represents a state space with axes corresponding to T and P, and curves are the boundaries between regions corresponding to particular phases. In an equlibrium two-component system with one phase, Gibb's phase rule gives

$$f = c - p + 2 = 2 - 1 + 2 = 3$$

so that there are three independent intensive variables, which we take to be T and P and one mole fraction. The full phase diagram therefore requires three dimensions. To make a two-dimensional phase diagram, we specify a fixed value for one variable. There are two principal types of two-dimensional phase diagrams for a two-component solution. One is the **pressure–composition phase diagram**, for which 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 solution obeying Raoult's law, the partial pressure of both components is given by Eq. (7.1-2), so the total vapor pressure is

$$P_{\text{tot}} = P_1^* x_1 + P_2^* x_2 = P_2^* + (P_1^* - P_2^*)x_1 \tag{7.1-24}$$

where we have used the relationship $x_2 = 1 - x_1$. This equation is represented by a straight line in the pressure–composition phase diagram.

Exercise 7.7

Show that the intercepts of the function in Eq. (7.1-24) 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 the liquid solution is not the same as the composition of the liquid solution. If we assume that the vapor phase is ideal, the mole fraction of component 1 in the vapor is given by Dalton's law of partial pressures:

$$y_1 = \frac{P_1}{P_{\text{tot}}} = \frac{P_1^* x_1}{P_2^* + (P_1^* - P_2^*)x_1} \tag{7.1-25}$$

where we denote the mole fraction of component 1 in the vapor phase by y_1.

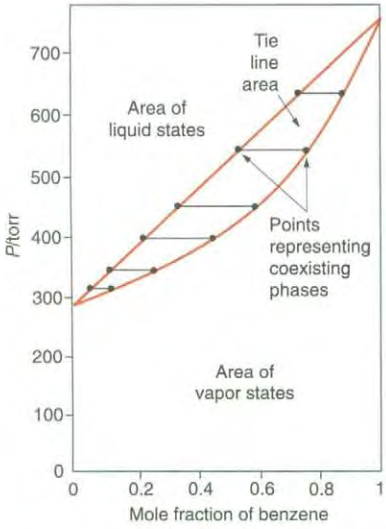

Figure 7.3. The Liquid–Vapor Pressure–Composition Phase Diagram of Benzene and Toluene at 80°C. The upper curve, which is the same as the upper curve in Figure 7.1, shows the pressure as a function of mole fraction in the liquid phase, and the lower curve shows the pressure as a function of mole fraction in the vapor phase. The two compositions that can coexist at a given pressure are given by the ends of the tie line at that pressure. Drawn from data of M. A. Rosanoff, C. W. Bacon, and F. W. Schulze, *J. Am. Chem. Soc.*, **36**, 1993 (1914).

EXAMPLE 7.2

The vapor pressure of pure benzene 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 composition of the vapor at equilibrium with the solution of Example 7.1.

Solution

Call benzene component 1 and toluene component 2:

$$P_1 = (0.48)(74.9\ \text{torr}) = 36.0\ \text{torr}$$

$$P_2 = (0.52)(21.6\ \text{torr}) = 11.2\ \text{torr}$$

$$P_{\text{tot}} = P_1 + P_2 = 47.2\ \text{torr}$$

$$y_1 = \frac{P_1}{P_{\text{tot}}} = \frac{36.0\ \text{torr}}{47.2\ \text{torr}} = 0.763$$

$$y_2 = \frac{P_2}{P_{\text{tot}}} = \frac{11.2\ \text{torr}}{47.2\ \text{torr}} = 0.237$$

The formula giving the total pressure as a function of y_1, the mole fraction of component 1 in the vapor phase, is

$$P_{\text{tot}} = \frac{P_1^* P_2^*}{P_1^* + y_1(P_2^* - P_1^*)} \tag{7.1-26}$$

The derivation of this formula is left as a problem (Problem 7.37).

Figure 7.3 shows the liquid–vapor pressure–composition phase diagram of benzene and toluene, which form a nearly ideal solution, at 80°C. The line represents Eq. (7.1-25), giving the pressure as a function of the benzene mole fraction in the liquid, and the other curve represents Eq. (7.1-26), giving the pressure as a function of the mole fraction of benzene in the vapor. The area below the curves represents possible equilibrium intensive states of the system when it is a one-phase vapor. The phase rule implies that there are three independent intensive variables for two components and one phase. In addition to the temperature, both the mole fraction and the pressure are independent, so that any point in this area represents a possible state of the system. The area above both curves represents possible equilibrium states of the system when it is a one-phase liquid, and any point in this area represents a possible state of the system.

The area between the curves represents two-phase states. In addition to the temperature (held fixed for this diagram) there is only one independent intensive variable. Therefore, a point in this area, corresponding to a value of P and a value of one mole fraction, cannot represent a possible intensive state of the system. A horizontal line segment, or **tie line**, between the two curves connects the state points for the two phases at equilibrium with each other. Several tie lines are shown in the figure. There is only one tie line for a given value of the pressure, so that the compositions of the two phases are dependent variables once the temperature and the pressure are chosen.

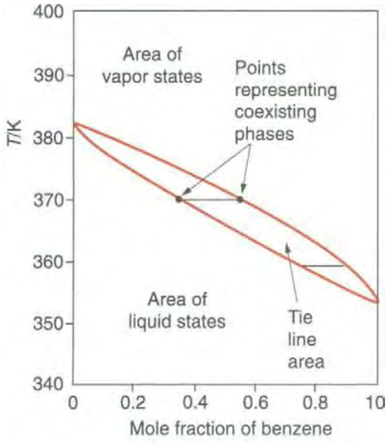

Figure 7.4. The Liquid–Vapor Temperature–Composition Phase Diagram of Benzene and Toluene at 1.000 atm. The lower curve shows the temperature as a function of the mole fraction in the liquid, and the upper curve shows the temperature as a function of the mole fraction in the vapor. Drawn from data of M. A. Rosanoff, C. W. Bacon, and F. W. Schulze, *J. Am. Chem. Soc.*, **36**, 1993 (1914).

The second common type of two-dimensional phase diagram for a two-component system is the **temperature–composition diagram**, in which the variables are the mole fraction of one component and the temperature, with the pressure held fixed. Figure 7.4 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. Tie lines drawn between the two curves connect values of the mole fraction in the two phases at equilibrium with each other. Each tie line in this diagram must correspond to a tie line in one of the pressure–composition diagrams.

A constant-pressure **distillation process** can be described with the temperature–composition phase diagram, as depicted in Figure 7.5. 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 further up the column, giving a liquid corresponding to point e. This process corresponds to two theoretical plates, with a temperature that changes as one moves up the column. A continuation of the process leads to a staircase pattern in the diagram, with one step for each theoretical plate. 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.

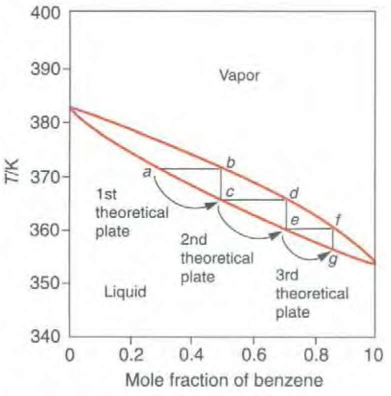

Figure 7.5. Diagram Representing a Constant-Pressure Distillation Process. Each theoretical plate corresponds to one step in the "staircase."

*Exercise 7.8

Estimate from Figure 7.5 the composition and boiling temperature of the condensate produced from the liquid at point a by a still with three theoretical plates.

The solid–liquid phase diagrams for a two-component mixture are similar to liquid–vapor phase diagrams if the solids are at least partially miscible. Figure 7.6 shows the temperature–composition phase diagram of silicon and germanium, which are miscible in the solid phase and form a nearly ideal solid solution. Note the similarity with Figure 7.4, which shows a liquid–vapor equilibrium of benzene and toluene. The area below the two curves in Figure 7.6 represents one-phase solid states (solid solutions), and the area above the two curves represents one-phase liquid states (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 7.7.

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 7.8, which represents the liquid–vapor equilibrium of a nearly ideal liquid solution. The compositions of the liquid and of the vapor at equilibrium with each other are represented by two surfaces, and tie-lines parallel to the composition axis connect coexisting states on these two surfaces. A pressure–composition diagram is created by passing a plane of constant temperature through the three-dimensional graph, and a temperature–composition diagram is created by passing a plane of constant pressure through the three-dimensional graph. The intersection of these two planes contains the common tie line of the two diagrams, as shown in the figure.

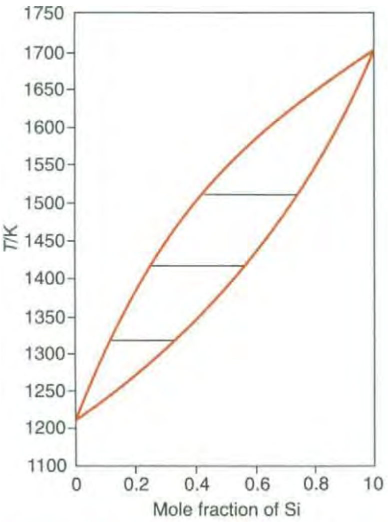

Figure 7.6. The Solid–Liquid Temperature–Composition Phase Diagram of Silicon and Germanium. Since both the solid and liquid phases are nearly ideal solutions, this diagram resembles the liquid–vapor phase diagram of an ideal liquid solution. From. D. Thurmond, *J. Phys. Chem.*, **57**, 827 (1953).

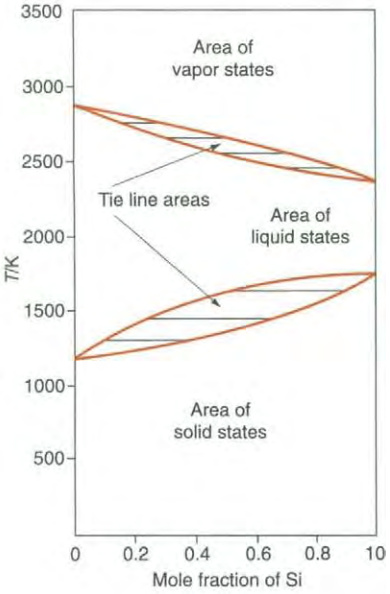

Figure 7.7. The Solid–Liquid and Liquid–Vapor Phase Diagram of Silicon and Germanium (Schematic). This diagram shows both the solid–liquid and liquid–vapor phase transitions.

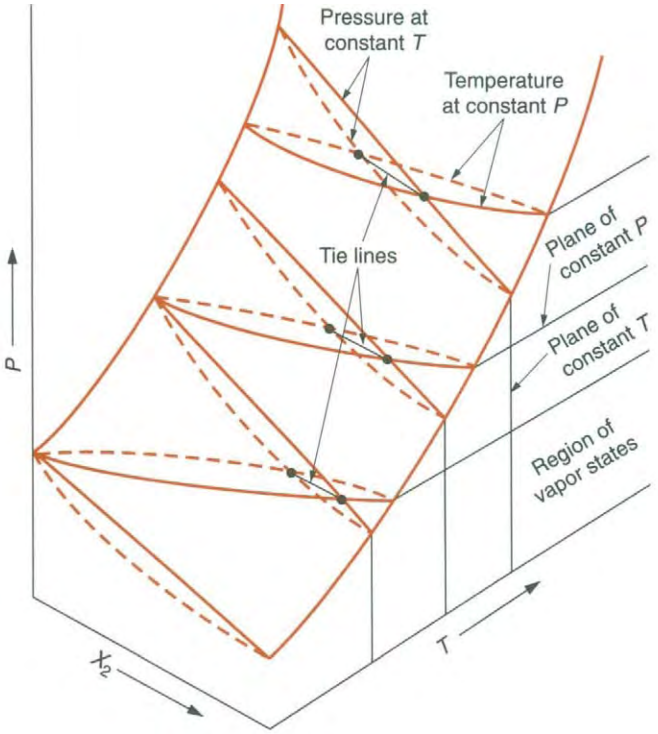

Figure 7.8. The Three-Dimensional Liquid–Vapor Phase Diagram for an Ideal Solution (Schematic). This diagram shows how both the temperature–composition phase diagram and the pressure–composition phase diagrams are obtained by passing planes through the same three-dimensional diagram.

7.2 Henry's Law and Dilute Nonelectrolyte Solutions

Most liquid and solid solutions are not well described by Raoult's law. Figure 7.9 shows the partial vapor pressures and total vapor pressure of a mixture of diethyl ether (component 1) and ethanol (component 2) at 20°C. In this system, the partial vapor pressures of both components are greater than predicted by Raoult's law, which is represented by broken lines. This behavior is called **positive deviation** from Raoult's law. Since both types of molecules have a greater tendency by move from the solution into the vapor phase than in an ideal solution, this corresponds to greater repulsions between unlike molecules than between like molecules and/or to lesser attractions

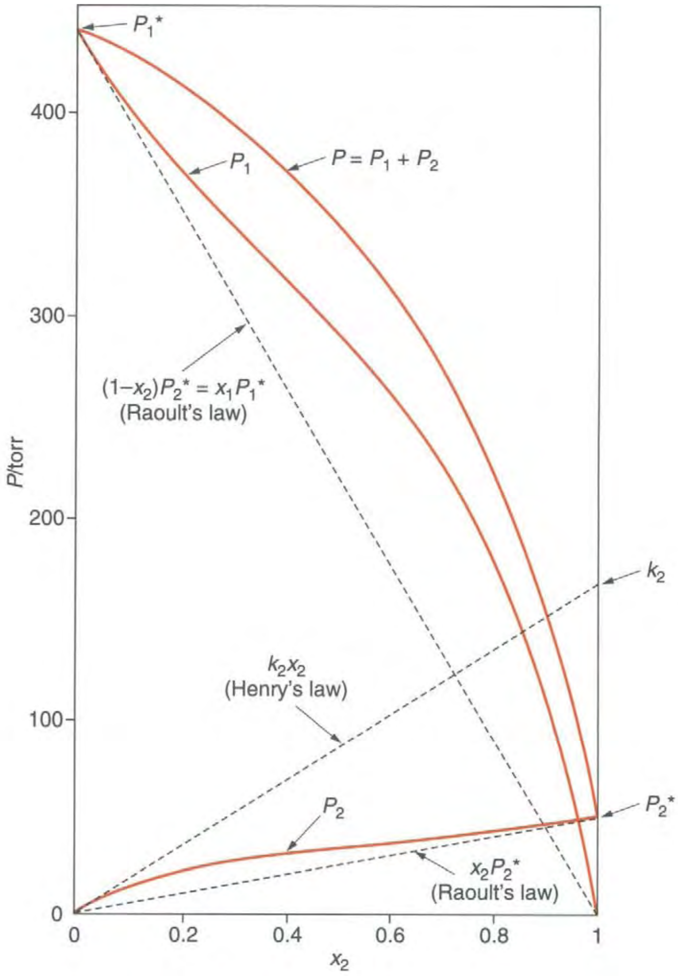

Figure 7.9. Partial Vapor Pressures of Ethanol (Component 2) and Diethyl Ether in a Solution at 20°C, Showing Positive Deviation from Raoult's Law. In addition to the actual behavior, this diagram shows the Raoult's-law behavior for both substances, and the Henry's law behavior for ethanol. Drawn from data of J. Timmermans, *Physicochemical Constants of Binary Systems*, Vol. 2, Interscience Publishers, New York, 1959, p. 401.

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. 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 7.9

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, 2–2 molecular interactions?

There are two features of Figure 7.9 that are typical for nonionic substances. The first is that for small values of x_1 the curve representing P_1 is nearly straight, and for small values of x_2 the curve representing P_2 is nearly straight. The second is that the curve representing P_1 nearly coincides with the line representing Raoult's law for values of x_1 near unity. The same is true of the curve representing P_2 for values of x_2 near unity. These properties can be summarized: A nearly pure component approximately obeys Raoult's law, and a dilute component approximately obeys **Henry's law**, which is written

$$P_i = k_i x_i \qquad (x_i \ll 1) \quad \text{(Henry's law)} \tag{7.2-1}$$

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 the atomic theory.

where k_i is called the **Henry's law constant** for substance i. It does not depend on the mole fraction, but depends on temperature and on the identities of all substances present. This situation is different from Raoult's law, in which the constant P_i^* depends only on temperature and the identity of substance i, and not on the identities of the other substances present.

A **dilute solution** is one in which the solute or solutes have small mole fractions, and in which the solvent has a mole fraction nearly equal to unity. In such a solution the solvent approximately obeys Raoult's law and the solutes approximately obey Henry's law. Most nonelectrolyte solutions behave like this at sufficiently low mole fractions of the solutes. The extrapolated line corresponding to Henry's law for ethanol (the solute) in diethyl ether (the solvent) is shown in Figure 7.9. The intercept of this line with the edge of the graph is equal to the value of Henry's law constant for ethanol in diethyl ether, approximately 160 torr at the temperature of the figure. The Henry's law constant for ethanol in solution with some solvent other than diethyl ether would have a different value.

Figure 7.9 could also represent a dilute solution of diethyl ether in ethanol, using the portion of the figure near the right edge. The diagram shows that ethanol nearly obeys Raoult's law for values of x_2 near unity, and that diethyl ether nearly obeys Henry's law for small values of x_1, although the line representing Henry's law for diethyl ether is not shown in the diagram.

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[1] See M. L. McGlashan, *J. Chem. Educ.*, **40**, 516 (1963).

EXAMPLE 7.3

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 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 7.10**

Find the value of 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. State any assumptions.

The Chemical Potential in a Dilute Solution

Consider a dilute solution in which the partial vapor pressure of the solute is large enough to measure. We equilibrate the solution with a vapor phase, which we assume to be ideal. Using Henry's law, Eq. (7.2-1), for the partial vapor pressure of substance number i (a solute), we have from the fundamental fact of phase equilibrium:

$$\mu_i^{(\text{soln})} = \mu_i^{(\text{gas})} = \mu_i^{\circ(\text{gas})} + RT\ \ln\left(\frac{k_i x_i}{P^\circ}\right)$$

To make this equation resemble Eq. (7.1-9), we write

$$\mu_i^{(\text{soln})} = \mu_i^{\circ(\text{H})} + RT\ \ln(x_i) \quad \text{(dilute solute)} \tag{7.2-2}$$

where

$$\mu_i^{\circ(\text{H})} = \mu_i^{\circ(\text{gas})} + RT\ \ln\left(\frac{k_i}{P^\circ}\right) \tag{7.2-3}$$

Since $\mu_i^{\circ(\text{H})}$ is equal to the chemical potential of component i in the vapor phase when the partial pressure P_i is equal to k_i, it is equal to the chemical potential that the pure liquid would have if it obeyed Henry's law for for $x_i = 1$. We define this "hypothetical" pure liquid to be the **standard state** for substance i in the dilute solution. We refer to $\mu_i^{\circ(\text{H})}$ as the standard-state chemical potential of substance i for this particular standard state. This standard state depends on the temperature and on the identity of the solvent as well as on the identity of the solute. As with the standard state of a component of an ideal solution, we specify a pressure of exactly 1 bar for this standard state, in order for all of our standard states to be at the same pressure. This would require a small correction term like that in Eq. (7.1-5). We neglect this correction. It may seem strange at first glance to have a standard state that corresponds to a hypothetical pure substance when we are discussing a dilute solute. The reason for this choice is that it allows us to write Eq. (7.2-2) in the same form as Eq. (7.1-9).

Distribution of a Solute between Two Solvents

Consider the equilibrium of two solutions containing the same solute but with different solvents that do not mix appreciably. If iodine is dissolved in water most of the iodine can be extracted from the water by equilibrating this phase with carbon tetrachloride or another nonpolar solvent. Assuming that Henry's law is obeyed in both solutions, the equilibrium mole fraction of iodine in the water phase is proportional to the mole fraction of iodine in the carbon tetrachloride phase. This fact is called **Nernst's distribution law**. The proportionality constant K_d is called the **distribution constant**, and is given by

$$K_d = \frac{x_{i(\mathrm{II})}^{(\mathrm{eq})}}{x_{i(\mathrm{I})}^{(\mathrm{eq})}} \quad \text{(definition)} \tag{7.2-4}$$

where iodine is called substance i, and where the labels I and II denote two phases. For example, we could denote the carbon tetrachloride phase by I and the aqueous phase by II. In addition to depending on the identity of the solute, the value of K_d depends on temperature and on the identities of the two solvents.

We use the fundamental fact of phase equilibrium to derive Eq. (7.2-4). The chemical potential of iodine in the two phases is given by

$$\mu_{i(\mathrm{I})} = \mu_{i(\mathrm{I})}^{\circ(\mathrm{H})} + RT\ \ln(x_{i(\mathrm{I})}) \tag{7.2-5a}$$

and

$$\mu_{i(\mathrm{II})} = \mu_{i(\mathrm{II})}^{\circ(\mathrm{H})} + RT\ \ln(x_{i(\mathrm{II})}) \tag{7.2-5b}$$

where we add a subscript to specify the phase. At equilibrium,

$$\mu_{i(\mathrm{I})} = \mu_{i(\mathrm{II})}$$

We solve Eq. (7.2-5a) for $x_{i(\mathrm{I})}$ and solve Eq. (7.2-5b) for $x_{i(\mathrm{II})}$, and after using Eq. (7.2-3), we can write

$$K_d = \frac{x_{i(\mathrm{II})}^{(\mathrm{eq})}}{x_{i(\mathrm{I})}^{\mathrm{eq})}} = \exp\left[\frac{\mu_{i(\mathrm{I})}^{\circ(\mathrm{H})} - \mu_{i(\mathrm{II})}^{\circ(\mathrm{H})}}{RT}\right] = \frac{k_i^{(\mathrm{I})}}{k_i^{(\mathrm{II})}} \tag{7.2-6}$$

where $k_{i(\mathrm{I})}$ and $k_{i(\mathrm{II})}$ are the Henry's law constants for substance i in phases I and II, respectively.

Exercise 7.11

a. Carry out the steps to obtain Eq. (7.2-6).

***b.** The value of the distribution coefficient for iodine between water (phase II) and carbon tetrachloride (phase I) is approximately equal to 0.0022 at 25.0°C. If a solution containing 0.0100 mol of iodine 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. Neglect any water that dissolves in the carbon tetrachloride phase and any carbon tetrachloride that dissolves in the aqueous phase.

The **molality** of component i in a solution is defined by

$$m_i = \frac{n_i}{w_1} \quad (i = 2, 3, \ldots, c) \quad \text{(definition)} \tag{7.2-7}$$

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}, also referred to as "molal." We use the symbol w_1 for the mass of the solvent because m_i is the accepted symbol for the molality and another quantity denoted by the letter m would be confusing. For small amounts of the solute, the molality is nearly proportional to the mole fraction. If M_1 is the molar mass of the solvent, then

$$w_1 = n_1 M_1 \tag{7.2-8}$$

so that the mole fraction of component i is given by

$$x_i = \frac{n_i}{n_1 + n_2 + \cdots + n_c} = \frac{n_i}{(w_1/M_1) + n_2 + \cdots + n_c} \tag{7.2-9}$$

For a dilute solution, n_1 is much larger than the other amounts, so that

$$x_i \approx \frac{n_i M_1}{w_1} = m_i M_1 \tag{7.2-10}$$

In this case, Henry's law can be expressed in terms of the molality:

$$P_i = k_i m_i M_1 = k_i^{(m)} m_i \quad \text{(dilute solution)} \tag{7.2-11}$$

where $k_i^{(m)} = k_i M_1$ is the **molality Henry's law constant** for substance i. Like the Henry's law constant of Eq. (7.2-1) it depends not only on the identity of substance i but also on the identity of the solvent and on the temperature. Equation (7.2-11) is valid only for a dilute solution, as is generally the case with Henry's law.

EXAMPLE 7.4

a. From the value of k_2 for ethanol (substance 2) in Example 7.3, find the value of $k_2^{(m)}$.
b. Find the vapor pressure of a 0.0500 mol kg^{-1} solution of ethanol in benzene.

Solution

a.

$$k_2^{(m)} = (1.51 \times 10^3 \text{ torr})(0.07812 \text{ kg mol}^{-1}) = 118 \text{ torr (mol kg}^{-1})^{-1}$$

b.

$$P_2 = [118 \text{ torr (mol kg}^{-1})^{-1}][0.0500 \text{ mol kg}^{-1}] = 5.90 \text{ torr}$$

For a dilute solution, the chemical potential can be expressed in terms of the molality in an equation similar to Eqs. (7.2-2) and (7.1-9). Using Eqs. (7.2-2) and (7.2-10),

$$\mu_i = \mu_i^{\circ(H)} + RT \ln(m_i M_1) = \mu_i^{\circ(m)} + RT \ln(m_i/m^\circ) \quad \text{(dilute solution)} \tag{7.2-12}$$

where $\mu_i^{\circ(m)} = \mu_i^{\circ(H)} + RT \ln(M_1 m^\circ)$ and where m° is defined to equal 1 mol kg^{-1} (exactly).

The quantity $\mu_i^{\circ(m)}$ is the chemical potential of substance i in its **molality standard state**. This standard state of component i is that of a substance in a "hypothetical" solution with m_i equal to m° ($1\,\mathrm{mol\,kg^{-1}}$) and with Henry's law in the form of Eq. (7.2-11) valid at this molality. Again we specify a pressure of exactly 1 bar for this standard state.

Exercise 7.12

Show that $\mu_i^{\circ(\mathrm{m})}$ is equal to the chemical potential of i in the vapor phase at equilibrium with a $1.000\,\mathrm{mol\,kg^{-1}}$ solution if Eq. (7.2-11) is valid at this molality.

The **molar concentration** of component i is defined by

$$c_i = \frac{n_i}{V} \tag{7.2-13}$$

where n_i is the amount of the solute in moles and V is the volume of the solution. The term "concentration" is sometimes used to refer to the mass of a solute per unit volume, but we will not use this measure of composition, and will usually refer to the molar concentration simply as the concentration. The SI unit of volume is $\mathrm{m^3}$, but we will also use the liter. If the volume is measured in liters, the molar concentration is commonly called the **molarity**. A common symbol for the molarity is the formula for the substance inside square brackets:

$$c_i = [\mathscr{F}_i] \tag{7.2-14}$$

where $\mathscr{F}_i$ is an abbreviation for the formula of substance i. Although molarity is commonly used in general chemistry courses and in spite of its convenience in volumetric analyses, the molality is more commonly used in physical chemistry courses because the molarity depends on temperature while the molality does not.

*Exercise 7.13

Assuming that the coefficient of thermal expansion of an aqueous solution is the same as that of water, $2.0661 \times 10^{-4}\,\mathrm{K^{-1}}$, determine the molarity at 25°C of a solution that has a molarity of $0.1000\,\mathrm{mol\,L^{-1}}$ at 20.0°C.

Henry's law can be expressed in terms of concentration. By Euler's theorem, Eq. (5.6-4), the volume of a dilute solution is

$$V = \sum_{i=1}^{c} n_i \bar{V}_i \approx n_1 \bar{V}_1 \approx n_1 V^*_{\mathrm{m},1} \tag{7.2-15}$$

where the approximate equality holds for a dilute solution, in which n_1 is much larger than the amounts of the solutes. In this case

$$c_i \approx \frac{n_i}{n_1 V^*_{\mathrm{m},1}} \approx \frac{x_i}{V^*_{\mathrm{m},1}} \quad \text{(dilute solutions)} \tag{7.2-16}$$

Exercise 7.14

a. Show that for a dilute solution, Henry's law becomes

$$P_i = k_i V^*_{\mathrm{m},1} c_i = k_i^{(\mathrm{c})} c_i \tag{7.2-17}$$

b. Show that for a dilute solution, the chemical potential can be expressed in terms of the concentration:

$$\mu_i = \mu_i^{\circ(c)} + RT\ln\left(\frac{c_i}{c^\circ}\right) \qquad (7.2\text{-}18)$$

where $\mu_i^{\circ(c)} = \mu_i^{\circ(H)} + RT\ \ln(c^\circ V_{m,1}^*)$ and where $c^\circ = 1\,\text{mol}$ per unit volume (exactly). Interpret the molarity standard state, at which the chemical potential is equal to $\mu_i^{\circ(c)}$.

In addition to the mole fraction, molality, and concentration, other measures are used to express the composition of solutions, including percentage by mass, percentage by volume, and parts per million by mass. 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 for sufficiently dilute solutions.

***Exercise 7.15**

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

Henry's law, which applies to equilibrium between a solution and a gas phase, can be used to express the maximum solubility of gases in liquids. At equilibrium the amount of a gas dissolved in a liquid is proportional to the partial pressure of the gas. The only difference from the usual version of Henry's law is that instead of thinking of a solution producing a vapor phase at equilibrium with the solution, we think of a gas dissolving to produce a solution at equilibrium with the gas phase.

EXAMPLE 7.5

At 25°C, water at equilibrium with air at 1.000 atm contains about 8.3 ppm of dissolved oxygen by mass. Compute the Henry's law constant. 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

$$x_2 = \left(\frac{8.3\ \text{g}}{32.0\ \text{g mol}^{-1}}\right)\left(\frac{18.0\ \text{g mol}^{-1}}{1\times 10^6\ \text{g}}\right) = 4.7\times 10^{-6}$$

and the Henry's law constant is

$$k_2 = \frac{0.203\ \text{atm}}{4.7\times 10^{-6}} = 4.3\times 10^4\ \text{atm}$$

The Solvent in a Dilute Solution Obeys Raoult's Law

If all solutes in a solution obey Henry's law over some dilute range of composition, the solvent obeys Raoult's law over this range of composition. We show this fact for a two-component solution, leaving the proof for several components as a problem at the end of the chapter (Problem 7.46). We begin with the Gibbs–Duhem relation for constant pressure and temperature:

$$x_1\left(\frac{\partial \mu_1}{\partial x_2}\right)_{T,P}+x_2\left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P}=0 \tag{7.2-19}$$

This equation requires that the pressure exerted on the solution is constant. The vapor phase must have an additional gas or gases (such as air) present to keep the pressure constant. The small amount of air that dissolves in the solution can be ignored, and the small effect of a modest change in pressure on the chemical potentials in the solution is negligible (see Example 6.5).

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

$$\left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P}=RT\left(\frac{d\ \ln(x_2)}{dx_2}\right)=\frac{RT}{x_2} \tag{7.2-20}$$

Since $x_1 + x_2 = 1$, $dx_2 = -dx_1$. Therefore, by Eq. (7.2-19)

$$x_1\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P}=x_2\left(\frac{\partial \mu_2}{\partial x_2}\right)_{T,P}=\frac{x_2RT}{x_2}=RT \tag{7.2-21}$$

Dividing this equation by x_1 and multiplying by dx_1, we obtain

$$\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P}dx_1=\left(\frac{RT}{x_1}\right)dx_1 \tag{7.22}$$

Integrating this equation from $x_1 = 1$ to $x_1 = x_1' = 1 - x_2'$, we obtain

$$\mu_1(x_1')-\mu_1(1)=RT[\ln(x_1')-\ln(1)]$$

which is the same as

$$\mu_1(x_1)=\mu_1^*+RT\ \ln(x_1) \tag{7.2-23}$$

where we recognize $\mu_1(1)$ as μ_1^*, and where we have dropped the prime (′) on the value of x_1. Equation (7.2-23) is the same as Eq. (7.1-1) for an ideal solution, and leads to Raoult's law for the solvent, as in Eq. (7.1-2). We define the standard state for the solvent in a dilute solution to be the pure substance at pressure P° (exactly 1 bar). Again, this would require a small correction term like that in Eq. (7.1-5). We neglect this correction.

7.3 The Activity and the Description of General Systems

Most solutions are neither ideal or dilute. To describe all possible cases, including pure substances as well as solution components, we define the **activity** a_i of substance i by

$$\mu_i=\mu_i^\circ+RT\ \ln(a_i)\quad \text{(general definition of the activity } a_i\text{)} \tag{7.3-1}$$

where μ_i° is the chemical potential of substance i in the appropriate standard state. The relation shown in Eq. (7.3-1) is a general equation, to be used for pure substances and components of mixtures in solid, liquid, or gaseous phases. Notice the similarity of this equation with Eqs. (7.1-9), (7.2-2), (7.2-12), and (7.2-18). An important property of the activity is that it is equal to unity if the substance is in its standard state, since the logarithm of unity is equal to zero. However, we will have different kinds of standard states for different kinds of systems.

The Activity of a Pure Solid or Liquid

The standard state of a pure solid or liquid is the substance at pressure P°. This choice means that the activity of the pure substance is equal to unity if the pure substance is at pressure P°. If the substance is at a pressure other than P°,

$$\mu_i(P') = \bar{G}_i(P') = \mu_i^\circ + \int_{P^\circ}^{P'} V^*_{\mathrm{m},i}\, dP = \mu_i^\circ + V^*_{\mathrm{m},i}(P' - P^\circ) \qquad (7.3\text{-}2)$$

where we have used Eq. (5.3-11) and where we assume the substance to be incompressible. The activity at pressure P is given by

$$RT\ \ln(a_i) = V^*_{\mathrm{m},i}(P - P^\circ) \qquad (7.3\text{-}3)$$

which is equivalent to

$$\boxed{a_i = \exp\left(\frac{V^*_{\mathrm{m},i}(P - P^\circ)}{RT}\right) \quad \text{(pure solid or liquid)}} \qquad (7.3\text{-}4)$$

where we have dropped the prime (′) label. The exponent in Eq. (7.3-4) is generally quite small unless P differs greatly from P°.

EXAMPLE 7.6

Find the activity of pure liquid water at a pressure of 2.00 atm and a temperature of 298.15 K.

Solution

$$\ln(a) = \frac{(1.805 \times 10^{-6}\ \mathrm{m^3\ mol^{-1}})(1.00\ \mathrm{atm})(101{,}325\ \mathrm{N\ m^{-2}\ atm^{-1}})}{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})}$$

$$= 0.0007378$$

$$a = e^{0.0007378} = 1.000738$$

*Exercise 7.16

Find the pressure such that the activity of liquid water is equal to 1.0100 at 298.15 K.

For ordinary pressures we will assume that the activity of a pure solid or liquid is equal to unity.

The Activity of an Ideal Gas

The standard state for the activity of an ideal gas is the same as that used for the Gibbs energy: the pure ideal gas at whatever temperature we wish to discuss and at pressure P°. Comparison of Eq. (7.3-1) with Eq. (5.3-5) shows that

$$\boxed{a_i = \frac{P_i}{P^\circ} \quad \text{(ideal gas)}} \qquad (7.3\text{-}5)$$

where P_i is the pressure (or partial pressure) of the gas. Since each gas in an ideal gas mixture behaves as though it were the only gas present, Eq. (7.3-5) can also be used for components of ideal gas mixtures.

Activities in Ideal Solutions

For a component of an ideal liquid or solid solution, the composition is most conveniently expressed in terms of the mole fractions of the components. Comparison of Eq. (7.3-1) with Eq. (7.1-9) shows that

$$a_i = x_i \quad \text{(ideal solution)} \tag{7.3-6a}$$

$$\mu_i^\circ = \mu_i^*(T, P^\circ) \quad \text{(ideal solution)} \tag{7.3-6b}$$

where the standard state is the pure substance at the temperature of the solution and at pressure P°, and in the same phase as the solution. If the solution is a liquid, the standard state must be the substance in the liquid phase.

An example of a solution that is nearly ideal is a liquid mixture of benzene and naphthalene. However, benzene does not mix with solid naphthalene. This is a common occurrence. For a substance to mix with another substance that is a solid it must fit into its crystal lattice. The same is not required for a liquid, so that miscibility is much more common in the liquid phase than in the solid phase. Since naphthalene is a solid at room temperature the standard state of naphthalene for the liquid solution must be pure supercooled liquid naphthalene at the temperature of the solution. Since the chemical potential of the supercooled (metastable) liquid is higher than that of the solid at temperatures lower than the melting temperature, 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. Solutions in this range exceed the maximum solubility of naphthalene in benzene, and if they occur they are metastable and are called **supersaturated**. Figure 7.10 schematically shows the vapor pressure and chemical potential of naphthalene in a solution with benzene near room temperature.

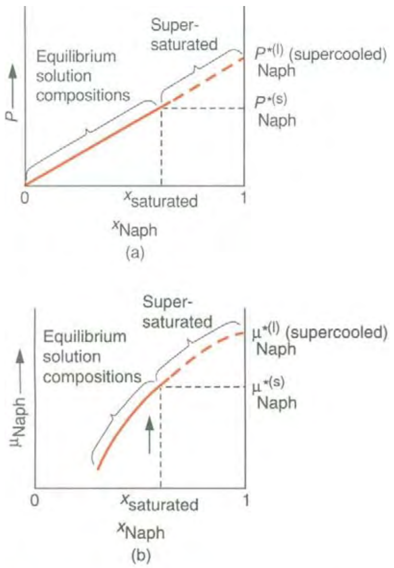

Figure 7.10. Naphthalene in an Ideal Solution (Schematic). (a) **The vapor pressure as a function of composition.** The composition at which the vapor pressure is equal to that of solid naphthalene is the composition of maximum solubility (saturation). (b) **The chemical potential as a function of composition.** The composition at which the chemical potential is equal to that of solid naphthalene is the composition of maximum solubility.

Exercise 7.17

Show that the maximum solubility of a solid such as naphthalene is independent of the identity of the liquid solvent if the two substances form an ideal solution.

Activities in Nonideal Systems. The Activity Coefficient

The activity of a component of a nonideal system is defined in whatever way is needed to make Eq. (7.3-1) valid. It is always necessary to define the standard state. The extent to which the actual activity deviates from the ideal activity is specified by the **activity coefficient** γ, defined as the ratio

$$\gamma_i = \frac{a_i(\text{real})}{a_i(\text{ideal})} \quad \text{(definition)} \tag{7.3-7}$$

The Activity and Activity Coefficient of a Nonideal Gas

The standard state for the activity of a nonideal gas is the hypothetical ideal gas at the standard-state pressure P°. Comparison of Eq. (7.3-1) with Eq. (5.3-6) shows that the activity of a nonideal gas is the ratio of the fugacity to P°:

$$a_i = \frac{f_i}{P^\circ} \quad \text{(any gas)} \tag{7.3-8}$$

In the case of an nonideal gas, a_i(ideal) in Eq. (7.3-7) is the activity of the ideal gas, P_i/P°, where P_i is partial pressure of the gas.

The activity coefficient is given by Eq. (7.3-7) as

$$\gamma_i = \frac{f_i/P^\circ}{P_i/P^\circ} = \frac{f_i}{P_i} \tag{7.3-9}$$

It is also known as the **fugacity coefficient**, and is sometimes denoted by ϕ_i instead of by γ_i. The activity coefficient of an ideal gas equals unity.

The chemical potential of a nonideal gas can be written

$$\mu_i = \mu_i^\circ + RT\ \ln(a_i) = \mu_i^\circ + RT\ \ln\left(\frac{f_i}{P^\circ}\right) = \mu_i^\circ + RT\ \ln\left(\frac{\gamma_i P_i}{P^\circ}\right) \tag{7.3-10}$$

If the value of the activity coefficient 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 Nonideal Solutions

The activities of the components of a nonideal solution are specified in different ways, depending on whether one of the components is designated as the solvent and depending on the variables used for specifying the composition of the solution. We will discuss first the descriptions based on mole fractions, and will discuss molality and concentration descriptions later in this section.

Convention I. In this treatment all of the components are treated on an equal footing, with no substance designated as the solvent and with mole fractions used to specify the composition. 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. For a solution of volatile substances at equilibrium with a vapor phase, 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. (7.3-1) and assume the vapor to be an ideal gas,

$$\mu_i^{\circ(\mathrm{I})} + RT \ln[a_i^{(\mathrm{I})}] = \mu_i^{\circ(\mathrm{gas})} + RT\ \ln\left(\frac{P_i}{P^\circ}\right) \tag{7.3-11}$$

where we attach the superscript (I) to specify 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^*. The relation of Eq. (7.3-11) becomes

$$\mu_i^{\circ(\text{gas})} + RT\ \ln\left(\frac{P_i^*}{P^\circ}\right) + RT\ \ln(a_i^{(\text{I})}) = \mu_i^{\circ(\text{gas})} + RT\ \ln\left(\frac{P_i}{P^\circ}\right) \tag{7.3-12}$$

Canceling equal terms and taking antilogarithms in Eq. (7.3-12) gives

$$P_i = P_i^* a_i^{(\text{I})} \tag{7.3-13}$$

which is just like Raoult's law, Eq. (7.1-2), except that the activity $a_i^{(\text{I})}$ occurs instead of the mole fraction x_i. The activity acts as an "effective" mole fraction in determining the partial vapor pressure of the substance. Equation (7.3-13) is equivalent to

$$a_i^{(\text{I})} = \frac{P_i}{P_i^*} \tag{7.3-14}$$

The activity coefficient is equal to the actual vapor pressure divided by the value of the vapor pressure predicted by Raoult's law:

$$\gamma_i^{(\text{I})} = \frac{a_i^{(\text{I})}}{x_i} = \frac{P_i/P^\circ}{P_{i(\text{ideal})}/P^\circ} = \frac{P_i}{P_i^* x_i} \tag{7.3-15}$$

Convention I is the most convenient description when a solution deviates only slightly from Raoult's law.

EXAMPLE 7.7

Find the value of the activity and the activity coefficient of 2,2,4-trimethylpentane (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

$$a_2^{(\text{I})} = \frac{48.31\ \text{torr}}{59.03\ \text{torr}} = 0.8184$$

$$\gamma_2^{(\text{I})} = 0.8184/0.2748 = 2.978$$

*Exercise 7.18

Find the value of the activity and the activity coefficient of ethanol in the solution of Example 7.7, 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. In this description the mole fractions of all components are used to specify the composition, but one of the components (which we choose to be substance number 1) is designated as the solvent and is treated just as in Convention I:

$$a_1^{(\mathrm{II})} = a_1^{(\mathrm{I})} = \frac{P_1}{P_1^*} \quad \text{(solvent = component 1)} \tag{7.3-16}$$

$$\gamma_1^{(\mathrm{II})} = \gamma_1^{(\mathrm{I})} = \frac{a_1^{(\mathrm{I})}}{x_1} = \frac{P_1/P^\circ}{P_{1(\text{ideal})}/P^\circ} = \frac{P_1}{P_1^* x_1} \tag{7.3-17}$$

(When one component is designated as the solvent, we will call it component number 1.) Instead of specifying the deviation from Raoult's law for a solute, we specify its deviation from Henry's law. This means that the standard state for the activity of a solute is a hypothetical pure liquid or solid with a vapor pressure equal to Henry's law constant, just as for a solute in a dilute solution.

From the fundamental fact of phase equilibrium, we write for a solute in its standard state

$$\mu_i^{\circ(\mathrm{II})} = \mu_i^{\circ(\mathrm{H})} = \mu_i^{\circ(\text{gas})} + RT \ln\left(\frac{k_i}{P^\circ}\right) \quad (i \neq 1) \tag{7.3-18}$$

The activity takes on the value that is needed to make Eq. (7.3-1) valid:

$$\mu_i = \mu_i^{\circ(\mathrm{II})} + RT \ln(a_i^{(\mathrm{II})}) \tag{7.3-19}$$

Equation (7.3-18) is substituted into Eq. (7.3-19) and the chemical potential of substance *i* in the solution is equated to its chemical potential in the gas phase. This gives

$$\mu_i^{\circ(\text{gas})} + RT \ln\left(\frac{k_i}{P^\circ}\right) + RT \ln(a_i^{(\mathrm{II})}) = \mu_i^{\circ(\text{gas})} + RT \ln\left(\frac{P_i}{P^\circ}\right) \tag{7.3-20}$$

Cancelation and taking antilogarithms leads to

$$P_i = k_i a_i^{(\mathrm{II})} \quad (i \neq 1) \tag{7.3-21}$$

This equation is just like Henry's law, Eq. (7.2-1), except for the occurrence of the activity instead of the mole fraction. If Henry's law is obeyed, the activity and the mole fraction are equal to each other. If not, the activity is an "effective" mole fraction in expressing the chemical potential and the partial vapor pressure. Equation (7.3-21) is equivalent to

$$a_i^{(\mathrm{II})} = \frac{P_i}{k_i} \quad (i \neq 1) \tag{7.3-22}$$

The activity coefficient 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:

$$\gamma_i^{(\mathrm{II})} = \frac{a_i^{(\mathrm{II})}}{x_i} = \frac{P_i}{k_i x_i} \tag{7.3-23}$$

Equation (7.3-19) can now be written

$$\mu_i = \mu_i^{\circ(\mathrm{II})} + RT \ln(\gamma_i^{(\mathrm{II})} x_i) \tag{7.3-24}$$

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. If Henry's law is nearly obeyed by solutes, the use of Convention II gives solute activity coefficients nearly equal to unity as well as a solvent activity coefficient nearly equal to unity, while Convention I gives activity coefficients nearly equal to unity if Raoult's law is nearly obeyed by all substances.

EXAMPLE 7.8

The value of Henry's law constant for ethanol in diethyl ether at 20°C is 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

Convention I:

$$a_2^{(\mathrm{I})} = \frac{P_2}{P_2^*} = \frac{12.45\ \mathrm{torr}}{44.40\ \mathrm{torr}} = 0.280$$

$$\gamma_2^{(\mathrm{I})} = \frac{0.280}{0.100} = 2.80$$

Convention II:

$$a_2^{(\mathrm{II})} = \frac{P_2}{k_2} = \frac{12.45\ \mathrm{torr}}{160\ \mathrm{torr}} = 0.0778$$

$$\gamma_2^{(\mathrm{II})} = \frac{a_2}{x_2} = \frac{0.0778}{0.100} = 0.778$$

***Exercise 7.19**

Using Convention I, find the activity and activity coefficient for diethyl ether in the solution of Example 7.8. 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.

Activities and activity coefficients of solutes are also defined to be used with molalities and concentrations instead of mole fractions. Once again, we require that Eq. (7.3-1) be valid, and choose standard states so that the activity is numerically equal to the molality if Eq. (7.2-10) is valid or to the concentration if Eq. (7.2-15) is valid.

The Molality Description

From Eq. (7.2-7), the molality of component i is

$$m_i = \frac{n_i}{w_1} = \frac{n_i}{n_1 M_1} = \frac{x_i}{x_1 M_1} \quad (\text{definition}, i \neq 1) \tag{7.3-25}$$

where M_1 is the molar mass of the solvent and w_1 is the mass of the solvent. Using the relation of Eq. (7.3-25) in Eq. (7.3-24), we write

$$\mu_i = \mu_i^{\circ(\mathrm{II})} + RT\ \ln(M_1 m^\circ) + RT\ \ln\left(\frac{\gamma_i^{(\mathrm{II})} x_1 m_i}{m^\circ}\right) \tag{7.3-26}$$

where m° is defined to equal $1\ \mathrm{mol\,kg^{-1}}$ (exactly). This equation is in the form of Eq. (7.3-1):

$$\mu_i = \mu_i^{\circ(\mathrm{m})} + RT\ \ln(a_i^{(\mathrm{m})}) \tag{7.3-27}$$

where

$$a_i^{(\mathrm{m})} = \frac{\gamma_i^{(\mathrm{II})} x_1 m_i}{m^\circ} \tag{7.3-28}$$

and

$$\mu_i^{\circ(\mathrm{m})} = \mu_i^{\circ(\mathrm{II})} + RT\ \ln(M_1 m^\circ) \tag{7.3-29}$$

As in the molality description of a dilute solution, the standard state is the hypothetical solution with molality equal to $1\ \mathrm{mol\,kg^{-1}}$ and obeying the molality version of Henry's law, Eq. (7.2-11). We define the **molality activity coefficient**

$$\gamma_i^{(\mathrm{m})} = \gamma_i^{(\mathrm{II})} x_1 \tag{7.3-30}$$

so that Eq. (7.3-27) can be written

$$\mu_i = \mu_i^{\circ(\mathrm{m})} + RT\ \ln\left(\frac{\gamma_i^{(\mathrm{m})} m_i}{m^\circ}\right) \tag{7.3-31}$$

Since x_1, the mole fraction of the solvent, is approximately equal to unity in dilute solutions, the molality activity coefficient and the mole fraction activity coefficient are nearly equal in dilute solutions.

Equation (7.3-31) is the same as Eq. (7.2-12) 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, which describes how the solute deviates from the molality description of a dilute solution. This is generally true: inclusion of the effects of nonideality is accomplished by inserting an activity coefficient as a factor that multiplies the mole fraction, molality, or other composition variables.

The Concentration Description

The concentration is given by Eq. (7.2-13),

$$c_i = \frac{n_i}{V} = \frac{x_i}{V_\mathrm{m}} \tag{7.3-32}$$

where V_m is the mean molar volume, V/n (n is the total amount of all substances). We want to write an equation of the form

$$\mu_i = \mu_i^{\circ(\mathrm{c})} + RT\ \ln\left(\frac{\gamma_i^{(\mathrm{c})} c_i}{c^\circ}\right) \tag{7.3-33}$$

so that the activity in the concentration description is

$$a_i^{(c)} = \frac{\gamma_i^{(c)} c_i}{c^\circ} \tag{7.3-34}$$

where c° is defined to equal 1 mol L^{-1} or 1 mol m^{-3}. Equation (7.3-33) is valid if

$$\mu_i^{\circ(c)} = \mu_i^{(II)} + RT\ \ln(V_{m,1}^* c^\circ) \tag{7.3-35}$$

and

$$\gamma_i^{(c)} = \frac{\gamma_i^{(II)} \bar{V}}{V_{m,1}^*} \tag{7.3-36}$$

The standard-state chemical potential is that of a hypothetical solution with a concentration of substance i equal to 1 mol L^{-1} (or 1 mol m^{-3}) and obeying Henry's law in the concentration description, as in Eq. (7.2-15). Correction is made for the fact that the mean molar volume is not equal to the molar volume of the solvent except in the limit of infinite dilution.

In all our descriptions, the solvent is treated in the same way as in Convention I. Its activity is always its mole fraction times its activity coefficient:

$$a_1 = \gamma_1 x_1 \quad \text{(solvent, all descriptions)} \tag{7.3-37}$$

Since the activities and activity coefficients of the same solute in two different descriptions are not necessarily equal to each other we have attached superscripts to specify which description is being used. We sometimes omit these superscripts, relying on the context to make clear which description is being used. Inspection of Eqs. (7.3-33) and (7.3-36) shows that all of the solute activity coefficients become equal to each other in the limit of infinite dilution.

Activities of Nonvolatile Solutes. The Gibbs–Duhem Integration

If a solute has a small vapor pressure that cannot be measured conveniently, another method must be found to determine its activity. For a two-component solution with a volatile solvent and a nonvolatile solute, the activity coefficient of the solute can be determined by measuring the vapor pressure of the solvent over a range of composition and then integrating the Gibbs–Duhem relation. For constant pressure and temperature, the Gibbs–Duhem relation is given by Eq. (5.6-11). When we substitute Eq. (7.3-1) into this equation for the case of two components, we obtain

$$x_1 RT\ d[\ln(a_1)] + x_2 RT\ d[\ln(a_2)] = 0 \tag{7.3-38}$$

We use Convention II. For both components, $a_i = \gamma_i x_i$, where we omit superscripts. Using the fact that $x_i\ d[\ln(x_i)] = dx_i$, we obtain

$$x_1 RT\ d[\ln(\gamma_1)] + RT\ dx_1 + x_2 RT\ d[\ln(\gamma_2)] + RT\ dx_2 = 0$$

Since $x_1 + x_2 = 1$, $dx_1 + dx_2 = 0$, and two terms cancel. We divide by x_2 and obtain the equation

$$d[\ln(\gamma_2)] = -\frac{x_1}{1 - x_1} d[\ln(\gamma_1)] \tag{7.3-39}$$

The vapor pressure of the solvent (component 1) is measured over a range of compositions beginning with pure solvent and extending to the composition at which we want the value of γ_2, denoted by $x_1 = x_1'$ or $x_2 = x_2' = 1 - x_1'$. From the vapor pressure, the activity coefficient of the solvent, γ_1 is calculated for a number of compositions within the range of interest. Equation (7.3-39) is then integrated from $x_1 = x_1''$ to $x_1 = x_1'$, where x_1'' is a value of x_1 close enough to unity that Raoult's law is obeyed by the solvent and Henry's law is obeyed by the solute. At $x_1 = x_1''$, γ_2 is equal to unity, so that

$$\ln[\gamma_2(x_1')] = -\int_{x_1=x_1''}^{x_i=x_i'} \frac{x_1}{1-x_1}\, d[\ln(\gamma_1)] \tag{7.3-40}$$

where we consider both γ_2 and γ_1 to be functions of x_1. The lower limit x_1'' cannot be taken equal to unity, because the denominator $1 - x_1$ goes to zero in this case.

Unless the data are fit to some formula, this integral is approximated numerically. Before the advent of digital computers it was often done graphically, with the integrand $x_1/(1 - x_1)$ plotted on the vertical axis and $\ln(\gamma_1)$ plotted on the horizontal axis.

Thermodynamic Functions of Nonideal Solutions

The thermodynamic functions of solutions are generally expressed in terms of the changes in the variables produced by mixing the pure components to from the solution at a fixed temperature and pressure. We begin with the Gibbs energy change of mixing. From Euler's theorem and Eq. (7.3-1), the Gibbs energy of a nonideal solution can be written in a way that is analogous to Eq. (7.1-11) for an ideal solution:

$$G_{(\text{soln})} = \sum_{i=1}^{c} n_i[\mu_i^{\circ(\text{I})} + RT\ \ln(a_i^{(\text{I})})] \tag{7.3-41}$$

The actual value of the Gibbs energy or any other energy-related variable can always be modified by adding a constant to the potential energy. Therefore, only changes in any such variables are unambiguous. We must write an equation for ΔG for a process of interest instead of for G. For Convention I the standard states are the pure components, so that

$$G_{(\text{unmixed})} = \sum_{i=1}^{c} n_i\mu_i^* = \sum_{i=1}^{c} n_i\mu_i^{\circ(\text{I})} \tag{7.3-42}$$

The change in Gibbs energy for producing the solution from the pure substances is

$$\Delta G_{\text{mix}} = RT\sum_{i=1}^{c} n_i\ \ln(a_i^{(\text{I})}) \tag{7.3-43}$$

We can rewrite this equation in terms of the activity coefficients:

$$\begin{aligned}\Delta G_{\text{mix}} &= RT\sum_{i=1}^{c} n_i\ \ln(\gamma_i^{(\text{I})}x_i)\\ &= RT\sum_{i=1}^{c} n_i\ \ln(x_i) + RT\sum_{i=1}^{c} n_i\ \ln(\gamma_i^{(\text{I})})\end{aligned} \tag{7.3-44}$$

The first sum in the right-hand-side of the final version of the equation is the same as for an ideal solution, and the second sum represents a correction for the nonideality of the solution. This correction is called the **excess Gibbs energy**, and is denoted by G^{E}:

$$\begin{aligned} G^{\mathrm{E}} &= \Delta G_{\mathrm{mix}}(\mathrm{actual}) - \Delta G_{\mathrm{mix}}(\mathrm{ideal}) \\ &= RT\sum_{i=1}^{c} n_i \ln(\gamma_i^{(\mathrm{I})}) \end{aligned} \tag{7.3-45}$$

so that

$$\Delta G_{\mathrm{mix}} = \Delta G_{\mathrm{mix}}(\mathrm{ideal}) + G^{\mathrm{E}} \tag{7.3-46}$$

The **excess enthalpy**, **excess energy**, **excess entropy**, etc., can all be defined for a nonideal solution:

$$H^{\mathrm{E}} = \Delta H_{\mathrm{mix}}(\mathrm{actual}) - \Delta H_{\mathrm{mix}}(\mathrm{ideal}) \tag{7.3-47a}$$

$$U^{\mathrm{E}} = \Delta U_{\mathrm{mix}}(\mathrm{actual}) - \Delta U_{\mathrm{mix}}(\mathrm{ideal}) \tag{7.3-47b}$$

$$S^{\mathrm{E}} = \Delta S_{\mathrm{mix}}(\mathrm{actual}) - \Delta S_{\mathrm{mix}}(\mathrm{ideal}) \tag{7.3-47c}$$

$$V^{\mathrm{E}} = \Delta V_{\mathrm{mix}}(\mathrm{actual}) - \Delta V_{\mathrm{mix}}(\mathrm{ideal}) \tag{7.3-47d}$$

Exercise 7.20

Show that

$$S^{\mathrm{E}} = -R\sum_{i=1}^{c} n_i \ln[\gamma_i^{(\mathrm{I})}] - RT\sum_{i=1}^{c} n_i \left(\frac{\partial \ln(\gamma_i^{(\mathrm{I})})}{\partial T}\right)_P \tag{7.3-48}$$

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 component 2 is defined by

$$\Delta H_{\mathrm{int},1} = \frac{\Delta H_{\mathrm{mix}}}{n_1} \tag{7.3-49}$$

and the molar integral heat of solution of component 2 is defined by

$$\Delta H_{\mathrm{int},2} = \frac{\Delta H_{\mathrm{mix}}}{n_2} \tag{7.3-50}$$

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 7.9

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

$$\Delta H_{\mathrm{int},2} = -\frac{9.17\ \mathrm{kJ}}{2.00\ \mathrm{mol}} = -4.58\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta H_{\mathrm{int},1} = -\frac{9.17\ \mathrm{kJ}}{10.00\ \mathrm{mol}} = -0.917\ \mathrm{kJ\ mol^{-1}}$$

Using the relation for a two-component solution

$$\Delta H_{\mathrm{mix}} = n_1\bar{H}_1 + n_2\bar{H}_2 - (n_1 H^*_{\mathrm{m},1} + n_2 H^*_{\mathrm{m},2}) \tag{7.3-51}$$

the integral heat of mixing of a component of a two-component solution can be written in terms of the partial molar enthalpies:

$$\begin{aligned}\Delta H_{\mathrm{int},2} &= \frac{1}{n_2}[n_1(\bar{H}_1 - H^*_{m,1}) + n_2(\bar{H}_2 - H^*_{\mathrm{m},2})] \\ &= \frac{n_1}{n_2}(\bar{H}_1 - H^*_{\mathrm{m},1}) + \bar{H}_2 - H^*_{\mathrm{m},2}\end{aligned} \tag{7.3-52}$$

The integral heat of solution is the enthalpy change per mole of solute for the entire process of making the solution, starting with pure solvent and adding the pure solute to make the desired concentration. It is therefore a kind of average molar quantity for making the solution of the desired concentration. In the limit of zero concentration it approaches a limit that depends only on the temperature, the pressure, the identity of the other substance.

The **differential heat of solution** is defined by

$$\Delta H_{\mathrm{diff},2} = \left(\frac{\partial\,\Delta H_{\mathrm{mix}}}{\partial n_2}\right)_{T,P,n'} \quad \text{(definition)} \tag{7.3-53}$$

The differential heat of solution is the enthalpy change per mole of solute for adding an infinitesimal amount of solute to the solution (not changing its composition), or equivalently for adding 1 mol of solution to a very large amount of the solution (again not changing its composition). From Eqs. (7.3-51) and (7.3-53),

$$\Delta H_{\mathrm{diff},i} = \bar{H}_i - H^*_{\mathrm{m},i} \tag{7.3-54}$$

Equation (7.3-54) is valid for any number of components, while Eq. (7.3-52) is valid only for a two-component solution.

Exercise 7.21

Write the version of Eq. (7.3-52) that applies to a solution of c components.

Tabulated Thermodynamic Properties for Solution Components

In Chapters 3 and 5 we discussed enthalpy and Gibbs energy 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 one mole of substance i in a large amount of the solution of the specified composition. A large amount of solution is used so that the addition of the solute does not appreciably change its composition. The enthalpy change of formation is related to the differential heat of solution, not the integral heat of solution. The Gibbs energy change of formation is analogous; it is the change in Gibbs energy to produce one mole of the substance from the necessary elements in their most stable forms, and then to dissolve it in a large amount of the solution of the specified composition. These quantities do not include the enthalpy change or the Gibbs energy change to produce the large amount of solution to which the substance is added.

The composition of the solution must be specified. The tabulated values of enthalpy changes and Gibbs energy changes of formation of solutes in Table A.8 are for standard states. The notation (ao) in the table means that the value is for the hypothetical $1\ \mathrm{mol\ kg^{-1}}$ solution with activity coefficient set equal to unity. The notation (ai) means the same thing, but for a complete ionization of a weak electrolyte. For all standard states the pressure is specified to equal P°. The standard-state enthalpy change of formation is defined by

$$\Delta H_\mathrm{f}^\circ(i,\mathrm{soln}) = \bar{H}_i^\circ - H^\circ(\mathrm{elements}) \tag{7.3-55}$$

and the standard-state Gibbs energy of formation is given by

$$\Delta G_\mathrm{f}^\circ(i,\mathrm{soln}) = \mu_i^\circ - G^\circ(\mathrm{elements}) \tag{7.3-56}$$

EXAMPLE 7.10

The following are values for ethanol at 298.15 K:

	$\Delta H_\mathrm{f}^\circ/\mathrm{kJ\ mol^{-1}}$	$\Delta G_\mathrm{f}^\circ/\mathrm{kJ\ mol^{-1}}$
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 $\mu^{\circ(\mathrm{m})} - G_\mathrm{m}^*(\mathrm{liq})$ for ethanol in H_2O at 298.15 K.

Solution

a. Call ethanol component number 2:

$$\begin{aligned}\Delta H_{\mathrm{diff},2}^\circ &= H_{\mathrm{m},2}^{\circ(\mathrm{m})} - H_{\mathrm{m},2}^*(\mathrm{liq}) = \Delta H_\mathrm{f}^\circ(2,\mathrm{ao}) - \Delta \mathrm{H}_\mathrm{f}^\circ(2,\mathrm{liq})\\ &= -288.3\ \mathrm{kJ\ mol^{-1}} - (277.69\ \mathrm{kJ\ mol^{-1}}) = -10.6\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

Note the difference in value between this quantity and the integral heat of solution in Example 7.9.

b.

$$\begin{aligned}\mu_2^{\circ(\mathrm{m})} - G_{\mathrm{m},2}^*(\mathrm{liq}) &= \Delta G_\mathrm{f}^\circ(2,\mathrm{ao}) - \Delta G_f^\circ(2,\mathrm{liq})\\ &= -181.64\ \mathrm{kJ\ mol^{-1}} - (-174.78\ \mathrm{kJ\ mol^{-1}}) = -6.86\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

7.4 Activity Coefficients in Electrolyte Solutions

Some compounds ionize or dissociate to form electrically charged ions in a solution with water and some other solvents. The electrical forces between these ions in solution are strong, and act over a large distance compared to molecular dimensions. They are

Coulomb's law is named for Charles Augustin de Coulomb, 1736–1806, the French physicist who discovered the law.

said to be **long-range forces**. The force on a macroscopic object with charge Q_1 due to one of charge Q_2 is given by Coulomb's law

$$\mathbf{F}_{12} = \mathbf{e}_r \frac{Q_1 Q_2}{4\pi\varepsilon r_{12}^2} \qquad (7.4\text{-}1)$$

where r_{12} is the distance between the centers of the objects, and where the charges are measured in coulombs (C). The constant ε depends on the identity of the substance (medium) between the charges, and is called the **permittivity** of the medium. The permittivity of a vacuum is denoted by ε_0, and is equal to 8.85419×10^{-12} $\mathrm{C^2\ N^{-1}\ m^{-2}}$. The permittivities of various substances have various values, always larger than that of a vacuum. The force is a vector that is proportional to the unit vector $\mathbf{e}_r$, which points from object 2 toward object 1. If the two charges have the same sign the force is a repulsion and if they have opposite signs the force is an attraction. By Newton's third law, the force on object 2 due to object 1 is the negative of the force on object 1 due to object 2. Although Eq. (7.4-1) was deduced for macroscopic charged objects, it is assumed to hold also for ions in a solution with the appropriate value of the permittivity of water.

The ratio of the permittivity of a given substance to that of a vacuum is called the **dielectric constant** and denoted by ε_{rel}. The dielectric constant of water is larger than that of most substances, and at 25°C is equal to 78.54. Although the electrostatic forces between ions in water are weaker than in a vacuum by this factor, these forces are of long range and have significant effects on the behavior of the solution. There are two principal equilibrium effects of the elctrostatic forces: The first is that the long-range electrostatic forces cause significant deviations from ordinary dilute behavior even at low concentrations. The second is that the chemical equilibrium between the ions and the unionized or undissociated compound produces a behavior of the chemical potential that is qualitatively different from that of nonelectrolyte solutes. We will discuss the first effect in this section, and will discuss the second effect in Chapter 8, when we discuss the thermodynamics of chemical equilibrium.

In an ideal solution the effective molecular environment of the molecules of any substance must be composition-independent, which can happen if the intermolecular forces between unlike molecules and like molecules are the same. In a sufficiently dilute solution, almost all solute molecules are surrounded only by molecules of the solvent. If the intermolecular forces are short-rane forces, the molecular environment is independent of compositions so long as the solution remains dilute. However, in an electrolyte solution the long-range electrostatic interaction between the ions makes fairly distant ions influence a given ion, and electrolyte solutions deviate from dilute behavior except for extremely low concentrations.

The Debye–Hückel theory is named for Peter J. W. Debye, 1884–1966, Dutch-American physicist and chemist who received the Nobel Prize for chemistry in 1936 for his work on the dipole moments of molecules, and for Erich Hückel, 1896–1980, German chemist who is also known for an approximation scheme used in molecular quantum mechanics.

The Debye–Hückel Theory

There is a molecular theory for the activity coefficients of an electrolyte solution, due to Debye and Hückel. We will not discuss their theory except to mention its underlying ideas and to quote its principal result.[2]

The Debye–Hückel theory begins with the assumption that a pair of ions exert forces on each other given by Eq. (7.4-1), except that the centers of two ions cannot approach

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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).

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, so that there is no other contribution to the activity coefficient.

The main idea of the Debye–Hückel derivation was to pretend that the ions in a solution could somehow have their changes varied reversibly from zero to the actual values, and to determine the consequences of this process from electrostatic theory and statistical mechanical theory. During the reversible charging process, an "ion atmosphere" is created, consisting of an excess of ions of the opposite charge in the vicinity of any given ion. An equation for the statistical average distribution of ions around the fixed ion was derived by combining the Poisson equation of electrostatics (which we will not discuss) and the Boltzmann probability distribution of Eq. (1.7-25) into an equation called the **Poisson–Boltzmann equation**. The reversible work of creating the ion atmosphere was calculated from electrostatic theory. According to Eq. (5.1-27), the net work done on the system in a reversible process is equal to the change in the Gibbs energy, which leads to equations for the electrostatic contribution to chemical potential and the activity coefficient.

The first major result of the Debye–Hückel theory is a formula for the statistical distribution of charge around a given ion in the solution:

$$n_j(r) = \frac{-z_j e^2 \exp[-\kappa(r-a)]}{4\pi\varepsilon r(1+\kappa a)} \tag{7.4-2}$$

where r is the distance from the center of the given ion of valence z_j, where $n_j(r)$ represents the average net charge per unit volume at a distance r from a given ion, and where e is the charge on a proton, 1.6022×10^{-19} C. The quantity κ is

$$\kappa = e\left(\frac{2N_{\text{Av}}\rho_1 I}{\varepsilon k_{\text{B}} T}\right)^{1/2} \tag{7.4-3}$$

where N_{Av} is Avogadro's number, ρ_1 is the density of the solvent, k_{B} is Boltzmann's constant, and T is the temperature. The quantity I is the **ionic strength**, defined for a solution with s different charged species by

$$I = \frac{1}{2}\sum_{i=1}^{s} m_i z_i^2 \quad \text{(definition of ionic strength)} \tag{7.4-4}$$

where m_i is the modality of species i and z_i is its valence (number of proton charges per ion).

EXAMPLE 7.11

Calculate the ionic strength of a solution that is $0.100\ \text{mol kg}^{-1}$ in NaCl and $0.200\ \text{mol kg}^{-1}$ in $CaCl_2$. Assume complete dissociation.

Solution

$$I = \tfrac{1}{2}[m(\mathrm{Na}^+)(+1)^2 + m(\mathrm{Ca}^{2+})(+2)^2 + m(\mathrm{Cl}^-)(-1)^2]$$
$$= \tfrac{1}{2}[(0.100\ \mathrm{mol\ kg^{-1}}) + (0.200\ \mathrm{mol\ kg^{-1}})(2^2) + (0.500\ \mathrm{mol\ kg^{-1}})]$$
$$= 0.700\ \mathrm{mol\ kg^{-1}}$$

Notice the large contribution of a multiply charged species like Ca^{2+}.

*Exercise 7.22

Calculate the ionic strength of a solution that is 0.150 mol kg^{-1} in K_2SO_4 and 0.050 mol kg^{-1} in Na_2SO_4. Assume complete dissociation.

The expression for κ can be written

$$\kappa = \beta I^{1/2} \tag{7.4-5}$$

where β is a parameter that depends only on the temperature and the properties of the solvent:

$$\beta = e\left(\frac{2N_{\mathrm{Av}}\rho_1}{\varepsilon k_{\mathrm{B}}T}\right)^{1/2} \tag{7.4-6}$$

The reciprocal of κ is called the **Debye length**. This length is a measure of the effective range of the net electrostatic interaction of the ions in the solution.

Exercise 7.23

Show that for water at 298.15 K,

$$\beta = 3.281 \times 10^9\ \mathrm{kg^{1/2}\ mol^{-1/2}\ m^{-1}} \quad \text{(water, 298.15 K)} \tag{7.4-7}$$

The density of water at 298.15 K is equal to 997.14 kg m^{-3}.

The total net charge in a spherical shell of thickness dr and radius r centered on a given ion of valence z_j is given by

$$dQ_{\mathrm{shell}} = 4\pi r^2 n_j(r)\,dr \tag{7.4-8}$$

where the factor $4\pi r^2\,dr$ is the volume of the spherical shell. Figure 7.11 shows $|4\pi r^2 n_+(r)|$ around an anion of a 1–1 electrolyte at a molality of 0.005 mol kg^{-1}. The maximum in the curve is at the Debye length ($r = 1/\kappa$), which for this case is approximately 43 Å (4300 pm or 4.3×10^{-9} m), illustrating the relatively long range of the net electrostatic forces.

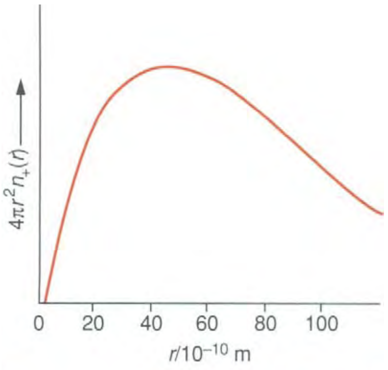

Figure 7.11. The Distribution of Charge around a Central Ion According to the Debye–Hückel Theory. This diagram shows the charge density in spherical shells around a given ion.

Exercise 7.24

Show that the maximum in the curve of Figure 7.11 is at $r = 1/\kappa$ and verify the value of the distance to the maximum for a 1–1 electrolyte at 0.005 mol kg^{-1}.

The second major result of the Debye–Hückel theory is obtained from equating the reversible work to form the ionic atmosphere with the change in the Gibbs energy. We obtain from this a formula for the activity coefficient of ions of valence z:

$$\ln(\gamma_i) = -\frac{z_i^2 \alpha I^{1/2}}{1 + \beta a I^{1/2}} \tag{7.4-9}$$

The quantity α is a second function of temperature and of the properties of the solvent:

$$\alpha = (2\pi N_{\mathrm{Av}} \rho_1)^{1/2} \left(\frac{e^2}{4\pi \varepsilon k T}\right)^{3/2} \tag{7.4-10}$$

Equation (7.4-9) is commonly used for the activity coefficient in both the molality and molarity descriptions, since these activity coefficients are nearly equal in a dilute aqueous solution.

Exercise 7.25

Show that for water at 298.15 K, the value of α is

$$\alpha = 1.171\ \mathrm{kg^{1/2}\ mol^{-1/2}} \quad \text{(water, 298.15 K)} \tag{7.4-11}$$

The chemical potentials and activity coefficients of individual ions cannot be measured, because the chemical potential is a partial derivative with respect to the amount of the given substance, keeping the amounts of other substances fixed. The amount of energy required to add ions of one charge without adding ions of the opposite charge is so large that it is not possible to add a significant amount of one kind of ion to a system without adding some ions of the other charge at the same time. For an electrolyte solute represented by the formula $M_{\nu_+}X_{\nu_-}$, where ν_+ and ν_- represent the numbers of cations and anions, respectively, in the formula of the solute, it is customary to define the **mean ionic activity coefficient**

$$\gamma_\pm = (\gamma_+^{\nu_+} \gamma_-^{\nu_-})^{1/\nu} \tag{7.4-12}$$

where $\nu = \nu_+ + \nu_-$, the total number of ions in the formula. From Eq. (7.4-9) we can obtain

$$\ln(\gamma_\pm) = -z_+ |z_-| \frac{\alpha I^{1/2}}{1 + \beta a I^{1/2}} \tag{7.4-13}$$

Exercise 7.26

Carry out the algebraic steps to obtain Eq. (7.4-13).

EXAMPLE 7.12

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. This distance gives a value of βa equal to 1.00 kg$^{1/2}$ mol$^{-1/2}$.

Solution

$$\ln(\gamma_\pm) = -\frac{(1.171\ \mathrm{kg}^{1/2}\mathrm{mol}^{-1/2})(0.01\ \mathrm{mol\ kg}^{-1})^{1/2}}{1+(1.00\ \mathrm{kg}^{1/2}\ \mathrm{mol}^{-1/2})(0.01\ \mathrm{mol\ kg}^{-1})^{1/2}} = -0.1065$$

$$\gamma_\pm = 0.899$$

The Debye–Hückel theory has been shown experimentally to be an accurate **limiting law**. That is, it gives the correct behavior as the concentration is made very small. In practice, it is accurate enough for some purposes for ionic strengths up to about $0.01\ \mathrm{mol\,kg}^{-1}$, but often fails badly for ordinary concentrations. Figure 7.12 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 same slope.

Since βa is approximately equal to $1.0\ \mathrm{kg}^{-1}\ \mathrm{mol}^{-1}$ for many ions, as in Example 7.12, we write as an approximation

$$\ln(\gamma_\pm) = -z_+|z_-|\frac{\alpha I^{1/2}}{1+(I/m^\circ)^{1/2}} \tag{7.4-14}$$

where $m^\circ = 1\ \mathrm{mol\ kg}^{-1}$ (exactly). For small values of the ionic strength the $\beta a I^{1/2}$ term in the denominator of Eq. (7.4-13) is relatively small compared with unity, and the Debye–Hückel equation is similar to the first term in an empirical equation of Brønsted that predated the theory of Debye and Hückel.[3]

$$\ln(\gamma_\pm) = -\alpha m^{1/2} + 2\beta m \tag{7.4-15}$$

Much work has been done to extend the Debye–Hückel theory, beginning in 1926 with a theory of Bjerrum[4] in which it was assumed that two ions of opposite charge closer to each other than a certain distance comprised an ion pair that could be treated as a single chemical species in chemical equilibrium with the dissociated ions. These ion pairs do not constitute molecules with an ionic chemical bond, because they are separated by water molecules that are strongly attached to the ions. In this regard they differ from such complexes as AgCl_2^-, which has coordinate covalent bonds between the silver ion and the chloride ion. There appear to be many such ion pairs in an electrolyte solution.[5] Later research is largely based on theoretical work of Mayer,[6] in which 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]:

$$\ln(\gamma_\pm) = -z_+|z_-|\left(\frac{\alpha I^{1/2}}{1+(I/m^\circ)^{1/2}} + \frac{2\nu_+\nu_-}{\nu}bm\right. \tag{7.4-16}$$

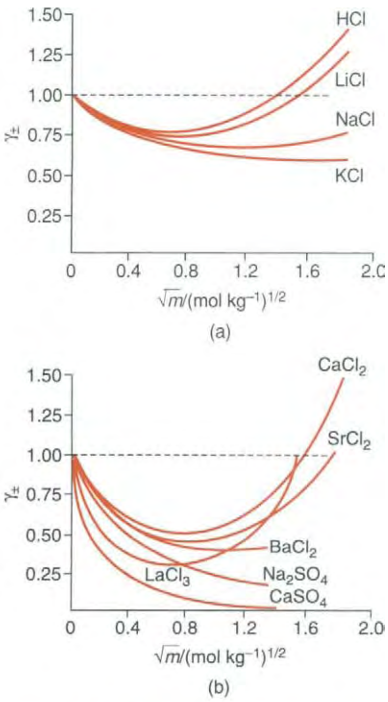

Figure 7.12. The Mean Ionic Activity Coefficients of Several Electrolyte Solutes as a Function of the Square Root of the Ionic Strength. According to the Debye–Hückel theory, the curves should coincide for a set of electrolytes with the same value of $z_+|z_-|$, as they do for a small region near zero value of the ionic strength.

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[3] J. N. Brønsted, *J. Am. Chem. Soc.*, **44**, 938 (1922).

[4] N. Bjerrum, *Kgl. Danske Vidensk. Selskab.*, **7**, no. 9 (1926).

[5] 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.

[6] J. E. Mayer, *J. Chem. Phys.*, **18**, 1426 (1950); K. S. Pitzer, *Acc. Chem. Res.*, **10**, 317, (1977).

[7] E. A. Guggenheim, *Phil. Mag.*, **19**, 588 (1935); E. A. Guggenheim and J. C. Turgeon, *Trans. Faraday Soc.*, **51**, 747 (1955).

where b is a parameter that is evaluated experimentally for each electrolyte solute. The **Davies equation**[8] assumes that a fixed value of this constant can be used for all electrolyte solvents. For water as the solvent and for a temperature of 298.15 K, the Davies equation is

$$\log_{10}(\gamma_{\pm}) = -0.510z_+|z_-|\left[\frac{(I/m^{\circ})^{1/2}}{1+(I/m^{\circ})^{1/2}} - 0.30\frac{I}{m^{\circ}}\right] \qquad (7.4\text{-}17)$$

This equation has no adjustable parameters in it, and is used when no experimental information is available for an ionic solute. In some cases it can give usable results for activity coefficients up to ionic strength 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, Eq. (7.4-13), with βa taken equal to unity, and of the Davies equation, Eq. (7.4-17).

Exercise 7.27

Calculate the activity coefficient for the solution of Example 7.12 using the Davies equation. Find the percent difference between the result of the Davies equation and the Debye–Hückel limiting law.

7.5 Phase Diagrams for Nonideal Mixtures

In this section, we present and discuss some temperature–composition and pressure–composition phase diagrams for nonideal two-component and three-component solutions.

Liquid–Vapor Phase Diagrams of Two-Component Nonideal Systems

Figure 7.13 shows a pressure–composition liquid–vapor phase diagram of ethanol and diethyl ether for a fixed temperature of 20°C. Figure 7.14 shows the temperature–composition phase diagram of the same mixture for a fixed pressure of 1.84 atm. Compare Figure 7.13 with Figure 7.3, which represents an ideal mixture. The curve in Figure 7.13 representing total vapor pressure as a function of liquid composition lies higher than the line segment that would represent Raoult's law. This is called **positive deviation from Raoult's law**. The curve representing the pressure as a function of vapor phase composition also lies higher than the ideal curve would. The corresponding temperature curves in Figure 7.14 lie lower than the curves for an ideal solution, since if the vapor pressure is larger than that of an ideal solution, the solution will boil at a lower temperature than an ideal solution. Deviation in the other direction also occurs with some mixtures, and this is called **negative deviation from Raoult's law**.

If the deviation from ideality is large enough, the curves in the phase diagram can exhibit a maximum or a minimum. Figure 7.15 shows the pressure–composition phase

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[8] C. W. Davies, *Ion Association*, Butterworth, London, 1962, pp. 35–52.

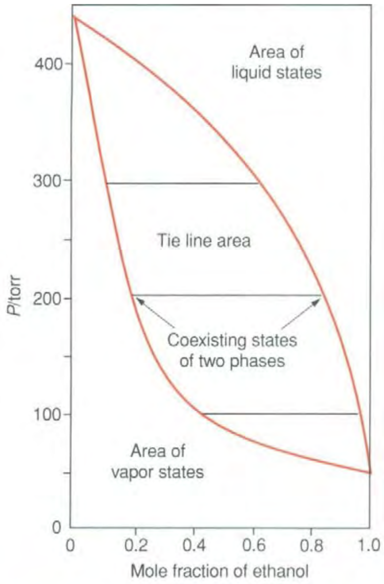

Figure 7.13. Pressure–Composition Phase Diagram for Diethyl Ether–Ethanol at 20°C. The lower curve shows the pressure as a function of mole fraction in the vapor, and the upper curve shows the pressure as a function of mole fraction in the liquid. Compare with Figure 7.3. Drawn from data in J. Timmermans, *Physicochemical Constants of Binary Systems*, Vol. 2, Interscience Publishers, New York, 1959, p. 401.

diagram of ethanol and benzene, which shows a maximum in the vapor pressure curve. A strong negative deviation can give a minimum in the vapor pressure curve. Either a maximum or minimum point in such a curve is called an **azeotrope**. The two curves representing liquid and vapor compositions are tangent at this point, so that the two phases have the same composition at an azeotrope. To show this fact we write the Gibbs–Duhem relation, Eq. (5.6-11), for the liquid phase at constant temperature and pressure. Using Eq. (7.3-1) and dividing by RT, we obtain

$$x_1\ d[\ln(a_1)] + d_2\ d[\ln(a_2)] = 0 \qquad (7.5\text{-}1)$$

where x_1 and x_2 are the mole fractions in the liquid. In order to have constant pressure, an additional gas, such as air, must be present in the gas phase. We neglect any of this gas that dissolves in the solution. Also, the effect of this added gas on the vapor pressure is small, as shown in Example 6.5, and we ignore it.

If the gas phase (assumed ideal) is at equilibrium with the solution, the chemical potential of component 1 has the same value in each phase. Assuming Convention I for the solution, we write

$$\mu_1^{\circ(\mathrm{l})} + RT\ \ln(a_1) = \mu_1^{\circ(\mathrm{gas})} + RT\ \ln(P_1/P^\circ)$$

For an infinitesimal equilibrium change in state at constant T and P,

$$RT\ d[\ln(a_1)] = RT\ d[\ln(P_1/P^\circ)] \qquad (7.5\text{-}2)$$

When Eq. (7.5-2) and the analogous equation for substance 2 are substituted in Eq. (7.5–1), we obtain for the vapor at equilibrium with the solution

$$x_1\ d[\ln(P_1/P^\circ)] + x_2\ d[\ln(P_2/P^\circ)] = 0$$

$$x_1 \frac{1}{P_1}\ dP_1 + x_2 \frac{1}{P_2}\ dP_2 = 0$$

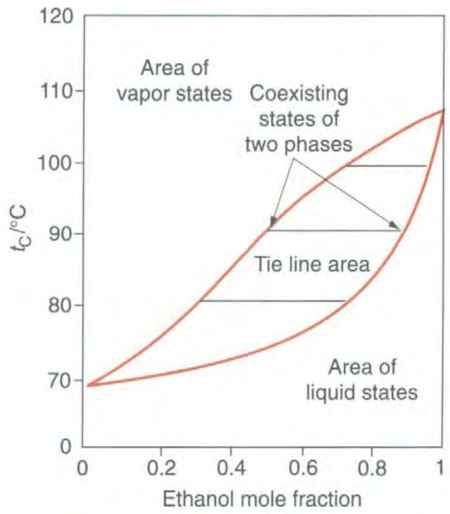

Figure 7.14. Temperature–Composition Phase Diagram for Diethyl Ether–Ethanol at 1.84 atm. The lower curve represents the temperature as a function of mole fraction in the liquid, and the upper curve represents the temperature as a function of mole fraction in the vapor. Compare with Figure 7.4 for a nearly ideal solution. Drawn from data in J. Timmermans, *Physicochemical Constants of Binary Systems*, Vol. 2, Interscience Publishers, New York, 1959, p. 401.

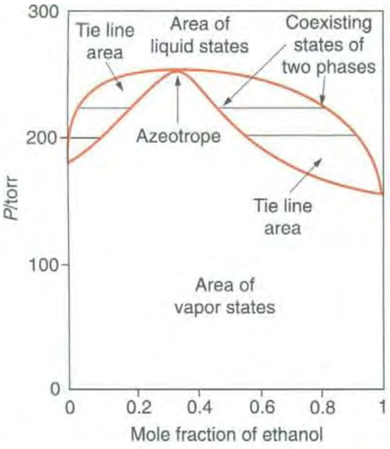

Figure 7.15. Liquid–Vapor Pressure–Composition Phase Diagram of Ethanol and Benzene, Showing an Azeotrope. In this diagram, we see a large positive deviation from ideality that produces a maximum in the curves. Drawn from data in J. Timmermans, *Physicochemical Constants of Binary Systems*, Vol. 2, Interscience Publishers, New York, 1959, p. 61.

where the mole fractions are those in the liquid solution. We convert this equation into a derivative equation:

$$\frac{x_1}{P_1}\left(\frac{\partial P_1}{\partial x_1}\right)_{T,P}+\frac{x_2}{P_2}\left(\frac{\partial P_2}{\partial x_1}\right)_{T,P}=0 \tag{7.5-3}$$

The total vapor pressure is the sum of the partial vapor pressures:

$$P_{\text{vap}}=P_1+P_2$$

At the azeotrope, the total vapor pressure is at a maximum or a minimum with respect to x_1, so that

$$\left(\frac{\partial P_{\text{vap}}}{\partial x_1}\right)_{T,P}=\left(\frac{\partial P_1}{\partial x_1}\right)_{T,P}+\left(\frac{\partial P_2}{\partial x_1}\right)_{T,P}=0 \tag{7.5-4}$$

When this equation is substituted into Eq. (7.5-3),

$$\frac{x_1}{P_1}=\frac{x_2}{P_2}$$

or

$$\frac{x_1}{x_2}=\frac{P_1}{P_2}=\frac{x_{1(\text{gas})}}{x_{2(\text{gas})}} \tag{7.5-5}$$

where we have used the fact that in an ideal gas mixture the mole fraction is proportional to the partial pressure (Dalton's law). We have shown that 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.

Azeotropes can occur with either positive or negative deviation from ideality. Figure 7.16 shows the temperature–composition phase diagram of acetone and chloroform, which exhibits an azeotrope. Since there is a maximum in the curves this diagram, a pressure–composition phase diagram would have a minimum, corresponding to a negative deviation from ideality. 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 have an azeotrope at 1.00 atm pressure at an ethanol mole fraction equal to 0.90. Any mixture of ethanol and water can be distilled to this composition, but no further.

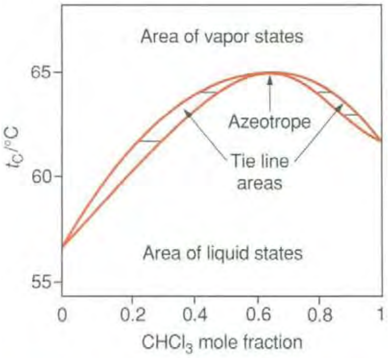

Figure 7.16. Liquid–Vapor Temperature–Composition Phase Diagram of Acetone and Chloroform. In this diagram we see a negative deviation from ideality that produces a maximum in the curves. This maximum corresponds to a minimum in the pressure–composition phase diagram.

Exercise 7.28

The normal boiling temperature of water is 100°C, and that of ethanol is 78.3°C. At 1.000 atm, the azeotrope boils at 78.17°C.

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 7.5, 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.

If a binary mixture has a sufficiently large positive deviation from ideality, there can be a separation into two liquid phases, each one of which is mostly one component saturated with the other component. Such phase separations are well known. ("Oil and water don't mix.") Figure 7.17 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 in the center of the diagram. Only the compositions to

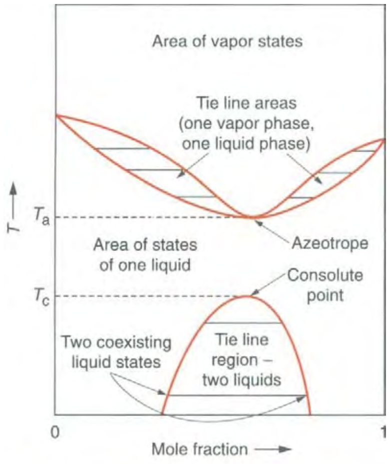

Figure 7.17. Temperature–Composition Phase Diagram of a System with Liquid–Liquid Phase Separation (Schematic). In this diagram, we see a large positive deviation from ideality that produces a phase separation into two liquid phases below a critical solution temperature T_c.

the right or to the left of this region are possible equilibrium compositions of a single liquid phase at temperatures below T_c. Any horizontal tie line connects points representing the compositions of the two liquids that can be at equilibrium with each other at the temperature of the tie line.

The highest point in the tie-line region is called an **upper critical solution point**, or an **upper consolate point**. It has a number of properties similar to those of the gas–liquid critical point in Figure 2.4. For example, 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. As its temperature is gradually raised, the meniscus between the phases becomes diffuse and disappears, in the same way that the meniscus between the liquid and vapor phases disappears as the liquid–vapor critical point is approached, as shown in Figure 2.5.

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. For example, below the lower consulute point at 61.5°C, water and nicotine mix in all proportions, and above the upper consolute temperature at 233.0°C, they also mix in all proportions.[9] Between these two temperatures, there is a tie-line region in the diagram and the liquids are only partially miscible. In this region, the Gibbs energy of the system is lower when it separates into two phases than it would be if it were in the (metastable) one-phase state. 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 7.17, the two-phase region can extend to the liquid–vapor region, and produce a phase diagram like that of Figure 7.18, which shows the temperature–composition phase diagram of furfural and water at 1.000 atm. The horizontal tie line at 97.90°C connects three points representing the compositions of the two liquid phases and one gas phase that can coexist at equilibrium. For two components and three phases, only one intensive variable is independent. Since the pressure is fixed for this diagram, no other variable is independent, and the compositions of all phases and the temperature are fixed for this state.

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 97.90°C at 1.000 atm. The vapor has a furfural mole fraction equal to 0.092, independent of the amounts of furfural and water. The vapor is condensed to a two-phase liquid, 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, which might decompose the organic substance.

Solid–Liquid Phase Diagrams

Figure 7.19 shows the solid–liquid temperature-composition phase diagram of gold and copper, which are completely miscible in both the solid and liquid phases. This diagram is similar in appearance to a liquid–vapor phase diagram such as the upper part of

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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).

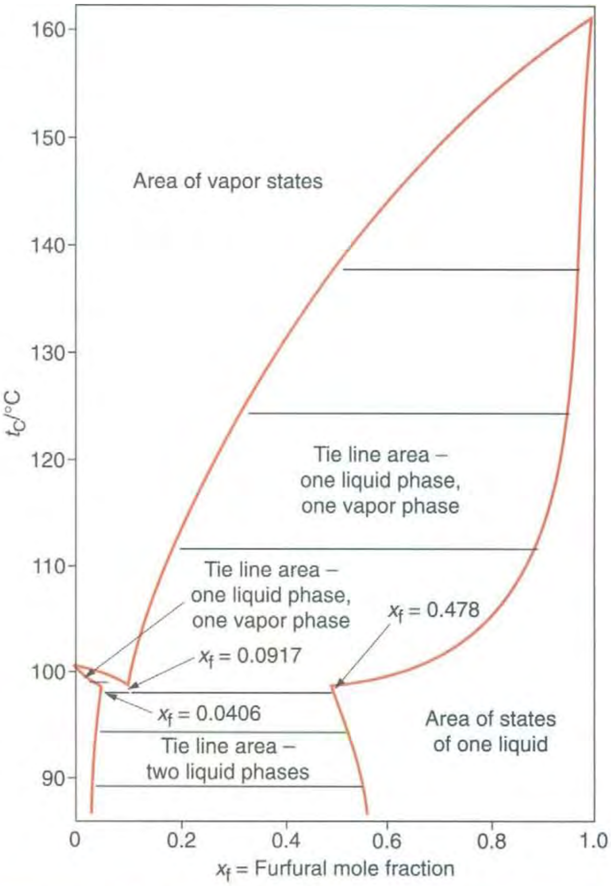


Figure 7.18. Liquid–Vapor Temperature–Composition Phase Diagram of Furfural and Water at 1.000 atm. In this diagram we see a large positive deviation from ideality that produces a phase separation into two liquid phases at all temperatures. (After G. H. Mains, *Chem. & Met. Eng.*, **26**, 779 (1922).

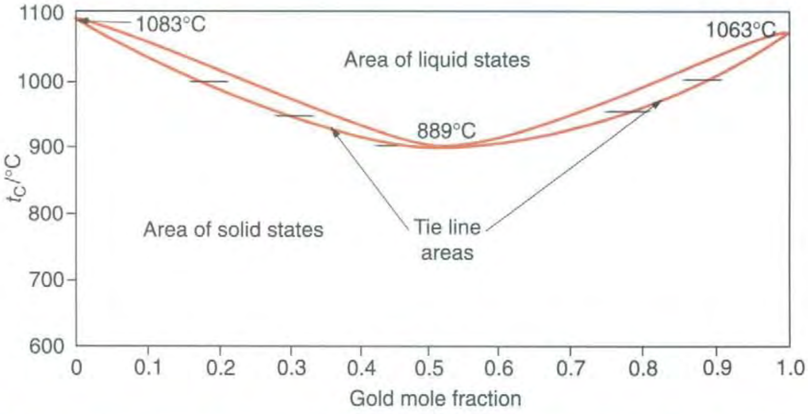


Figure 7.19. Solid–Liquid Temperature–Composition Phase Diagram of Gold and Copper. - Compare with Figure 7.17 for a liquid-vapor transition. From M. Hansen, *The Constitution of Binary Alloys*, McGraw-Hill, New York, 1958, p. 199.

Figure 7.17. Instead of a liquid solution, the lower area represents a solid solution, and instead of a gaseous mixture the area above the tie-line regions represents a liquid solution. The tie-line areas contain tie lines containing the composition of a solid solution and the composition of the liquid solution at equilibrium with that solid solution.

Just as liquids are sometimes purified by distillation, solids are sometimes purified by **zone refining**, in which a rod-shaped piece of the solid is gradually passed through a ring-shaped furnace. A zone of the solid melts as it passes into the furnace and refreezes as it passes 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 instead of a horizontal line segment. The liquid system is often not so easy to equilibrate as the vapor, but in many cases the solid that freezes out approximates the equilibrium composition at the other end of the tie line, being richer in the higher-melting component than the original solid. This is analogous to distillation in a still with one theoretical plate. A second pass through the furnace can lead to a further purification.

*Exercise 7.29

By drawing a "staircase" in Figure 7.19, 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 pases lead to if the curves had a maximum instead of a minimum?

Figure 7.20 shows the solid–liquid temperature–composition phase diagram of silver and copper at 1.00 atm. This diagram is similar in appearance to the liquid–vapor phase diagram of water and furfural in Figure 7.18, except that we have two coexisting solid solutions instead of two coexisting liquid solutions in the bottom area of the diagram.

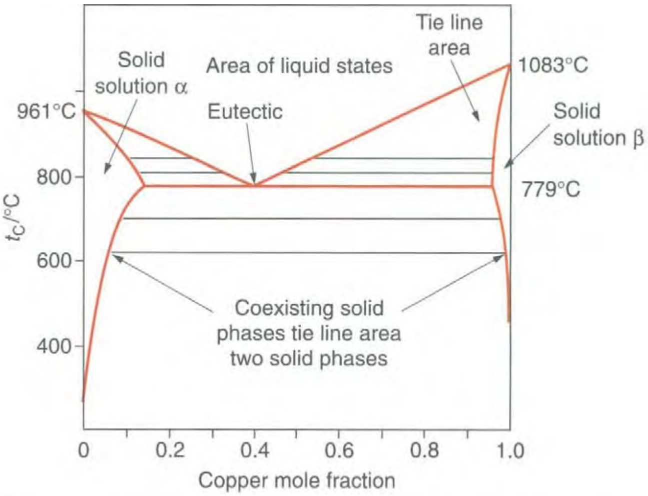


Figure 7.20. Solid–Liquid Temperature–Composition Phase Diagram of Silver and Copper. This diagram shows a sufficiently large deviation from ideality in the solid solutions that two different solid solution phases occur. From R. E. Dickerson, *Molecular Thermodynamics*, Benjamin, New York, 1969, p. 371.

Just as the tie line at 97.90°C in Figure 7.18 connects the state points representing two liquid phases and a vapor phase, the tie line at 779°C in Figure 7.20 connects the state points representing the two solid phases and one liquid phase that can be at equilibrium. The point representing the liquid phase at equilibrium with the two solid phases 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 the compositions represented by the ends of the tie line. This two-phase solid mixture can consist of very small grains of one phase imbedded in the other phase, so that it looks almost like a single phase unless viewed through a microscope.

Exercise 7.30

For each one-phase region in the phase diagram of Figure 7.20, 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.

Solid–liquid phase diagrams like that of Figure 7.20 are constructed by analyzing experiments in which a mixture of known composition is heated above its melting point and then allowed to cool slowly. Figure 7.21 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 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 rate of cooling becomes slower, since the enthalpy of freezing is evolved and since the composition of the liquid changes as the solid is removed. When the eutectic temperature is reached at 779°C, a second solid solution, rich in silver, 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 after the system is entirely frozen can the temperature drop further.

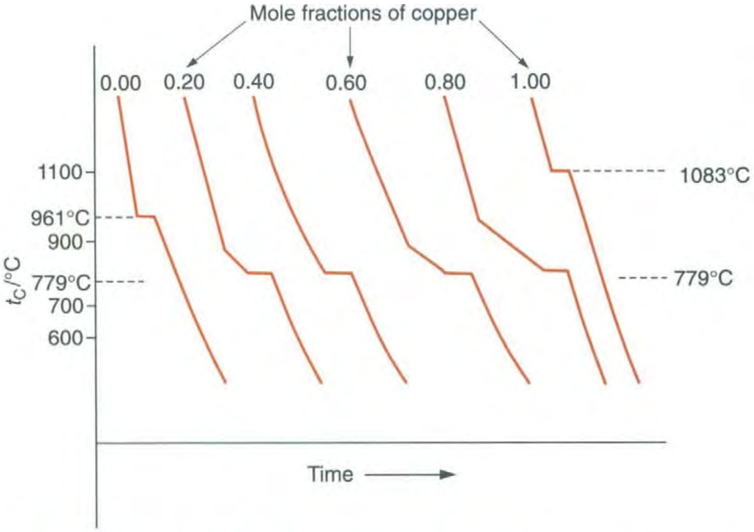


Figure 7.21. Cooling Curves for the Silver–Copper System. The first "break" in each curve represents the first appearance of a solid phase. The horizontal segments represent the eutectic, when three phases occur. From R. E. Dickerson, *Molecular Thermodynamics*, Benjamin, New York, 1969, p. 371.

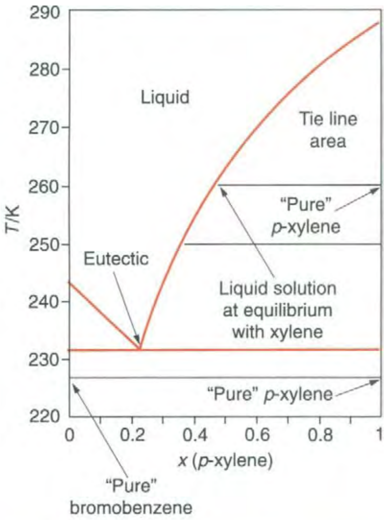


Figure 7.22. Solid–Liquid Temperature–Composition Phase Diagram of p-Xylene and Bromobenzene. There is a positive deviation from ideality that is sufficiently large to prevent any sig-nificant solid solubility. From M. L. McGlashan, *Chemical Thermodynamics*, Academic Press, New York, 1979, p. 268.

Figure 7.22 shows the solid–liquid pressure–composition phase diagram of *p*-xylene and bromobenzene at 1 atm. This diagram is similar to that of silver and copper in Figure 7.20 except that the solids are almost completely insoluble in each other. The regions of solid solubility are too small to show in the figure, and the two solids that equilibrate with each other are essentially pure substances.

Solid–Liquid Phase Diagrams with Compounds

Sometimes two substances form solid-state compounds, even if they do not react in the liquid or gas phase. Figure 7.23 shows the solid–liquid temperature–composition phase diagram of aniline (A) and phenol (P), which exhibit a one-to-one compound (AP) in the solid state and are completely miscible in the liquid phase. The existence of such a compound depends not only on the interaction between the reactant molecules but also on the crystal lattice. The compound AP exists only in the solid state. When it melts, an equimolar liquid solution of aniline and phenol results.

The phase diagram resembles two phase diagrams set side by side, and that is essentially what it is. The vertical line at mole fraction 0.5 represents the compound $C_6H_5OH{\cdot}C_6H_5NH_2$, which we abbreviate by AP. 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. Each diagram contains a eutectic point,

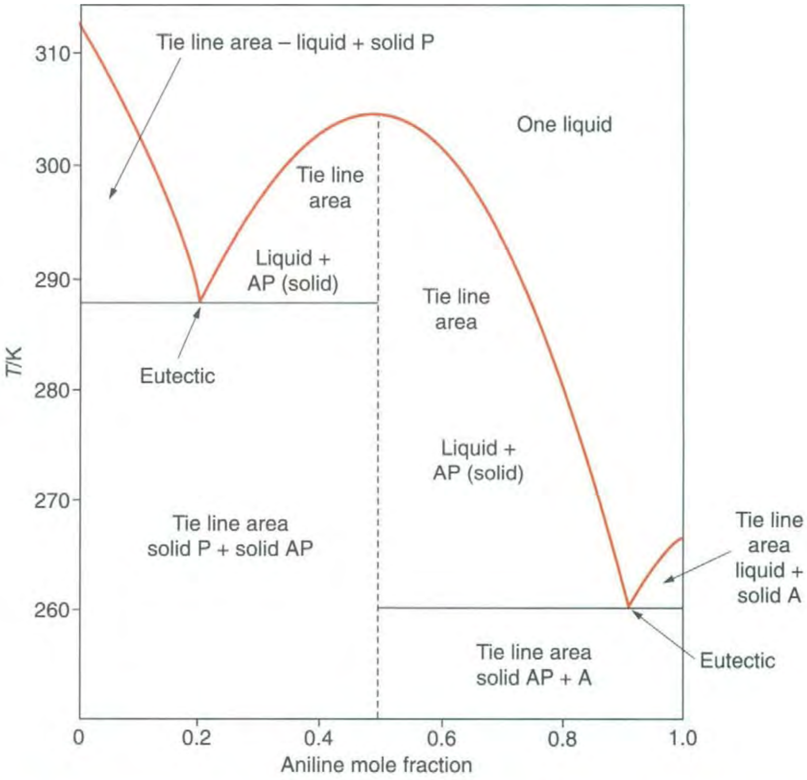


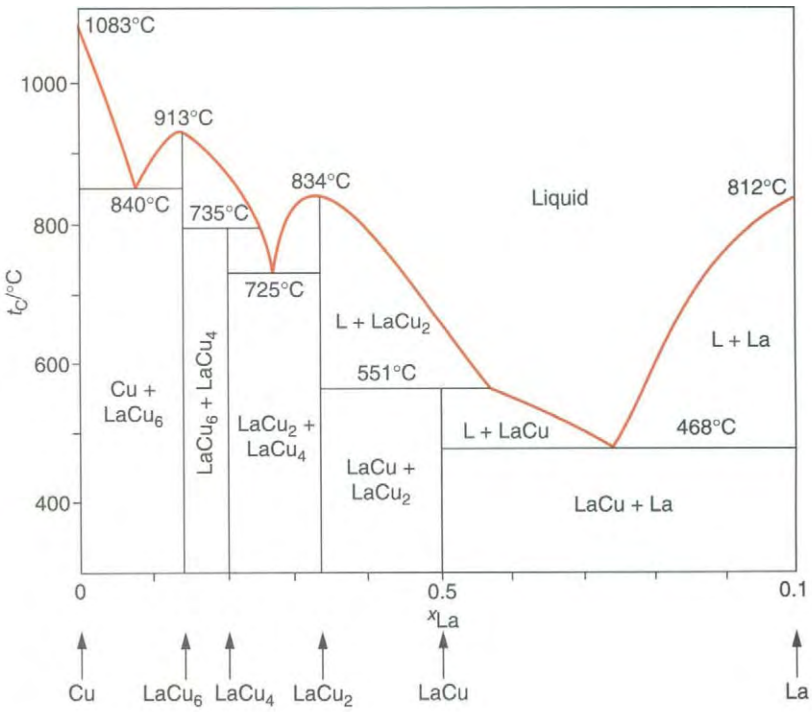
Figure 7.23. Solid–Liquid Temperature–Composition Phase Diagram of Phenol and Aniline. In this diagram we see the occurrence of a stoichiometric compound of the two substances, containing the same number of moles of each substance.

below which the two nearly pure solid substances can coexist. Either A or P can coexist with the compound AP, but they cannot coexist with each other at equilibrium because of the existence of the compound.

If more than one solid compound occurs a solid–liquid phase diagram can be quite complicated. Figure 7.24 shows the temperature–composition phase diagram of copper and lanthanum, with four different compounds. There are only two maxima in the diagram, for the compounds $LaCu_2$ and $LaCu_6$. The two compounds $LaCu_4$ and LaCu do not melt in the same way as does the compound of aniline and phenol and the compounds $LaCu_2$ and $LaCu_6$. For example, at 551°C, LaCu melts to form a liquid phase with lanthanum mole fraction equal to 0.57 plus solid $LaCu_2$, as indicated by the tie line. This phenomenon is called **incongruent melting**, because the liquid phase does not have the same composition as the solid phase from which it arose. The point representing the composition of the liquid at 551°C is called a **peritectic point**.

Exercise 7.31

For each area in Figure 7.24, tell what phase or phases occur, and give the number of independent intensive variables.



7.24. Solid–Liquid Temperature–Composition Phase Diagram of Copper and Lanthanum. There are four compounds. There is no eutectic between LaCu and $LaCu_2$. The compound LaCu melts incongruently to give solid $LaCu_2$ and a liquid solution. From R. E. Dickerson, *Molecular Thermodynamics*, Benjamin, New York, 1969, p. 379.

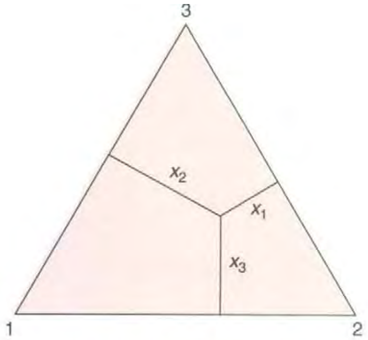


Figure 7.25. Mole Fractions of a Three-Component System Plotted in an Equilateral Triangle. The three perpendicular distances from any interior point to the three sides of an equilateral triangle have a constant sum.

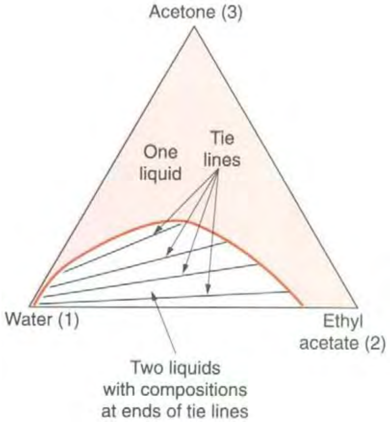


Figure 7.26. Liquid–Liquid Composition–Composition Phase Diagram of Water, Acetone, and Ethyl Acetate at 1 atm and 30°C. The region at the bottom of the diagram corresponds to separation of two liquid phases, as shown by the ends of the tie lines.

Three-Component Phase Diagrams

For three components and one phase, $f = 3 - 1 + 2 = 4$. We have already had to keep one variable fixed in order to draw a two-dimensional phase diagram for two components. For three components we must keep two variables fixed to have a two-dimensional phase diagram. If the amount of one substance is held fixed at zero, we have an ordinary two-component phase diagram. If the temperature and the pressure are both held fixed, we have a composition–composition phase diagram, since two mole fractions are independent if there is a single phase.

For a composition–composition phase diagram at a fixed temperature and a fixed pressure, an equilateral triangle is customarily used, as depicted in Figure 7.25, instead of a plane with two perpendicular axes. There is a theorem of plane geometry that asserts that the sum of the three perpendicular distances to the sides has the same value for any point inside an equilateral 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, which must add to unity. Each vertex of the triangle represents a different pure component, and the pependicular distance from the opposite side to any point inside the triangle equals the mole fraction of the component represented by that point.

Figure 7.26 shows the liquid–liquid composition–composition phase diagram of water, acetone, and ethyl acetate at 30°C and 1.00 atm. The tie lines in the two-phase region connect points 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 any side of the triangle or to each other. Their directions must be determined experimentally.

In order to display a temperature–composition phase diagram at constant pressure, a three-dimensional space must be used. Figure 7.27 shows a perspective view of a partial solid–liquid phase diagram for bismuth, tin, and lead. These substances actually dissolve appreciably in each other in the solid phases, but the solid solution regions are artificially shrunk to zero to simplify the diagram. Each face of the triangular prism is a two-component temperature–composition diagram. Each two-component diagram has a single eutectic, and the bismuth–lead diagram also has a peritectic point, but we will ignore this in describing the phases that can occur. The interior of the prism represents compositions in which all three components are present. There is a **triple eutectic** at 96°C. The surface shown in the diagram is the lower boundary of the three-dimensional one-phase liquid region. This surface has three grooves in it that lead down to the triple eutectic from the three two-component eutectics.

Below the surface lie regions corresponding to two, three, or four phases. Figure 7.28 shows schematically a composition–composition phase diagram obtained by passing a plane through the prism slightly above the triple eutectic. The central roughly triangular region is a one-phase liquid region inside which all points represent possible compositions of a single liquid phase. Each tie line from an edge of this region connects to a corner of the diagram. This means that only one solid phase freezes out from a composition corresponding to a point on the edge of the region. At a composition corresponding to a corner of the region, two components freeze out, as in a two-component eutectic. The triangular regions along the sides of the triangle are three-phase regions. Just as the two ends of a tie line give the possible compositions of two phases, the corners of these regions give the compositions of three coexisting phases (the liquid with a composition corresponding to the corner of the liquid region, and the two solids). There are no tie lines in these regions and each region could be called a "tie triangle."

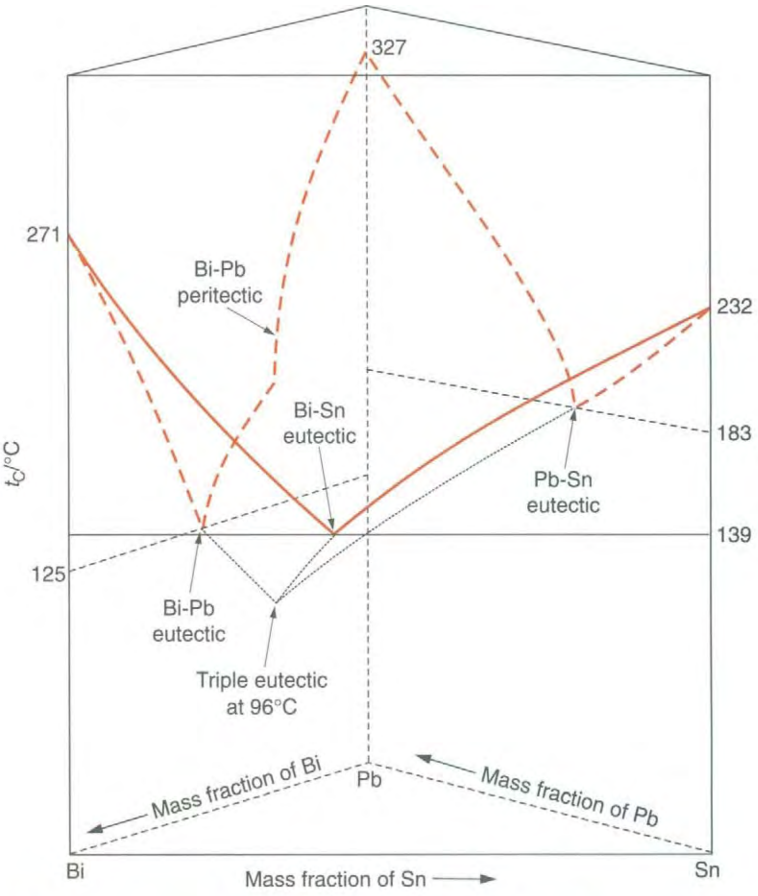


Figure 7.27. Perspective View of 3-Dimensional Temperature–Composition Phase Diagram of Bismuth, Tin, and Lead at 1 atm. The diagram has been simplified by omission of the regions of solid solubility. Each face of the triangular prism is a two-component temperature–composition phase diagram with a eutectic. There is also a peritectic point in the Bi–Pb phase diagram. From F. T. Gucker and R. L. Seifert, *Physical Chemistry*, W. W. Norton, New York, 1966, p. 773.

At the triple eutectic temperature, the liquid region has shrunk to a point, from which three tie lines extend, one to each corner, indicating that at the triple eutectic three solid phases at equilibrium with the eutectic liquid. Four phases are at equilibrium, and if the pressure is fixed, the temperature and the compositions of the four phases are fixed.

7.6 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 the properties have on solute concentration. The four principal colligative properties are freezing point depression, boiling point elevation, vapor pressure lowering, and osmotic pressure. Discussing these four phenomena is like performing variations on a theme. The theme on which we will see four variations is the fundamental fact of phase equilibrium. We will assume that the

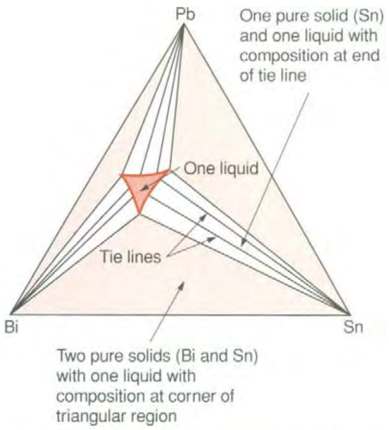


Figure 7.28. Schematic Solid–Liquid Composition–Phase Diagram of Bismuth, Tin, and Lead at 100°C and 1 atm. This temperature is slightly above the triple eutectic temperature. The diagram is produced by passing a horizontal plane through the three-dimensional diagram shown in Figure 7.27. The small roughly triangular liquid area is the only one-phase area in the diagram.

solution is dilute, so that the solutes obey Henry's law and the solvents obey Raoult's law.

Freezing Point Depression

Consider a system consisting of a liquid solution with a single solute at equilibrium with the pure solid solvent. We assume that the solute is completely insoluble in the frozen solvent. From the fundamental fact of phase equilibrium,

$$\mu_1(\text{liq}) = \mu_1^*(\text{solid}) \tag{7.6-1}$$

where the solvent is called component number 1. We assume that the solution is dilute, so that the solvent acts as it would in an ideal solution. Therefore,

$$\mu_1^*(\text{liq}) + RT\ln(x_1) = \mu_1^*(\text{solid}) \tag{7.6-2}$$

where x_1 is the mole fraction of the solvent in the solution. There are two phases and two components, so that by the Gibbs phase rule there are two independent intensive variables. If we regard pressure and temperature as independent, the mole fraction of the solvent becomes a dependent variable.

We divide Eq. (7.6-2) by T and then differentiate it with respect to temperature, keeping the pressure fixed:

$$\left(\frac{\partial(\mu_1^*(\text{liq})/T)}{\partial T}\right)_P + R\left(\frac{\partial\ln(x_1)}{\partial T}\right)_P = \left(\frac{\partial\mu_1^*(\text{solid})/T}{\partial T}\right)_P \tag{7.6-3}$$

We obtain an identity by use of thermodynamic relations:

$$\left(\frac{\partial(\mu_i^*/T)}{\partial T}\right)_P = \frac{T(\partial\mu_i^*/\partial T)_P - \mu_i^*}{T^2} = \frac{-TS_{\text{m},i}^* - \mu_i^*}{T^2} = -\frac{H_{\text{m},i}^*}{T^2} \tag{7.6-4}$$

Use of this identity in Eq. (7.6-3) gives

$$R\left(\frac{\partial\ln(x_1)}{\partial T}\right)_P = \frac{H_{\text{m},1}^*(\text{liq}) - H_{\text{m},1}^*(\text{solid})}{T^2} = \frac{\Delta_{\text{fus}}H_{\text{m},1}}{T^2} \tag{7.6-5}$$

where $\Delta_{\text{fus}}H_{\text{m},1}$ is the molar enthalpy change of fusion (melting) of the pure solvent. In Eq. (7.6-5), x_1 is a dependent variable since we have chosen T and P to be the two independent variables.

We multiply Eq. (7.6-5) by dT and integrate both sides of Eq. (7.6-5) from the normal melting temperature of the pure solvent $T_{\text{m},1}$ to some lower temperature T'.

$$R\int_{T_{\text{m},1}}^{T'}\left(\frac{\partial\ln(x_1)}{\partial T}\right)_P dT = \int_{T_{\text{m},1}}^{T'}\frac{\Delta_{\text{fus}}H_{\text{m},1}}{T^2}\,dT \tag{7.6-6}$$

To a good approximation, the enthalpy change of fusion is constant over a small range of temperature. The result of the integration is therefore

$$R\ln[x_1(T')] = -\Delta_{\text{fus}}H_{\text{m},1}\left(\frac{1}{T'} - \frac{1}{T_{\text{m},1}}\right) \tag{7.6-7}$$

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 the equilibrium value of $x_1 = 1$ at temperature $T_{\text{m},1}$.

Our present system (solid pure solvent plus liquid solution) is the same as the system that corresponds to one of the liquid composition curves in a solid–liquid phase diagram such as Figure 7.22, so that Eq. (7.6-7) is the equation for this curve if Raoult's law holds and if there is no appreciable solid solubility. In this case the curve is independent of the identity of the second component (except that it stops when it meets the other curve at the eutectic point).

For dilute solutions, Eq. (7.6-7) is simplified by using the first term of a Taylor series:

$$\ln(x_1) = \ln(1 - x_2) \approx -x_2 \tag{7.6-8}$$

This is valid only if x_2 is small compared with unity.

*Exercise 7.32

a. Write the next two terms in the Taylor series for $\ln(1 - x_2)$.

b. Evaluate the two terms of part (a) for $x_2 = 0.01$.

c. Find the percentage error for the approximation of Eq. (7.6-8) for $x_2 = 0.100$, 0.0100, 0.00100, and 0.000100.

Use of the approximation of Eq. (7.6-8) gives

$$x_2 \approx \Delta_{\text{fus}}H_{\text{m},1}\frac{T_{\text{m},1} - T}{RT_{\text{m},1}T} \tag{7.6-9a}$$

where we drop the prime symbol on the equilibrium temperature. Equation (7.6-9a) is accurate only for dilute solutions, in which case T is approximately equal to $T_{\text{m},1}$. We write as a further approximation

$$x_2 \approx \left(\frac{\Delta_{\text{fus}}H_{\text{m},1}}{RT_{\text{m},1}^2}\right)\Delta T_{\text{f}} \tag{7.6-9b}$$

where we use the symbol ΔT_{f} for $T_{\text{m},1} - T$, the freezing point depression.

Equation (7.6-9b) is often rewritten in terms of the molality, using Eq. (5.6-11) to relate the molality and the mole fraction for a dilute solution. The result is

$$\Delta T_{\text{f}} = K_{\text{f}1}m_2 \tag{7.6-10}$$

where m_2 is the molality of the solute (component 2) and where M_1 is the molar mass of the solvent (measured in kilograms). The quantity $K_{\text{f}1}$ is called the **freezing point depression constant**.

$$K_{\text{f}1} = \frac{M_1RT_{\text{m},1}^2}{\Delta_{\text{fus}}H_{\text{m},1}} \tag{7.6-11}$$

The freezing point depression constant has a different value for each solvent, but is independent of the identity of the solute. Equation (7.6-11) is still valid if there are several solutes, in which case m_2 is replaced by the sum of the molalities of all solutes. If a solute dissociates or ionizes, the total molality of all species must be used.

Exercise 7.33

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 7.13

Find the freezing point depression of a solution of 10.00 g of sucrose in 1.000 kg of water.

Solution

$$m_2 = \frac{10.00\ \text{g sucrose}\left(\dfrac{1\ \text{mol sucrose}}{342.30\ \text{g sucrose}}\right)}{1.000\ \text{kg}} = 0.02921\ \text{mol kg}^{-1}$$

$$\Delta T = (1.86\ \text{K kg mol}^{-1})(0.02921\ \text{mol kg}^{-1}) = 0.0543\ \text{K}$$

Boiling Point Elevation

Consider a volatile solvent (component 1) and a nonvolatile solute (component 2) in a solution that is at equlibrium with pure component 1 in a vapor phase. We assume that the dilute solution approximation is valid, that the gas phase is ideal, and that our system is at a fixed pressure P. The fundamental fact of phase equilibrium gives

$$\frac{\mu^*_{1(\text{liq})}}{T} + R\ \ln(x_{1(\text{liq})}) = \frac{\mu_{1(\text{gas})}}{T} \tag{7.6-12}$$

where we have divided the equation by T. Differentiation of this equation with respect to T at constant P and use of the identity of Eq. (7.6-4) gives

$$R\left(\frac{\ln(\partial x_{1(\text{liq})})}{\partial T}\right)_P = -\frac{H_{\text{m},1(\text{gas})}}{T^2} + \frac{H_{\text{m},1(\text{liq})}}{T_2} = -\frac{\Delta_{\text{vap}}H_{\text{m},1}}{T^2} \tag{7.6-13}$$

where $\Delta_{\text{vap}}H_{\text{m},1}$ is the molar enthalpy change of vaporization of the pure liquid component 1. This equation is similar to Eq. (7.6-5) except that the right-hand side of Eq. (7.6-13) is a negative quantity, while that of Eq. (7.6-5) is a positive quantity. The reason for this difference is that going from the liquid phase to the vapor phase is an endothermic process, while going from the liquid phase to the solid phase is an exothermic process.

We now multiply Eq. (7.6-13) 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, giving an equation analogous to Eq. (7.6-7):

$$R\ \ln(x_1^{(\text{liq})}) = \Delta_{\text{vap}}H_{\text{m},1}\left(\frac{1}{T'} - \frac{1}{T_{\text{b},1}}\right) \tag{7.6-14}$$

Equation (7.6-14) can be simplified in the case of small boiling point elevations by using the same approximations as were used in Eq. (7.6-9b), with the result

$$x_2 = \left(\frac{\Delta_{\text{vap}}H_{\text{m},1}}{RT^2_{\text{b},1}}\right)\Delta T_{\text{b}} \tag{7.6-15}$$

where $\Delta T_{\text{b}} = T - T_{\text{b},1}$ is the boiling point elevation (a positive quantity). Notice how similar the boiling point elevation equation is to the freezing point depression equation.

When Eq. (7.6-15) is solved for the boiling point elevation and written in terms of the molality, the result is analogous to Eq. (7.6-10):

$$\Delta T_{\text{b}} = K_{\text{b}1}m_2 \tag{7.6-16}$$

where the boiling point elevation constant for component 1 is given by

$$K_{b1} = \frac{M_1 R T_{b,1}^2}{\Delta_{vap} H_{m,1}} \tag{7.6-17}$$

Again, this quantity is different for each solvent, but does not depend on the identity of the solute or solutes. If more than one solute is present, the molality m_2 is replaced by the sum of the molalities of all solutes.

***Exercise 7.34**

a. Find the value of the boiling point elevation constant for water. The molar enthalpy change of vaporization is equal to $40.67\,\mathrm{kJ\,mol^{-1}}$.

b. Find the boiling temperature at 1.00 atm of a solution of glucose with 5.00 g of glucose in 1.000 kg of water.

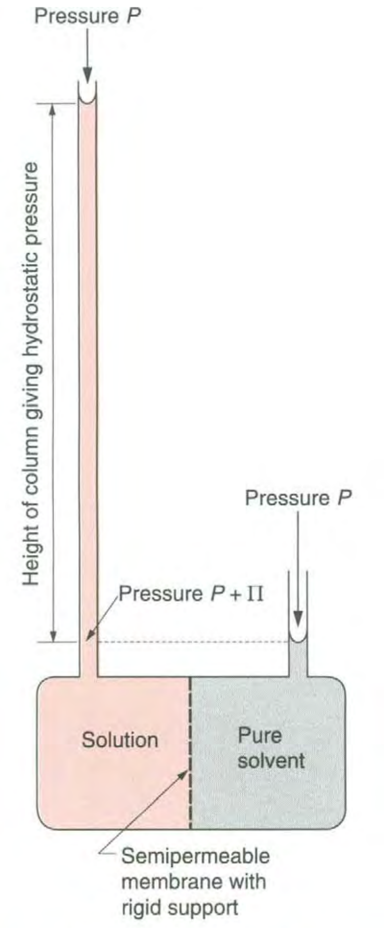


Figure 7.29. An Osmometer (Schematic). The system is equilibrated by the hydrostatic pressure of the column of solution in the left tube.

Vapor Pressure Lowering

For a nonvolatile solute and a volatile solvent that obeys Raoult's law, the total vapor pressure is equal to the partial vapor pressure of the solvent, given by

$$P_{vap(total)} = x_1 P_1^* \tag{7.6-18}$$

where P_1^* is the vapor pressure of the pure solvent (component 1). The lowering of the vapor pressure is given by

$$\Delta P_{vap} = P_1^* - x_1 P_1^* = P_1^*(1 - x_1) = P_1^* x_2 \tag{7.6-19}$$

***Exercise 7.35**

a. Calculate the vapor pressure at 100.0°C of the solution in Exercise 7.34b.

b. From Eq. (7.6-19), obtain an expression for the vapor pressure lowing of a dilute solution in terms of the molality.

Osmotic Pressure

This colligative property involves the equilibrium of a liquid solution and its pure liquid solvent on opposite sides of a semipermeable membrane that allows only the solvent to pass and to be equilibrated between the two sides. The chemical potential of the solvent is made to have equal values in the two phases by having the two phases at different pressures. A simple apparatus in which this equilibrium can be accomplished is shown in Figure 7.29. The left side of the apparatus contains a solution containing a solute (component 2) dissolved in a solvent (component 1), and the right side contains the same 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, and the entire apparatus is held at constant temperature. Let the pressure on the pure solvent on the right side of the semipermeable membrane be called P, and the pressure on the solution of the left side be called $P + \Pi$. The difference Π is the **osmotic pressure**.

At equilibrium, the value of the chemical potential of the solvent must be the same on both sides of the membrane:

$$\mu_1^*(T,P) = \mu_1(T,P+\Pi) = \mu_1^*(T,P+\Pi) + RT\ \ln(x_1) \qquad (7.6\text{-}20)$$

From Eq. (5.3-10), if the molar volume of the pure liquid is nearly independent of pressure (a good approximation),

$$\mu_1^*(T,P+\Pi) - \mu_1^*(T,P) = \int_P^{P+\Pi} V_{\mathrm{m},1}^*\,dP \approx \Pi V_{\mathrm{m},1}^* \qquad (7.6\text{-}21)$$

which gives

$$\Pi V_{\mathrm{m},1}^* = -RT\ \ln(x_1) = -RT\ \ln(1-x_2) \approx RTx_2 \qquad (7.6\text{-}22)$$

where the approximation of Eq. (7.6-8) for dilute solutions has been applied. It is customary to rewrite Eq. (7.6-22) 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

$$V = n_1\bar{V}_1 + n_2\bar{V}_2 \approx n_1 V_{\mathrm{m},1}^*$$

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 this work on osmotic pressure. He was also the first person to propose the tetrahedral carbon atom.

Use of these two equations gives

$$\Pi = \frac{n_2RT}{V} = c_2RT \qquad (7.6\text{-}23)$$

where c_2 is the concentration of the solute. Equation (7.6-23) is remarkably similar to the ideal gas equation of state. It is known as the **van't Hoff equation.**

Exercise 7.36

a. Verify Eq. (7.6-23).
***b.** Find the osmotic pressure of a solution of 5.00 g of glucose in enough water to make 1.000 L of solution.

For solutions of moderate concentration, the osmotic pressure is quite large. According to the van't Hoff equation, a 1.00 mol L^{-1} solution has an osmotic pressure of 24.4 atm at 25°C, corresponding to the hydrostatic pressure of a column of water roughly 250 m high.

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 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:

$$P_i = k_i x_i$$

A solution in which Henry's law is obeyed by the solutes is called a dilute solution.

The activity a_i is defined by the general 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

$$a_i^{(m)} = \frac{\gamma_i^{(m)} m_i}{m^\circ}$$

The Debye–Hückel theory provides an accurate limiting law for the activity coefficients of electrolyte solutes. A semiempirical 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, and a temperature–composition diagram is plotted in a (three-dimensional) triangular prism.

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.

PROBLEMS

Problems for Section 7.1

7.37. Derive Eq. (7.1-26).

7.38. 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.

***7.39.** Assume that a 1.000 molal solution of naphthalene in benzene is ideal. Calculate the value of the activity coefficient in the molality description and in the concentration description.

7.40. Assume that carbon tetrachloride and 1,1,1-trichloroethane (methylchloroform) 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).

7.41. 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).

Problems for Section 7.2

7.42. 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 at a gas at 1.000 atm and 20.0°C.

*7.43. **a.** From the value in Exercise 7.11, 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. (Two moles of thiosulfate are required to react with 1 mol of I_2.)

7.44. From the value in Exercise 7.11, find the value of the distribution coefficient for iodine between water and carbon tetrachloride at 25°C, using the molality description.

*7.45. From the value of Henry's law constant for ethanol in benzene at 40°C, calculate the value of Henry's law constant for ethanol in benzene at this temperature if mass fractions are used instead of mole fractions to describe the system.

7.46. 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.

Problems for Section 7.3

*7.47. Find the activity of pure liquid water at 1250 bar and 25°C.

7.48. Find the activity of graphite and that of diamond at the coexistence pressure at 298.15 K.

*7.49. 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.

7.50. 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 any solution that is equilibrated with solid naphthalene (a saturated solution) has the same mole fraction of naphthalene, independent of the solvent, if the solution is ideal.

*7.51. 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 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. 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.

7.52. **a.** From data in Problem 7.51, find the activity coefficient of chloroform in acetone for the solution of Problem 7.51, using the molality description and regarding acetone as the solvent.

b. Find the activity coefficient of acetone in the solution of Problem 7.51, using the molality description and regarding acetone as the solvent.

*7.53. **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. Note that tabulated values for strong electrolytes in solution are listed for the separate ions.

b. From data on Gibbs energy changes of formation in Table A.8, find the value of $\mu^{\circ(\text{m})} - G_{\text{m}}^*$ (solid) for KOH at 298.15 K.

7.54. The maximum solubility of iodine in water at 1.000 atm and 298.15 K is equal to 1.42×10^{-3} mol kg^{-1}. Find the value of $\mu^{\circ(\text{m})} - \mu^{*(\text{solid})}$ for I_2. State any assumptions.

Problems for Section 7.4

*7.55. **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 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.

7.56. **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. (7.4-13), and using a value of βa equal to 1.00 $\text{kg}^{1/2}$ $\text{mol}^{-1/2}$. Repeat the calculation for a 0.0075 molal $FeSO_4$ 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).

7.57. 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 7.12 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 7.12 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 7.12 and comment on any differences.

Problems for Section 7.5

7.58. Describe what happens if one begins with a fairly small amount of water at 99.0°C and gradually adds furfural to the water until one has a mixture that has a mole fraction of furfural equal to 0.90. The temperature is maintained at 99.0°C. Give the approximate mole fractions at which phase transitions occur.

7.59. 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.

7.60. Sketch cooling curves for mixtures of phenol (P) and aniline (A) with aniline mole fractions equal to 0.26 (at the eutectic between A and AP), 0.35, 0.50, and 0.90. Describe what happens at each break in each curve.

7.61. 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.[11] Label each area in the diagram with the number of independent intensive variables corresponding to that phase.

7.62. 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.[12]

7.63. 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.

7.64. 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.

b. Repeat part (a) for a mole fraction of lanthanum equal to 0.53.

7.65. 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.

7.66. Figure 7.30 shows a phase diagram of lithium sulfate, ammonium sulfate, and water. For each area in the diagram, say what phase or phases is present and give the number of independent intensive variables.

Problems for Section 7.6

7.67. Find the freezing point depression of a solution of 1.500 g of KCl in 1.000 kg of water. Assume that the KCl

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[11] J. B. Ott, J. R. Goates, D. R. Anderson, and H. T. Hall Jr., *Trans. Faraday Soc.*, **65**, 2876 (1969).

[12] The actual diagram might be more complicated. See Hansen, *The Constitution of Binary Alloys*, McGraw-Hill, New York, 1958, pp. 1238ff.

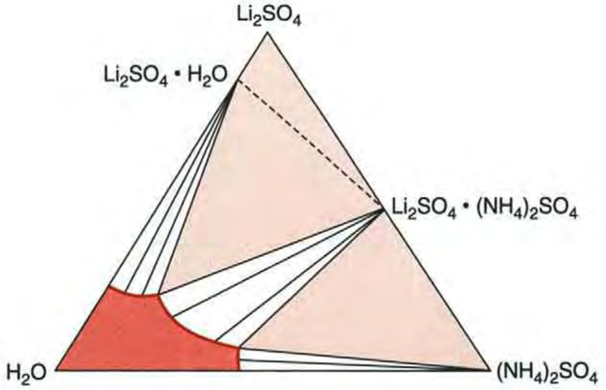

Figure 7.30. Concentration–Concentration Phase Diagram of Lithium Sulfate, Ammonium Sulfate, and Water at 30°C and 1.000 atm. Pure lithium sulfate and ammonium sulfate are solid at this temperature.

dissociates completely, so that two moles of dissolved ions result from one mole of KCl.

7.68. **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. (7.6-9b).

b. Calculate the freezing temperature of the solution of part (a) using Eq. (7.6-7).

c. Modify Eq. (7.6-7) 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).

***7.69.** **a.** Calculate the boiling temperature of the solution of Problem 7.68, using Eq. (7.6-14).

b. Repeat the calculation using Eq. (7.6-15) and calculate the percent difference of the boiling point elevation from that of part (a).

c. Repeat the calculation using Eq. (7.6-16) and calculate the difference of the boiling point elevation from that of part (a).

7.70. 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 mL^{-1}. The freezing temperature depression is 3.04°C. Find the molar mass of the solute.

7.71. 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.

7.72. The density of ethylene glycol is 1.1088 g 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. State any assumptions.

***7.73.** The molar enthalpy change of fusion of ethylene glycol is 11.23 kJ mol^{-1}. Its density is given in the preceding problem. Find the freezing temperature of a solution made from 0.500 L of water and 9.500 L of ethylene glycol. State any assumptions.

7.74. **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 7.5. 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.

***7.75.** **a.** Calculate the osmotic pressure at 20.00°C of a solution of 5.00 g of sucrose in 95.00 g of water, using Eq. (7.6-23). 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 7.29.

b. Repeat the calculation using the version of Eq. (7.6-22) with the natural logarithm in it.

c. Repeat the calculation, assuming the same value for the activity coefficient of water as found in part (c) of Problem 7.68.

7.76. 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}.

General Problems

***7.77.** 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, every activity coefficient is equal to unity.

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.

7.78. 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 7.31. The 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 distance $L_1^{(\beta)}$ 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.

7.79. The freezing temperature of CH_2OHCH_2OH, ethylene glycol (the main ingredient of automobile antifreeze), is −11.5°C. Its density is $1.1088\,\mathrm{g\,cm^{-3}}$, and its enthalpy change of fusion is $11.23\,\mathrm{kJ\,mol^{-1}}$.

a. Find the freezing point depression constant for solutions with ethylene glycol as the solvent.

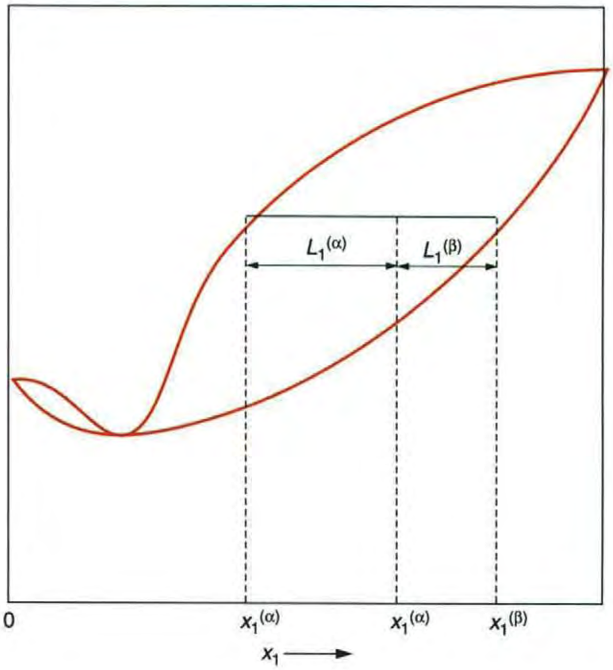

Figure 7.31. Phase Diagram Illustrating the Lever Rule. The lever rule is similar to the formula for levers, $F_1L_1 = F_2L_2$, where the Fs stand for forces and the Ls stand for the lengths of the lever arms.

b. Find the freezing temperature of a solution of 10.0 g of water in 1.000 kg of ethylene glycol.

c. Find the freezing temperature of a solution of 10.0 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. (7.6-7) 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?

8

The Thermodynamics of Chemical Equilibrium

OBJECTIVES

After studying this chapter, a student should:

1. understand the thermodynamic origin of equilibrium constant expressions;
2. be able to carry out equilibrium calculations on various kinds of chemical systems;
3. be able to apply the principle of Le Châtelier;
4. understand some models for the coupling of chemical reactions in biological systems.

PRINCIPAL FACTS AND IDEAS

1. The principles of thermodynamics determine the state of chemical equilibrium for any system.
2. The familiar equilibrium constant expression of elementary chemistry is equal to a constant at constant temperature and pressure, when modified to include activity coefficients.
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.

8.1 Gibbs Energy Changes and Equilibria of Chemical Reactions. The Equilibrium Constant

Equation (3.7-7) is a "generic" chemical equation that can stand for any chemical reaction:

$$0 = \sum_{i=1}^{c} \nu_i \mathcal{F}_i \tag{8.1-1}$$

where the formula of substance number i is denoted by $\mathcal{F}_i$ and its stoichiometric coefficient is denoted by ν_i. The stoichiometric coefficients of products are positive, and those of reactants are negative. For example, the equation for the ionization of acetic acid is written

$$C_2H_4O_2(aq) + H_2O \rightleftharpoons C_2H_3O_2^-(aq) + H_3O^+(aq) \tag{8.1-2a}$$

or

$$0 = C_2H_3O_2^-(aq) + H_3O^+(aq) - C_2H_4O_2(aq) - H_2O \tag{8.1-2b}$$

The arrow or double arrow that we ordinarily use is replaced by an equal sign. The inconvenience of writing chemical equations in this unfamiliar way is more than outweighed by the resulting ability to write thermodynamic equations in compact forms that apply to any chemical reaction.

We consider reactions in closed systems at constant pressure and temperature, and assume that the system can be considered to be in a metastable state at any time during the reaction, so that the Gibbs energy and other thermodynamic variables of the system have well-defined values as equlibrium is approached. The Gibbs energy of the system must decrease until it reaches a stable minimum value at equilibrium.

If an infinitesimal amount of reaction takes place at constant T and P, the change in the Gibbs energy is given by Eq. (5.4-3):

$$dG = \sum_{i=1}^{c} \mu_i \, dn_i \quad \text{(constant } T \text{ and } P\text{)} \tag{8.1-3}$$

To express dG in terms of the amount of reaction that takes place, we define the **extent of reaction** ξ by

$$n_i = n_i(\text{initial}) + \nu_i \xi \tag{8.1-4}$$

where n_i is the amount of substance i. Use of any substance in Eq. (8.1-4) gives the same value of ξ if only one chemical reaction can occur. The extent of reaction has the dimensions of moles. If ξ increases from zero to one mole, one mole of reaction has occurred. If so, 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. The meaning of one mole of reaction changes if the balancing of the reaction equation is changed. For example, if all stoichiometric coefficients are doubled, the equation is still balanced, but one mole of reaction now corresponds to twice the amount of each substance.

For an infinitesimal extent of reaction, $d\xi$, we can write a relation that is valid for any choice of substance i so long as it is involved in the reaction:

$$dn_i = \nu_i \, d\xi \tag{8.1-5}$$

Equation (8.1-3) now becomes

$$dG = \sum_{i=1}^{c} \mu_i \nu_i \, d\xi = \left(\sum_{i=1}^{c} \nu_i \mu_i \right) d\xi \quad (T \text{ and } P \text{ constant}) \tag{8.1-6}$$

where we factor a common factor $d\xi$ out of the sum. We can see that

$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P} = \sum_{i=1}^{c} \nu_i \mu_i \tag{8.1-7}$$

The quantity $(\partial G/\partial \xi)_{T,P}$ is the **rate of change of Gibbs energy per mole of reaction.** Since it is a derivative of an extensive quantity with respect to an extensive quantity, it is an intensive quantity.

At constant temperature and pressure, $dG < 0$ for a spontaneous reaction. This implies that if the forward reaction is spontaneous,

$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P} < 0 \quad \text{(forward reaction spontaneous)} \tag{8.1-8}$$

since the forward reaction corresponds to $d\xi > 0$. If the backward reaction is spontaneous,

$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P} > 0 \quad \text{(backward reaction spontaneous)} \tag{8.1-9}$$

If the equilibrium state has been attained, there is no tendency for reaction to occur, and

$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P} = \sum_{i=1}^{c} \nu_i \mu_i = 0 \quad \text{(equilibrium)} \tag{8.1-10}$$

The situation is as represented in Figure 8.1. 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.

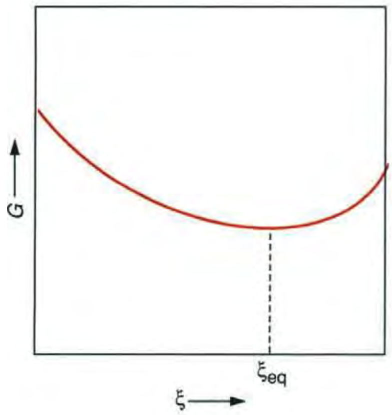

Figure 8.1. The Gibbs Energy of a Reacting System as a Function of the Progress Variable. The minimum in the curve corresponds to the equilibrium state, and other portions of the curve correspond to metastable states.

We now express the chemical potential in terms of the activity, using Eq. (7.3-1):

$$\mu_i = \mu_i^\circ + RT \ln(a_i) \tag{8.1-11}$$

where μ_i° is the chemical potential of substance i in whatever standard state applies. The expression of Eq. (7.3-1) is general. It applies to any substance in any kind of state, so the equilibrium expression in Eq. (8.1-11) is valid for any reaction.

The rate of change of the Gibbs energy per mole of reaction is

$$\left(\frac{\partial G}{\partial \xi} \right)_{T,P} = \sum_{i=1}^{c} \nu_i \mu_i^\circ + RT \sum_{i=1}^{c} \nu_i \ln(a_i) \tag{8.1-12}$$

If the reaction could be carried out with all of the reactants and products maintained in their standard states, all activities would equal unity, the second sum in the right-hand side of Eq. (8.1-12) would vanish, and the change in G for one mole of reaction would be equal to

$$\Delta G^\circ = \int_0^1 \left[\left(\frac{\partial G}{\partial \xi} \right)_{T,P} \bigg|_{\text{standard state}} \right] d\xi = \int_0^1 \left(\sum_{i=1}^{c} \nu_i \mu_i^\circ \right) d\xi = \left(\sum_{i=1}^{c} \nu_i \mu_i^\circ \right) \int_0^1 d\xi$$

$$\Delta G^\circ = \sum_{i=1}^{c} \nu_i \mu_i^\circ \quad \text{(standard-state reaction)} \tag{8.1-13}$$

The quantity ΔG° is called the **standard-state Gibbs energy change for one mole of reaction**. 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 Evaluation of the Standard-State Gibbs Energy Change

The Gibbs energy change of formation of a substance is defined as the Gibbs energy change to produce one mole of the substance from the appropriate elements in their most stable forms and is denoted by $\Delta_f G(i)$ for substance i. 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 white phosphorus is taken instead of the more stable red phosphorus. 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 3.

$$\Delta G^\circ = \sum_{i=1}^{c} \nu_i \, \Delta_f G^\circ(i) \tag{8.1-14}$$

where the Gibbs energy of formation $\Delta_f G^\circ(i)$ is the Gibbs energy change to form one mole of substance i from the elements in their most stable form. This equation is an exact analogue of Eq. (3.7-11) for the enthalpy change of the reaction, and follows from the fact that the Gibbs energy is a state function, as is the enthalpy. Values of standard-state Gibbs energy changes of formation for a number of substances are included in Table A.8 of Appendix A. This table also includes values of the quantity $-(G_\text{m}^\circ - H_{\text{m}298}^\circ)/T$, which can also be used to calculate ΔG° for a reaction, as is done in Example 8.1. The reason for including this function in the table is that it is found experimentally to be a more slowly varying function with temperature than is $\Delta_f G^\circ$. If a value for a temperature not in the table is needed, interpolation in its table gives greater accuracy than does interpolation in a table of $\Delta_f G^\circ$ values.

The Gibbs energy change of a constant-temperature reaction can also be calculated from

$$\Delta G = \Delta H - T\,\Delta S \tag{8.1-15}$$

where the enthalpy change is calculated from enthalpy changes of formation by Eq. (3.7–11) and the entropy change for a reaction is calculated from third-law ("absolute") entropies, using Eq. (4.5-6).

EXAMPLE 8.1

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 $-(G^\circ_\mathrm{m} - H^\circ_\mathrm{m298})/T$ and values of $\Delta_\mathrm{f}H^\circ$. Comment on the comparison of your answer with that of part (a).

Solution

a. From values in Table A.8 of Appendix A,

$$\begin{aligned}\Delta G^\circ &= 2\,\Delta_\mathrm{f}G^\circ(\mathrm{CO_2}) + (-2)\,\Delta_\mathrm{f}G^\circ(\mathrm{CO}) + (-1)\,\Delta_\mathrm{f}G^\circ(\mathrm{O_2})\\ &= 2(-394.389\ \mathrm{kJ\,mol^{-1}}) + (-2)(-137.163\ \mathrm{kJ\,mol^{-1}}) + (-1)(0)\\ &= -514.452\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

b. From values in Table A.8 of Appendix A,

$$\begin{aligned}\Delta H^\circ &= 2\,\Delta_\mathrm{f}H^\circ(\mathrm{CO_2}) + (-2)\,\Delta_\mathrm{f}H^\circ(\mathrm{CO}) + (-1)\,\Delta_\mathrm{f}H^\circ(\mathrm{O_2})\\ &= 2(-393.522\ \mathrm{kJ\,mol^{-1}}) + (-2)(-110.527\ \mathrm{kJ\,mol^{-1}}) + (-1)(0)\\ &= -565.990\ \mathrm{kJ\,mol^{-1}}\\ \Delta S^\circ &= 2S^\circ_\mathrm{m}(\mathrm{CO_2}) + (-2)S^\circ_\mathrm{m}(\mathrm{CO}) + (-1)S^\circ_\mathrm{m}(\mathrm{O_2})\\ &= 2(213.795\ \mathrm{J\,K^{-1}\,mol^{-1}}) + (-2)(197.653\ \mathrm{J\,K^{-1}\,mol^{-1}})\\ &\quad + (-1)(205.147\ \mathrm{J\,k^{-1}\,mol^{-1}}\\ &= -172.863\ \mathrm{J\,K^{-1}\,mol^{-1}}\\ \Delta G^\circ &= \Delta H^\circ - T\,\Delta S^\circ\\ &= -565.990\ \mathrm{kJ\,mol^{-1}} - (298.15\ \mathrm{K})(-172.863\ \mathrm{J\,K^{-1}\,mol^{-1}})\left(\frac{1\ \mathrm{kJ}}{1000\ \mathrm{J}}\right)\\ &= -514.451\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

c.

$$\begin{aligned}&T\,\Delta\left(\frac{-(G^\circ_\mathrm{m} - H^\circ_\mathrm{m298})}{T}\right)\\ &= (298.15\ \mathrm{K})[2(213.795\ \mathrm{J\,K^{-1}\,mol^{-1}}) - 2(197.653\ \mathrm{J\,K^{-1}\,mol^{-1}})\\ &\quad - 205.147\ \mathrm{J\,K^{-1}\,mol^{-1}}]\\ &= (298.15\ \mathrm{K})(-172.863\ \mathrm{J\,K^{-1}\,mol^{-1}})\left(\frac{1\ \mathrm{kJ}}{1000\ \mathrm{J}}\right) = -51.539\ \mathrm{kJ\,mol^{-1}}\\ \Delta G^\circ &= \Delta H^\circ_{298} - T\,\Delta\left(\frac{-(G^\circ_\mathrm{m} - H^\circ_\mathrm{m298})}{T}\right)\\ &= -565.990\ \mathrm{kJ\,mol^{-1}} + 51.539\ \mathrm{kJ\,mol^{-1}} = -514.451\ \mathrm{kJ\,mol^{-1}}\end{aligned}$$

Note that at 298.15 K, $-(G^\circ_\mathrm{m} - H^\circ_\mathrm{m298})/T = S^\circ_\mathrm{m}$. This is not true at other temperatures.

*Exercise 8.1

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 the standard-state enthalpy change and entropy change at 298.15 K for the same reaction.

c. Calculate the standard-state Gibbs energy change at 298.15 K for the same reaction using Eq. (8.1-15). Compare with the answer of part (a).

d. Calculate ΔG° at 298.15 K for the same reaction using values of $-(G^\circ_{\mathrm{m}} - H^\circ_{\mathrm{m}298})/T$ and the values 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. (8.1-12) in the form

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \Delta G^\circ + RT\ln(Q) \tag{8.1-16}$$

where

$$Q = a_1^{\nu_1} a_2^{\nu_2} \cdots a_c^{\nu_c} = \prod_{i=1}^{c} a_i^{\nu_i} \tag{8.1-17}$$

The notation $\prod$ denotes a product of factors, just as $\sum$ denotes a sum of terms. The quantity Q is called the **activity quotient**. It is called a quotient because its factors for reactants have negative exponents.

Exercise 8.2

Carry out the steps to obtain Eqs. (8.1-16) and (8.1-17).

If it is possible to keep the activity of every substance fixed during a chemical reaction, either by having a very large system or a small amount of reaction, or by adding reactants and removing products, the change in Gibbs energy for one mole of reaction can be written

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P}\bigg|_{\text{fixed comp}} = \Delta G\bigg|_{\text{fixed comp}}$$
$$= \int_0^1 [\Delta G^\circ + RT\ln(Q)]\,d\xi = [\Delta G^\circ + RT\ln(Q)]\int_0^1 d\xi$$

$$\Delta G\big|_{\text{fixed comp}} = \Delta G^\circ + RT\ln(Q) \tag{8.1-18}$$

*Exercise 8.3

a. Calculate the value of $\Delta G|_{\text{fixed comp}}$ at 298.15 K for the reaction of Exercise 8.1 if the partial pressure of PCl_5 is maintained equal to 0.100 bar, the partial pressure of PCl_3 is maintained equal to 0.600 bar, and the partial pressure of Cl_2 is maintained equal to 0.300 bar.

b. Repeat the calculation if the partial pressure of PCl_5 is maintained equal to 0.600 bar, the partial pressure of PCl_3 is maintained equal to 0.100 bar, and the partial pressure of Cl_2 is maintained equal to 0.300 bar.

The Thermodynamics of Chemical Equilibrium

At equilibrium, $(\partial G/\partial \xi)_{T,P} = 0$, and Eq. (8.1-16) becomes

$$0 = \Delta G^{\circ} + RT \ln(Q_{\text{eq}}) \tag{8.1-19}$$

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 called the **equilibrium constant**, K, or sometimes the **thermodynamic equilibrium constant**.

$$K = Q_{\text{eq}} = \prod_{i=1}^{c} a_i(\text{eq})^{\nu_i} = e^{-\Delta G^{\circ}/RT} \tag{8.1-20}$$

where $a_i(\text{eq})$ denotes the equilibrium value of a_i. Equation (8.1-20) is valid for any kind of reacting system.

The equilibrium constant is a quick indication of the equilibrium state of the system. If the equilibrium constant is greater than unity the equilibrium activities of the products will be greater than those of the reactants, and if the equilibrium constant is smaller than unity the equilibrium activities of the reactants will be larger.

8.2 Reactions Involving Gases and Pure Substances

For our first class of chemical reactions, we will assume that all gases can be assumed to be ideal and that all liquids and solids can be assumed to have constant volumes. The expressions for the activities these substances are relatively simple.

Gaseous Reactions

For reactions in which all substances are ideal gases, all of the activities are given by

$$a_i = \frac{P_i}{P^{\circ}} \quad \text{(ideal gas)} \tag{8.2-1}$$

Equation (8.1-20) for the equilibrium constant is

$$K_P = \prod_{i=1}^{c} \left(\frac{P_i(\text{eq})}{P^{\circ}}\right)^{\nu_i} \quad \text{(ideal gas reaction)} \tag{8.2-2}$$

where we attach the subscript P to indicate that all activities are expressed in terms of partial pressures. If the gases are not ideal gases, the partial pressures in Eq. (8.2-2) are replaced by fugacities. Some chemistry texts omit the P° divisors, giving the equilibrium constant the dimensions of pressure raised to the appropriate power, and others define two different equilibrium constants, one with the divisors and the other without them.

EXAMPLE 8.2

Consider the reaction

$$0 = 2NO_2(g) - N_2O_4(g)$$

a. Calculate the value of ΔG° at 298.15 K.

b. Calculate the value of K_P at 298.15 K.

c. Calculate the equilibrium pressure of a system that initially consists of 1.000 mol of dinitrogen tetroxide and that is confined in a fixed volume of 24.46 L at 298.15 K.

Solution

a. From the Gibbs energy changes of formation:

$$\begin{aligned}\Delta G^\circ &= 2\,\Delta_f G^\circ(NO_2) + (-1)\Delta_f G^\circ(N_2O_4)\\ &= (2)(51.258\text{ kJ mol}^{-1}) + (-1)(97.787\text{ kJ mol}^{-1}) = 4.729\text{ kJ mol}^{-1}\end{aligned}$$

b.

$$K = \exp\left(\frac{-4729\text{ J mol}^{-1}}{(8.3145\text{ J K}^{-1}\text{mol}^{-1})(298.15\text{ K})}\right) = 0.148$$

c. Let α be the degree of dissociation (the fraction of the initial N_2O_4 that dissociates). We assume ideal gas behavior:

$$P(NO_2) = \frac{n(NO_2)\mathrm{RT}}{V} = \frac{(1.000\text{ mol})(2\alpha)RT}{V}$$

$$P(N_2O_4) = \frac{n(N_2O_4)RT}{V} = \frac{(1.000\text{ mol})(1-\alpha)RT}{V}$$

We will sometimes label partial pressures, amounts, and activities with the formula for the substance inside parentheses instead of with a subscript. There is no difference between P_i and $P(i)$ or between n_i and $n(i)$. We now can write

$$\begin{aligned}K_P = 0.148 &= \frac{(2\alpha)^2}{1-\alpha}\frac{(1.000\text{ mol})RT}{P^\circ V}\\ &= \frac{4\alpha^2(1.0135)}{1-\alpha}\end{aligned}$$

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 discarded the negative root of the quadratic equation, since a negative value of α is not physically possible if no nitrogen dioxide is initially present. The total amount of gas is (1.000 mol) $(1 - \alpha + 2\alpha) = 1.174$ mol, so the total pressure is

$$\begin{aligned}P &= \frac{(1.174\text{ mol})(0.08206\text{ L atm K}^{-1}\text{ mol}^{-1})(298.15\text{ K})}{24.46\text{ L}}\\ &= 1.174\text{ atm} = 1.190\times 10^5\text{ Pa}\end{aligned}$$

Reactions Involving Pure Condensed Phases and Gases

If the pressure of the system does not differ very much from P°, then Eq. (7.3-4) gives for the activity of a pure liquid or solid:

$$a_i \approx 1 \quad \text{(Pure liquid or solid near } P^\circ\text{)} \qquad (8.2\text{-}3)$$

Substances that are pure liquids or solids contribute a factor nearly equal to unity to the equilibrium constant expression, and can be omitted from it.

EXAMPLE 8.3

a. Write the equilibrium constant quotient for the reaction

$$\mathrm{CaCO_3(s)} \rightleftharpoons \mathrm{CaO(s)} + \mathrm{CO_2(g)}$$

b. Find the value of the equilibrium constant at 298.15 K and the pressure of CO_2 at equilibrium with CaO(s) and $CaCO_3$(s) at 298.15 K.

Solution

a. Since the activities of the solids are nearly equal to unity,

$$K = \frac{a_{\mathrm{eq}}(\mathrm{CaO})a_{\mathrm{eq}}(\mathrm{CO_2})}{a_{\mathrm{eq}}(\mathrm{CaCO_3})} \approx a_{\mathrm{eq}}(\mathrm{CO_2}) \approx \frac{P_{\mathrm{eq}}(\mathrm{CO_2})}{P^\circ}$$

b. From the Gibbs energies of formation

$$\Delta G^\circ = (1)(-603.501\ \mathrm{kJ\ mol^{-1}}) + (1)(-394.389\ \mathrm{kJ\ mol^{-1}} + (-1)(-1128.79\ \mathrm{kJ\ mol^{-1}})$$
$$= 130.90\ \mathrm{kJ\ mol^{-1}}$$

$$K_P = \exp\left(-\frac{130900\ \mathrm{J\ mol^{-1}}}{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})}\right) = 1.17 \times 10^{-23}$$

$$P_{\mathrm{eq}}(\mathrm{CO_2}) = (P^\circ)(1.17 \times 10^{-23}) = 1.17 \times 10^{-23}\ \mathrm{bar} \approx 1.15 \times 10^{-23}\mathrm{atm}$$

This equilibrium constant is strongly temperature dependent, and becomes much larger at higher temperatures.

Those reactions that appear to proceed to completion are not fundamentally different from other reactions. They just have very large equilibrium constants.

EXAMPLE 8.4

a. Write the activity quotient for the combustion of propane, Problem 3.52, part (a), at 298.15 K.

b. Find the value of the equilibrium constant for this reaction.

Solution

a.

$$Q = \frac{(P(\mathrm{CO_2})/P^\circ)^3(1)^4}{(P(\mathrm{C_3H_8})/P^\circ)(\mathrm{P}(\mathrm{O_2})/P^\circ)^5}$$

b.

$$\Delta G^\circ = 3\Delta_f G^\circ(\mathrm{CO_2}) + 4\,\Delta_f G^\circ(\mathrm{H_2O}) + (-1)\,\Delta_f \mathrm{G}^\circ(\mathrm{C_3H_8}) + (-5)\,\Delta_f \mathrm{G}^\circ(\mathrm{O_2})$$
$$= (3)(-394.389\ \mathrm{kJ\ mol^{-1}}) + (4)(-237.141\ \mathrm{kJ\ mol^{-1}})$$
$$+ (-1)(-23.27\ \mathrm{kJ\ mol^{-1}}) + (-5)(0)$$
$$= -2108.46\ \mathrm{kJ\ mol^{-1}}$$

$$K = \exp\left(\frac{2108460\ \mathrm{J\ mol^{-1}}}{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})}\right) = e^{850.5} = 2 \times 10^{369}$$

***Exercise 8.4**

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 torr.

b. Find the volume containing one molecule of propane at the equilibrium of part (a). Comment on the magnitude of your result.

8.3 Chemical Equilibrium in Solution

For a component of a liquid or solid solution, the activity is given in one of several different ways, as described in Chapter 7. In discussing chemical equilibrium, one must specify which description is being used, since activities and standard states are different for different descriptions. We will usually use the molality description for aqueous solutions, but the molarity description and Convention II are also used. In the molality description, the activity of a solute is given by Eq. (7.3-28):

$$a_i = \frac{\gamma_i m_i}{m^\circ} \tag{8.3-1}$$

where m_i is the molality of substance number i, m° is equal to 1 mol kg^{-1} by definition, and γ_i is the activity coefficient of substance i. We omit superscripts on the activity coefficients. The activity of the solvent is given by Eq. (7.3-37):

$$a_1 = \gamma_1 x_1 \tag{8.3-2a}$$

where x_1 is the mole fraction of the solvent and γ_1 is its activity coefficient. In a dilute solution, both the activity coefficient and the mole fraction of the solvent are nearly equal to unity, so that

$$a_1 \approx 1 \tag{8.3-2b}$$

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. (8.1-14). Table A.8 of Appendix A includes some values of ΔG° for solids, liquids, gases, and some solutes in the molality standard state.

EXAMPLE 8.5

Using tabulated Giggs energy changes of formation, find the standard-state Gibbs energy change at 298.15 K for the reaction

$$2\mathrm{CO(aq)} + \mathrm{O_2(aq)} \rightleftharpoons 2\ \mathrm{CO_2(aq)}$$

Solution

From values in Table A.8 of Appendix A,

$$\begin{aligned} G^\circ &= 2\ \Delta_f G^\circ(\mathrm{CO_2}) + (-2)\ \Delta_f G^\circ(\mathrm{CO}) + (-1)\ \Delta_f G^\circ(\mathrm{O_2}) \\ &= 2(-385.98\ \mathrm{kJ\ mol^{-1}}) + (-2)(-119.90\ \mathrm{kJ\ mol^{-1}}) + (-1)(16.4\ \mathrm{kJ\ mol^{-1}}) \\ &= -548.56\ \mathrm{kJ\ mol^{-1}} \end{aligned}$$

This value compares with −514.452 kJ mol^{-1} for the gas-phase reaction at the same temperature.

***Exercise 8.5**

Find the value of ΔG° for the reaction of Example 8.4 using mole fractions according to Convention II instead of the molality description. State any assumptions.

The equilibrium constant for a reaction involving only solutes is given in the molality description by

$$K = Q_{\mathrm{eq}} = \prod_{i=2}^{c} \left(\frac{\gamma_i m_i(\mathrm{eq})}{m^\circ} \right)^{\nu_i} \tag{8.3-3}$$

Component number 1 (the solvent) is omitted from the product since it is not involved in the reaction. The equilibrium constant for a reaction involving the solvent is given by

$$K = Q_{\mathrm{eq}} = (\gamma_1 x_1)^{\nu_1} \prod_{i=2}^{c} \left(\frac{\gamma_i m_i(\mathrm{eq})}{m^\circ} \right)^{\nu_i} \tag{8.3-4}$$

For a dilute solution, x_1 and γ_1 are both nearly equal to unity, so that the activity factor for the solvent can be omitted to a good approximation, making Eq. (8.3-4) the same as Eq. (8.3-3). For a dilute solution in which the activity coefficients are nearly equal to unity, an approximate equilibrium constant is often written that omits all activity coefficients:

$$K_m = \prod_{i=2}^{c} (m_i(\mathrm{eq})/m^\circ)^{\nu_i} \tag{8.3-5}$$

Some authors also omit the m° factors, giving an equilibrium constant that has the dimensions of molality raised to some power. When the activity coefficients differ considerably from unity the use of K_m can be a poor approximation.

The value of the equilibrium constant for a solution reaction can be calculated from the Gibbs energy change of the standard-state reaction. 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.

EXAMPLE 8.6

a. Find the value of the equilibrium constant for the reaction of Example 8.5 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

The reaction is

$$2\mathrm{CO(aq)} + \mathrm{O_2(aq)} \rightleftharpoons 2\mathrm{CO_2(aq)}$$

From Example 8.5, $\Delta G^\circ = -548.56\ \mathrm{kJ\,mol^{-1}}$ at 298.15 K.

a.

$$K = e^{-\Delta G^\circ/RT} = \exp\left(\frac{548560\ \mathrm{J\,mol^{-1}}}{(8.3145\ \mathrm{J\,K^{-1}\,mol^{-1}})(298.15\ \mathrm{K})} \right)$$

$$= 1.27 \times 10^{96}$$

b.

$$
\begin{aligned}
(\partial G/\partial \xi)_{T,P} &= \Delta G^{\circ} + RT\ \ln(Q) \\
&= -548560\ \text{J mol}^{-1} \\
&\quad + (8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\text{K})\ \ln\left(\frac{(0.00015)^2}{(0.00010)^2(0.00020)}\right) \\
&= -548560\ \text{J mol}^{-1} + 23000\ \text{J mol}^{-1} = -525000\ \text{J mol}^{-1} \\
&= -525\ \text{kJ mol}^{-1}
\end{aligned}
$$

c. Let $m_{\text{eq}}(\text{CO})/m^{\circ} = 2x$, so that $m_{\text{eq}}(\text{O}_2)/\text{m}^{\circ} = 0.0002 + x$ and $m_{\text{eq}}(\text{CO}_2)/m^{\circ} = 0.00015 - 2x$:

$$K = 1.27 \times 10^{96} = \frac{[m_{\text{eq}}(\text{CO}_2)/m^{\circ}]^2}{[m_{\text{eq}}(\text{CO})/m^{\circ}]^2 m_{\text{eq}}(\text{O}_2)/m^{\circ}} = \left(\frac{(0.00015 - 2x)^2}{(2x)^2(0.00020 + x)}\right)$$

Since x will be very small,

$$x^2 \approx \left(\frac{(0.00015)^2}{4(1.27 \times 10^{96})(0.00020)}\right) = 2.21 \times 10^{-101}$$

$$x \approx 4.7 \times 10^{-51}; \qquad m_{\text{eq}}(\text{CO}) \approx 9.4 \times 10^{-51}\ \text{mol kg}^{-1}$$

8.4 Equilibria in Solutions of Strong Electrolytes

The foregoing discussion of chemical equilibrium provides the means to discuss some unique properties of the activities of strong electrolytes. We first consider a solution of a volatile strong electrolyte at equilibrium with a vapor phase, using hydrogen chloride as an example. From the fundamental fact of phase equilibrium,

$$\mu(\text{HCl, aq}) = \mu(\text{HCl, g}) \tag{8.4-1}$$

The HCl ionizes in solution according to the equation

$$\text{HCl(aq)} \rightleftharpoons \text{H}^+(\text{aq}) + \text{Cl}^-(\text{aq}) \tag{8.4-2}$$

Writing $\text{H}^+(\text{aq})$ does not express any particular assumption about hydration of the hydrogen ions. Some aqueous hydrogen ions are apparently bonded to a water molecule, forming H_3O^+, the hydronium ion, but even more are apparently attracted to water dimers, producing H_5O_2^+.[1] Others can be attached to trimers, and so on. The symbol $\text{H}^+(\text{aq})$ stands for all of these species taken together, just as we write, for example, $\text{Na}^+(\text{aq})$ for all of the variously hydrated sodium ions. The condition for equilibrium of the reaction of Eq. (8.4-2) is, from Eq. (8.1-10)

$$\mu(\text{HCl, aq}) = \mu(\text{H}^+) + \mu(\text{Cl}^-) \tag{8.4-3}$$

We use the molality description for the H^+ and Cl^- ions and omit the label "aq" since they occur only in the aqueous phase. For the aqueous HCl, we use a new molality description, in which m° (1 mol kg^{-1}) is replaced by m', a constant molality that is unspecified. This policy is necessary because the equilibrium constant for the ionization

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[1] H.-P. Cheng and J. L. Krause, *J. Chem. Phys.*, **107**, 8461 (1997).

of HCl is too large to be measured, and $m_{eq}(\mathrm{HCl})$ is too small to be measured. It allows us to avoid writing equations in which $m_{eq}(\mathrm{HCl})$ occurs.

The chemical potentials can be written in terms of activity coefficients and molalities:

$$\begin{aligned}\mu^{\circ}(\mathrm{HCl, aq}) + RT\ \ln[a(\mathrm{HCl, aq})] &= \mu^{\circ}(\mathrm{HCl, aq}) + RT\ \ln(\gamma(\mathrm{HCl})m_{eq}(\mathrm{HCl})/m') \\ &= \mu^{\circ}(\mathrm{H}^+) + RT\ \ln[\gamma(\mathrm{H}^+)m_{eq}(\mathrm{H}^+)/m^{\circ}] \\ &\quad + \mu^{\circ}(\mathrm{Cl}^-) + RT\ \ln[\gamma(\mathrm{Cl}^-)m_{eq}(\mathrm{Cl}^-)/m^{\circ}]\end{aligned} \tag{8.4-4}$$

The standard-state chemical potentials of H^+ and Cl^- refer to the hypothetical solution with molality m° (1 mol kg^{-1}) and activity coefficient equal to unity, but that of the HCl refers to the hypothetical solution with molality m' and unit activity coefficient.

Since the value of $m(\mathrm{HCl})$ is too small to measure, the value of m' is unmeasurable. To avoid use of the value of m' we specify that

$$\mu^{\circ}(\mathrm{HCl, aq}) = \mu^{\circ}(\mathrm{H}^+) + \mu^{\circ}(\mathrm{Cl}^-) \quad \text{(convention)} \tag{8.4-5}$$

which uniquely determines m', even though we still do not know its value. Combining Eq. (8.4-5) with Eq. (8.4-4) and taking antilogarithms, we obtain

$$\begin{aligned}a(\mathrm{HCl, aq}) &= \gamma(\mathrm{HCl})m(\mathrm{HCl})/m' = (\gamma(\mathrm{H}^+)m_{eq}(\mathrm{H}^+)/m^{\circ})(\gamma(\mathrm{Cl}^-)m_{eq}(\mathrm{Cl}^-)/m^{\circ}) \\ &= \frac{\gamma_+\gamma_- m_+ m_-}{m^{\circ 2}}\end{aligned} \tag{8.4-6}$$

where we have simplified the notation, replacing $m_{eq}(\mathrm{H}^+)$ by m_+ and $m_{eq}(\mathrm{Cl}^-)$ by m_-, with similar notation for the γ's. This allows us to replace $a(\mathrm{HCl, aq})$ by an expression containing only measurable quantities.

Exercise 8.6

Show that Eq. (8.4-6) is equivalent to Eq. (8.4-4).

Equation (8.4-5) is the same as requiring that

$$\Delta G^{\circ} = 0 \tag{8.4-7}$$

for the ionization reaction of Eq. (8.4-2), which means that the equilibrium constant for the reaction is given by

$$K = \frac{(\gamma_+ m_+/m^{\circ})(\gamma_- m_-/m^{\circ})}{(\gamma(\mathrm{HCl})m(\mathrm{HCl})/m')} = 1 \tag{8.4-8}$$

Equation (8.4-8) 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 assume that the vapor is an ideal gas, and write

$$\mu(\mathrm{HCl, g}) = \mu^{\circ}(\mathrm{HCl, g}) + RT\ \ln\left(\frac{P(\mathrm{HCl})}{P^{\circ}}\right) \tag{8.4-9}$$

and from Eqs. (8.4-1) and (8.4-4)

$$\mu^{\circ}(\mathrm{HCl, g}) + RT\ \ln(P(\mathrm{HCl})/P^{\circ}) = \mu^{\circ}_+ + \mu^{\circ}_- + RT\ \ln(\gamma_+\gamma_- m_+ m_-/m^{\circ 2}) \tag{8.4-10}$$

The **stoichiometric molality** m is defined to be the total amount of HCl per kilogram of solvent, including both ionized and unionized forms. Some authors call the stoichiometric molality the "gross molality." If no H^+ ions and Cl^- ions are added to the solution from other solutes and if the amount of H^+ ions from water can be neglected, m_+ and m_- are both equal to m since the molality of the unionized HCl is negligible. Equation (8.4-10) is equivalent to

$$P(\mathrm{HCl}) = k^{(m)}\gamma_+\gamma_- m^2 = k_{\pm}^{(m)} m^2 \gamma_{\pm}^2 \tag{8.4-11}$$

where

$$k_{\pm}^{(m)} = \left(\frac{P^\circ}{m^{\circ 2}}\right) \exp\left[\frac{\mu^\circ(H^+) + \mu^\circ(\mathrm{Cl}^-) - \mu^\circ(\mathrm{HCl, g})}{RT}\right] \tag{8.4-12}$$

and where $\gamma_{\pm}$ is the **mean ionic activity coefficient** of Eq. (7.4-12):

$$\gamma_{\pm} = (\gamma_+\gamma_-)^{1/2} \tag{8.4-13}$$

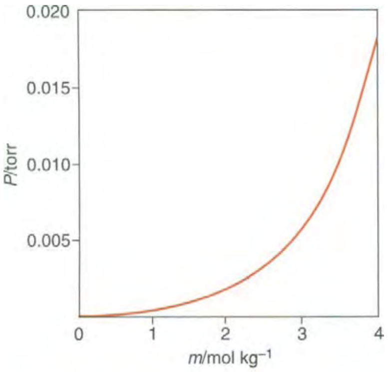

Figure 8.2. The Partial Vapor Pressure of HCl as a Function of Molality. In contrast with Henry's law, the curve in this diagram is quadratic instead of linear for small molality.

If the concentration of HCl is small enough, the activity coefficients are nearly equal to unity and the partial vapor pressure of HCl is nearly proportional to the square of the molality, not proportional to the molality as in Henry's law. Figure 8.2 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 coefficients determined by other techniques.

EXAMPLE 8.7

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.[2] The mean ionic activity coefficient is equal to 2.38. Find the value of $k_{\pm}^{(m)}$ and of $\mu^\circ(\mathrm{H}^+) + \mu^\circ(\mathrm{Cl}^-) - \mu^\circ(\mathrm{HCl, g})$.

Solution

$$k_{\pm}^{(m)} = \frac{P(\mathrm{HCl})}{\gamma_{\pm}^2 m^2} = \frac{6.97 \times 10^{-5}\ \mathrm{atm}}{(2.38)^2(5.00\ \mathrm{mol\ kg^{-1}})^2} = 4.92 \times 10^{-7}\ \mathrm{atm\ kg^2\ mol^{-2}}$$

$$\begin{aligned}\mu^\circ(\mathrm{H}^+) + \mu^\circ(\mathrm{Cl}^-) - \mu^\circ(\mathrm{HCl, g}) &= RT\ \ln\left(\frac{k_{\pm}^{(m)} m^{\circ 2}}{P^\circ}\right)\\ &= (8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})\\ &\quad \times \ln\left[\frac{(4.92 \times 10^{-7}\ \mathrm{atm})(1\ \mathrm{mol\ kg^{-1}})^2}{1\ \mathrm{bar}}\left(\frac{1.01325\ \mathrm{bar}}{1\ \mathrm{atm}}\right)\right]\\ &= -3.60 \times 10^4\ \mathrm{J\ mol^{-1}} = -36.0\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

Equations (8.4-4) through (8.4-8) are valid for a nonvolatile electrolyte such as NaCl or KOH as well as for a volatile electrolyte such as HCl or HNO_3. However, since the partial vapor pressure of these electrolytes is too small to measure, we cannot apply Eqs. (8.4-9) through (8.4-12) to these substances. For a general univalent–univalent electrolyte represented by the formula MX, we write the same equation as Eq. (8.4-6):

$$a(\mathrm{MX, aq}) = \gamma(\mathrm{M}^+)m(\mathrm{M}^+)\gamma(\mathrm{X}^-)m(\mathrm{X}^-)/m^{\circ 2} = \gamma_{\pm}^2 m_+ m_-/m^{\circ 2} \tag{8.4-14}$$

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[2] S. J. Bates and H. D. Kirschman, *J. Am. Chem. Soc.* **41**, 1991 (1919).

For $CaCl_2$,

$$CaCl_2 \rightleftharpoons Ca^{2+} + 2Cl^- \tag{8.4-15}$$

Setting ΔG° for this reaction equal to zero as in Eq. (8.4-7) leads to

$$a(CaCl_2) = (\gamma_+ m_+/m^\circ)(\gamma_- m_-/m^\circ)^2 \tag{8.4-16}$$

Exercise 8.7

Show that Eq. (8.4-16) is correct.

For $CaCl_2$, the **mean ionic activity coefficient** is defined to be

$$\gamma_\pm = (\gamma_+ \gamma_-^2)^{1/3} \tag{8.4-17}$$

and the **mean ionic molality** for $CaCl_2$ is defined to be

$$m_\pm = (m_+ m_-^2)^{1/3} \tag{8.4-18}$$

so that

$$a(CaCl_2) = (\gamma_\pm m_\pm)^3 \tag{8.4-19}$$

If there is no other source of Ca^{2+} or Cl^- than the $CaCl_2$,

$$m_+ = m, \qquad m_- = 2m \tag{8.4-20}$$

where m is the stoichiometric molality (total amount of $CaCl_2$ per kilogram of solvent), so that for $CaCl_2$:

$$m_\pm = m(2^2 1^1)^{1/3} = m\nu_\pm \tag{8.4-21}$$

where the second equality defines the quantity $\nu_\pm$ for $CaCl_2$ or a similar 1–2 electrolyte. We now write

$$a(CaCl_2) = (\gamma_\pm m_\pm/m^\circ)^3 = (\gamma_\pm \nu_\pm m/m^\circ)^3 \tag{8.4-22}$$

The analogous quantities are defined for any electrolyte. If the formula of the electrolyte is represented by $M_{\nu_+}X_{\nu_-}$, and if there is no other source of either ion,

$$a(M_{\nu_+}X_{\nu_-}) = (\gamma_\pm m_\pm/m^\circ)^{(\nu_+ + \nu_-)} \tag{8.4-23}$$

where, as in Eq. (7.4-12), the mean ionic activity coefficient is

$$\gamma_\pm = (\gamma_+^{\nu_+} \gamma_-^{\nu_-})^{1/(\nu_+ + \nu_-)} \tag{8.4-24}$$

and the mean ionic molality is

$$m_\pm = (m_+^{\nu_+} m_-^{\nu_-})^{1/(\nu_+ + \nu_-)} = m\nu_\pm = m(\nu_+^{\nu_+} \nu_-^{\nu_-})^{1/(\nu_+ + \nu_-)} \tag{8.4-25}$$

For example, the mean ionic molality of a 3–1 electrolyte such as $CrCl_3$ is equal to $27^{1/4}m$.

Exercise 8.8

a. Verify Eqs. (8.4-23) and (8.4-24).

***b.** Write expressions for $\gamma_\pm$ and $m_\pm$ for $Mg_3(PO_4)_2$ in terms of m, the stoichiometric molality, and the activity coefficients of the ions. Neglect hydrolysis (a poor approximation).

Tabulated Thermodynamic Values for Electrolytes

Gibbs energy changes of formation, activities, activity coefficients, etc., for separate ions cannot be measured because of the near impossibility of adding ions of one charge to a system without adding ions of the opposite charge. In spite of this fact, it is desirable to tabulate values of enthalpy changes of formation, Gibbs energies of formation, and absolute entropies for ions instead of for the neutral substances in order to have a shorter table. We make an arbitrary division of the Gibbs energy change of formation, enthalpy change of formation, entropy, etc., between the ions of one electrolyte, and make all other values consistent with this division. The arbitrary choice that is made is to assign zero values to the Gibbs energy change of formation, enthalpy change of formation, entropy, etc., 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 chloride ion, etc. This arbitrary convention does not change the value of ΔG or ΔS, etc, for a chemical reaction.

EXAMPLE 8.8

Using tabulated values in Table A.8 of Appendix A, calculate ΔH°, ΔG°, and ΔS° at 298.15 K for the reaction

$$0 = \mathrm{H_2O} + \mathrm{NaCl} - \mathrm{NaOH(aq)} - \mathrm{HCl(aq)}$$

Solution

We write the net ionic equation:

$$\begin{aligned}
0 &= \mathrm{H_2O} - \mathrm{OH^-} - \mathrm{H^+}\\
\Delta \mathrm{H}^\circ &= \Delta_f H^\circ(\mathrm{H_2O}) + (-1)\,\Delta_f H^\circ(\mathrm{OH^-}) + (-1)\,\Delta_f H^\circ(\mathrm{H^+})\\
&= (-285.830\ \mathrm{kJ\ mol^{-1}}) + (-1)(-229.994\ \mathrm{kJ\ mol^{-1}}) + (-1)0\\
&= -55.836\ \mathrm{kJ\ mol^{-1}}\\
\Delta G^\circ &= \Delta_f G^\circ(\mathrm{H_2O}) + (-1)\,\Delta_f G^\circ(\mathrm{OH^-}) + (-1)\,\Delta_f G^\circ(\mathrm{H^+})\\
&= (-237.141\ \mathrm{kJ\ mol^{-1}}) + (-1)(-157.244\ \mathrm{kJ\ mol^{-1}}) + (-1)0\\
&= -79.892\ \mathrm{kJ\ mol^{-1}}\\
\Delta S^\circ &= S_\mathrm{m}^\circ(\mathrm{H_2O}) + (-1)S_\mathrm{m}^\circ(\mathrm{OH^-}) + (-1)S_\mathrm{m}^\circ(\mathrm{H^+})\\
&= (69.95\ \mathrm{J\ K^{-1}\ mol^{-1}}) + (-1)(-10.75\ \mathrm{J\ K^{-1}\ mol^{-1}}) + (-1)0\\
&= 80.70\ \mathrm{J\ K^{-1}\ mol^{-1}}
\end{aligned}$$

Omission of the "spectator ions" from the calculation makes no difference, since their contributions cancel and since the standard state of each ion is independent of the other ions present.

8.5

Acid–Base Equilibrium Calculations

It is customary to specify the acidity of a solution in terms of the pH, which has been variously defined. We would like to be able to use the definition

$$\mathrm{pH} = -\log_{10}[a(\mathrm{H^+})] = -\log_{10}\left(\frac{\gamma(\mathrm{H^+})m(\mathrm{H^+})}{m^\circ}\right) \tag{8.5-1}$$

where $\log_{10}$ denotes the logarithm to the base 10 (the common logarithm). A version of the definition of Eq. (8.5-1) or of the analogous concentration definition that omits the activity coefficient is commonly found in elementary chemistry textbooks. The pH as defined in Eq. (8.5-1) cannot be measured exactly because of the impossibility of exact measurement of $\gamma(\mathrm{H}^+)$. However, we will assume that $\gamma(\mathrm{H}^+)$ can be approximated in some way so that we can use Eq. (8.5-1) as our definition of pH. We will describe the electrochemical method for determining pH in Chapter 9.

EXAMPLE 8.9

a. Find the value of the equilibrium constant at 298.15 K for the reaction

$$\mathrm{HA} \rightleftharpoons \mathrm{H}^+ + \mathrm{A}^-$$

where HA stands for acetic acid, CH_3COOH.

b. Find the molality of hydrogen ions 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.

Solution

a. From Gibbs energy changes of formation in Table A.8 of Appendix A,

$$\Delta G^\circ = \Delta_f G^\circ(\mathrm{A}^-) + \Delta_f G^\circ(\mathrm{H}^+) - \Delta_f G^\circ(\mathrm{HA})$$

$$= -396.46\ \mathrm{kJ\ mol^{-1}} + 0 - (-369.31\ \mathrm{kJ\ mol^{-1}}) = -27.15\ \mathrm{kJ\ mol^{-1}}$$

$$K = \exp\left[\frac{-27150\ \mathrm{J\ mol^{-1}}}{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})}\right] = 1.75 \times 10^{-5}$$

b. We assume that hydrogen ions from water can be neglected, and that the activity coefficient of the unionized acetic acid is equal to unity. We use a method of successive approximations. For our first approximation we assume that $\gamma_\pm$ is equal to unity:

$$K = 1.75 \times 10^{-5} = \frac{(m(\mathrm{H}^+)/m^\circ)(m(\mathrm{A}^-)/m^\circ)}{m(\mathrm{HA})/m^\circ} = \frac{x^2}{0.100 - x}$$

where we let $x = m(\mathrm{H}^+)/m^\circ = m(\mathrm{A}^-)/m^\circ$. This equation is the same as

$$x^2 + 1.75 \times 10^{-5}x - 1.75 \times 10^{-6} = 0$$

Use of the quadratic formula gives

$$x = 1.31 \times 10^{-3}, \qquad m(\mathrm{H}^+) = 1.31 \times 10^{-3}\ \mathrm{mol\ kg^{-1}}$$

where a negative root has been disregarded.

We now use the Davies equation to obtain an approximate value for the activity coefficients of the hydrogen ions and acetate ions at the molality we have found. From the Davies equation, Eq. (7.4-15), with I equal to $1.31 \times 10^{-3}\ \mathrm{mol\ kg^{-1}}$, we find that $\gamma_\pm$ is equal to 0.959.

We now obtain a second approximation by substituting this value of $\gamma_\pm$ into the equilibrium expression:

$$K = \frac{(0.959)^2 x^2}{0.100 - x}$$

This equation is solved, with the result that

$$x = 1.37 \times 10^{-3}, \qquad m(\mathrm{H}^+) = 1.37 \times 10^{-3}\ \mathrm{mol\ kg^{-1}}$$

Using the value of γ from the Davies equation,

$$\mathrm{pH} = 2.88$$

Since further iterations would not change the activity coefficient appreciably, we stop with this second approximation.

*Exercise 8.9

a. Find the standard-state Gibbs energy change and the equilibrium constant at 298.15 K for the ionization of water, which is the reverse reaction from that of Example 8.8.

b. Calculate the molalities of hydrogen and hydroxide ions in pure water at 298.15 K. Use the Davies equation to estimate activity coefficients.

The calculation of pH in aqueous solutions is not always as simple as it was in Example 8.9. If a weak acid is quite dilute, the hydrogen ions that come from the water ionization cannot be neglected, and this complicates the calculation.

EXAMPLE 8.10

Find the pH of a solution made from 1.00×10^{-7} mol of acetic acid and 1.000 kg of water and maintained at 298.15 K.

Solution

We must solve two simultaneous equations:

$$K = 1.75 \times 10^{-5} = \frac{(\gamma(\mathrm{H}^+)m(\mathrm{H}^+)/m^\circ)(\gamma(\mathrm{A}^-)m(\mathrm{A}^-)/m^\circ)}{\gamma(\mathrm{HA})m(\mathrm{HA})/m^\circ}$$

and

$$K_\mathrm{w} = 1.0 \times 10^{-14} = [\gamma(\mathrm{H}^+)m(\mathrm{H}^+)/m^\circ][\gamma(\mathrm{OH}^-)m(\mathrm{OH}^-)/m^\circ] \qquad (8.5\text{-}2)$$

We assume that γ_{HA} is equal to unity, since HA is uncharged. Since all of the ions are univalent, we assume that all of their activity coefficients are equal, as would be predicted by the Davies equation. We represent them by γ.

We let

$$z = \frac{m(\mathrm{H}^+)}{m^\circ}, \qquad y = \frac{m(\mathrm{OH}^-)}{m^\circ}$$

There are two equations, and although they contain four molalities, only two are independent. We express the other variables 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 one H^+ ion released from the acid, so that

$$\frac{m(\mathrm{A}^-)}{m^\circ} = z - y, \qquad \frac{m(\mathrm{HA})}{m^\circ} = \frac{m}{m^\circ} - (z - y)$$

where m is the stoichiometric molality. From the water ionization equilibrium expression,

$$y = \frac{K_\mathrm{w}}{\gamma^2 z}$$

After $m(A^-)$ and $m(\mathrm{HA})$ are eliminated and this expression is substituted into the acid equilibrium expression, it becomes

$$K = \frac{\gamma^2 z[z - K_\mathrm{w}/(\gamma^2 z)]}{m/m^\circ - z + K_\mathrm{w}/(\gamma^2 z)}$$

When we multiply this equation out, we obtain a cubic equation:

$$\gamma^2 z^3 + Kz^2 - [(m/m^\circ)K + K_w]z - KK_w/\gamma^2 = 0$$

For our first approximation, we assume that the activity coefficient is equal to unity and solve for z. Use of a computer program to obtain a numerical approximation to the root of this cubic equation gives $m(\mathrm{H}^+) = 1.61 \times 10^{-7}$ mol kg^{-1}, only 61% higher than in pure water. Use of the Davies equation gives a value of 0.999999 for γ, so that no repetition of the calculation is necessary. The value of the pH is 6.79. If the hydrogen ions from water are ignored, the method of Example 8.9 gives $m(\mathrm{H}^+) = 9.9 \times 10^{-8}$ mol kg^{-1}, which is in error by 38%, and is smaller than the value of $m(\mathrm{H}^+)$ in pure water.

*Exercise 8.10

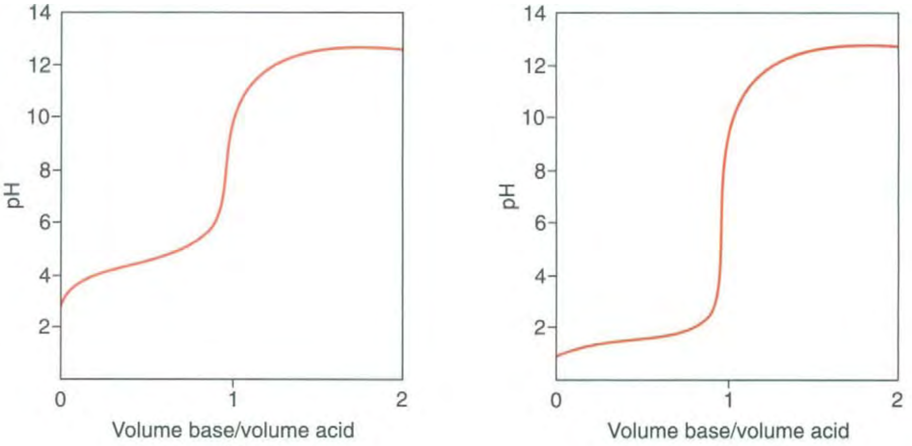
Another possible complication is that some acids are polyprotic, which means that one molecule of the acid ionizes successively to give more than one hydrogen ion. Find the pH of a solution made from 1.000 kg of water and 0.100 mol of phosphoric acid, H_3PO_4, for which the three acid dissociation constants are

$$K_1 = 7.52 \times 10^{-3}, \qquad K_2 = 6.23 \times 10^{-8}, \qquad K_3 = 2.2 \times 10^{-13}$$

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.

Buffer Solutions

In the titration of a weak acid with a strong base, the pH changes only slowly with addition of more base when about half of the acid has been neutralized. Figure 8.3a shows the titration curve of 0.100 molal acetic acid with 0.100 molal sodium hydroxide, and Figure 8.3b shows the titration curve of 0.100 molal hydrochloric acid with 0.100 molal sodium hydroxide. Near the neutral pH value of 7, the curve has a large positive



(a)

(b)

Figure 8.3. Titration Curves. (a) **Curve for a solution of acetic acid and a strong base.** (b) **Curve for a solution of hydrochloric acid.** For the acetic acid solution, there is a buffering region around pH 5.

slope in both diagrams, but near a pH value of 5, the acetic acid curve has a much smaller slope than does the hydrochloric acid curve.

A solution that resists changes in pH is called a **buffer solution**. A buffer solution can be produced by adding both the weak acid and its salt or by partially titrating the acid. Consider a solution with n_a mol of a weak acid and n_s mol of salt of this acid added to 1.000 kg of water. The acid will ionize slightly, and the anion will hydroyze slightly. These effects will nearly cancel, and we can write to a good approximation

$$m(\mathrm{HA}) = \frac{n_a}{1.000\ \mathrm{kg}}, \qquad m(\mathrm{A}^-) = \frac{n_s}{1.000\ \mathrm{kg}}$$

Assuming γ_{HA} to equal unity (a good approximation), the equilibrium expression is

$$K = \frac{(\gamma(\mathrm{H}^+)m(\mathrm{H}^+)/m^\circ)(\gamma(\mathrm{A}^-)m(\mathrm{A}^-)/m^\circ)}{m(\mathrm{HA})/m^\circ} = \frac{a(\mathrm{H}^+)\gamma(\mathrm{A}^-)n_s}{n_a} \tag{8.5-3}$$

If $\gamma(\mathrm{A}^-)$ is also assumed to equal unity, this equation can be written

$$\mathrm{pH} = \mathrm{p}K_a + \log_{10}\left(\frac{n_s}{n_a}\right) \tag{8.5-4}$$

where

$$\mathrm{p}K_a = -\log_{10}(K) \quad \text{(definition)} \tag{8.5-5}$$

and where $\log_{10}$ denotes the common logarithm (logarithm to the base 10). Equation (8.5-4) is known as the **Henderson–Hasselbalch equation**. This equation is used frequently in making buffer solutions. If greater accuracy is desired than the Henderson–Hasselbalch equation affords, one must use Eq. (8.5-3) with experimental or theoretical values of the activity coefficient of A^-.

EXAMPLE 8.11

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. (8.5-3) and the Davies equation.

Solution

a. Using the value $K_a = 1.75 \times 10^{-5}$,

$$\mathrm{pH} = 4.757 + \log_{10}\left(\frac{0.600\ \mathrm{mol}}{0.400\ \mathrm{mol}}\right) = 4.932$$

b. Let m_a be the molality of acid and m_s be the molality of the anion that would occur if the acid did not ionize and 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 $\gamma(\mathrm{HA})$ is equal to unity.

The hydrolysis of the salt is represented by

$$\mathrm{A}^- + \mathrm{H_2O} \rightleftharpoons \mathrm{HA} + \mathrm{OH}^-$$

We let $m(\mathrm{OH}^-)/m^\circ = y$ and $m(\mathrm{H}^+)/m^\circ = x$.

$$K = \frac{\gamma^2 x(m_s/m^\circ + x - y)}{m_a/m^\circ - x + y}$$

When y is replaced by $K_w/\gamma^2 x$, we obtain the equation

$$\gamma^2 x^3 + (\gamma^2 m_s/m^\circ + K)x^2 - (K_w + K m_a/m^\circ)x - K K_w/\gamma^2 = 0 \qquad (8.5\text{-}6)$$

The ionic strength of the solution is equal to $m_s + x$, so that the activity coefficient γ can be approximated by setting $I = m_s$ in the Davies equation for the initial calculation, and can be approximated more nearly exactly by successive approximation. Equation (8.5-6) is solved by successive approximation. 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 in part (a) is in error by 0.130.

Exercise 8.11

a. Verify Eq. (8.5-6).

b. Substitute the numerical result of part (b) of Example 8.11 into the equilibrium expression, Eq. (8.5-3), to verify its correctness.

Biological Buffering

The principal buffering system in mammalian blood is that of carbonic acid, which can equilibrate with its two anions and with gaseous and aqueous carbon dioxide through the reactions:

$$\mathrm{CO_2(g)} \rightleftharpoons \mathrm{CO_2(aq)} \qquad (8.5\text{-}7a)$$

$$\mathrm{CO_2(aq)} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_2CO_3(aq)} \qquad (8.5\text{-}7b)$$

$$\mathrm{H_2CO_3(aq)} \rightleftharpoons \mathrm{H^+} + \mathrm{HCO_3^-} \qquad (8.5\text{-}7c)$$

$$\mathrm{HCO_3^-} \rightleftharpoons \mathrm{H^+} + \mathrm{CO_3^{2-}} \qquad (8.5\text{-}7d)$$

*Exercise 8.12

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 (8.5-7b) is equal to 2.58×10^{-3}, that for reaction (8.5-7c) is equal to 1.70×10^{-4}, and that for reaction (8.5-7d) is equal to 4.69×10^{-11}. It is not possible by chemical analysis to distinguish CO_2(aq) from H_2CO_3. If the combined concentration of CO_2(aq) and H_2CO_3 is used in the equilibrium expression, a different value for the first acid ionization is found. (The molality of CO_2(aq) is larger than that of H_2CO_3.)

a. Find the value of the first ionization constant of carbonic acid, using the combined molalities of CO_2(aq) and H_2CO_3 in the equilibrium expression instead of the molality of H_2CO_3. Explain why reaction (8.5-7c) can act as an effective buffering reaction near the normal pH of blood, around pH 7.4.

b. Find the pH of a solution produced by equilibrating water with carbon dioxide gas at 760 torr at 25°C. Assume all activity coefficients are equal to unity.

c. 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. (8.5-7b) 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. (8.5-7b) and (8.5-7c) shifts 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.

8.6 Temperature Dependence of Equilibrium Constants. The Principle of Le Châtelier

The temperature derivative of ΔG° at constant pressure is given by differentiation of Eq. (8.1-13):

$$\frac{d\,\Delta G^\circ}{dT} = \sum_{i=1}^{c} \nu_i \left(\frac{\partial \mu_i^\circ}{\partial T}\right)_{P,n} \tag{8.6-1}$$

The derivatives on the right-hand side of this equation are at fixed P and n because each standard state corresponds to a specified fixed composition and pressure. From Eq. (5.5-10)

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n} = -\bar{S}_i \tag{8.6-2}$$

Substitution of the standard-state version of Eq. (8.6-2) into Eq. (8.6-1) gives

$$\frac{d\,\Delta G^\circ}{dT} = -\sum_{i=1}^{c} \nu_i \bar{S}_i^\circ = -\Delta S^\circ \tag{8.6-3}$$

where ΔS° is the entropy change for one mole of the standard-state reaction. It is convenient to write

$$\frac{d(\Delta G^\circ/T)}{dT} = \frac{1}{T}\frac{d\,\Delta G^\circ}{dT} - \frac{1}{T^2}\Delta G^\circ$$

which is equivalent to

$$\frac{d(\Delta G^\circ/T)}{dT} = -\frac{\Delta S^\circ}{T} - \frac{\Delta G^\circ}{T^2} = -\frac{\Delta H^\circ}{T^2} \tag{8.6-4}$$

The relation shown in Eq. (8.6-4) is the differential version of the **Gibbs–Helmholtz equation**. This equation holds only for a reaction that begins and ends at the same temperature. The value of ΔG is not defined for a temperature change, because at constant pressure a temperature change would produce a change in the Gibbs energy given by

$$\Delta G = \int_{T_1}^{T_2} dG = -\int_{T_1}^{T_2} \left(\frac{\partial G}{\partial T}\right)_{P,n} dT = -\int_{T_1}^{T_2} S\,dT \tag{8.6-5}$$

This expression cannot be evaluated because the actual value of the entropy of the system is not known. The third law implies only that the entropy can consistently be chosen to equal zero at zero temperature, not that it is known to vanish. The fact that ΔG is defined only for a constant-temperature process means that the derivative in Eq. (8.6-4) has the interpretation that ΔG values for constant-temperature processes at different temperatures can be compared.

Exercise 8.13

Show that

$$\frac{d(\Delta G^\circ/T)}{d(1/T)} = \Delta H^\circ \tag{8.6-6}$$

Equation (8.1-20) can be written

$$\ln(K) = -\frac{\Delta G^\circ}{RT} \tag{8.6-7}$$

From this equation and the Gibbs–Helmholtz equation, we can write

$$\frac{d\ln(K)}{dT} = \frac{\Delta H^\circ}{RT^2} \tag{8.6-8}$$

or

$$\frac{d\ln(K)}{d(1/T)} = -\frac{\Delta H^\circ}{R} \tag{8.6-9}$$

Exercise 8.14

Verify Eqs. (8.6-8) and (8.6-9).

If the value of ΔH° is known as a function of temperature, Eq. (8.6-8) can be integrated to obtain the value of K at one temperature from the value at another temperature:

$$\ln\left(\frac{K(T_2)}{K(T_1)}\right) = \frac{1}{R}\int_{T_1}^{T_2} \frac{\Delta H^\circ}{T^2}\, dT \tag{8.6-10}$$

which is equivalent to

$$\frac{\Delta G^\circ(T_2)}{T_2} - \frac{\Delta G^\circ(T_1)}{T_1} = -\int_{T_1}^{T_2} \frac{\Delta H^\circ}{T^2}\, dT \tag{8.6-11}$$

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. (8.6-10) becomes

$$\ln\left(\frac{K(T_2)}{K(T_1)}\right) = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{8.6-12}$$

and Eq. (8.6-11) becomes

$$\frac{\Delta G^\circ(T_2)}{T_2} - \frac{\Delta G^\circ(T_1)}{T_1} = \Delta H^\circ\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{8.6-13}$$

which is the integral version of the **Gibbs–Helmholtz equation**.

Exercise 8.15

Carry out the integrations to obtain Eqs. (8.6-12) and (8.6-13).

EXAMPLE 8.12

Assuming that ΔH° is temperature-independent, calculate the value of the equilibrium constant and of ΔG° at 100°C for the reaction:

$$0 = 2NO_2(g) - N_2O_4(g)$$

Solution

$$\begin{aligned}\Delta H^\circ &= 2\,\Delta_f H^\circ(NO_2) - \Delta_f H^\circ(N_2O_4)\\ &= 2(33.095\ \text{kJ mol}^{-1}) + (-1)(9.179\ \text{kJ mol}^{-1}) = 58.011\ \text{kJ mol}^{-1}\end{aligned}$$

$$\ln\left(\frac{K(373.15)}{K(298.15)}\right) = -\frac{57011\ \text{J mol}^{-1}}{8.3145\ \text{J K}^{-1}\ \text{mol}^{-1}}\left[\frac{1}{373.15\ K} - \frac{1}{298.15\ \text{K}}\right] = 4.622$$

Using the value of $K(298.15)$ from Example 8.2,

$$K(373.15) = K(298.15)e^{4.622} = (0.148)(101.7) = 14.92$$

$$\begin{aligned}\Delta G^\circ &= -RT\ \ln(K) = -(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(373.15\ \text{K})\ln(14.92)\\ &= -8390\ \text{J mol}^{-1} = -8.39\ \text{kJ mol}^{-1}\end{aligned}$$

***Exercise 8.16**

Find the value of K_P for the reaction of Example 8.3 at 1000 K. State any assumptions

If the assumption of constant ΔH° is not sufficiently accurate, the next simplest assumption is that the heat capacities are constant, so that

$$\Delta H^\circ(T) = \Delta H^\circ(T_1) + \Delta C_P(T - T_1) \tag{8.6-14}$$

When Eq. (8.6-14) is substituted into Eq. (8.6-8) and an integration is carried out from T_1 to T_2, the result is

$$\ln\left(\frac{K(T_2)}{K(T_1)}\right) = -\frac{\Delta H^\circ(T_1)}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \frac{\Delta C_P}{R}\left[\ln\left(\frac{T_2}{T_1}\right) + \frac{T_1}{T_2} - 1\right] \tag{8.6-15}$$

Exercise 8.17

a. Verify Eq. (8.6-15).

***b.** Using heat-capacity data from Appendix A and assuming the heat capacities to be temperature-independent, evaluate K and ΔG° for the reaction of Example 8.12 at 100°C. Calculate the percent difference between your value for K and that in Example 8.12.

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 that if possible a system will respond to a "stress" placed upon it by reacting in the direction that minimizes the effect of that stress on intensive properties of the system.[3]

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[3] 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.

Consider first the case that the transfer of heat to the system is the applied stress. From Eq. (8.6-8) 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), absorbing part of the heat put into the system. The temperature of the system rises by a smaller amount than if the reaction were somehow "frozen" and could not shift its reaction equilibrium. This 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. An increase in temperature shifts a chemical reaction in the endothermic direction.

The principle of Le Châtelier can also be applied to a 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, given by Dalton's law (assuming ideal gases) as

$$x_i = \frac{P_i}{P_{\text{tot}}} \tag{8.6-16}$$

where P_{tot} is the total pressure. Equation (8.2-2) becomes

$$K_P = \prod_{i=1}^{c} (x_i P_{\text{tot}}/P^\circ)^{\nu_i} = (P_{\text{tot}}/P^\circ)^{\Delta\nu} \prod_{i=1}^{c} (x_i)^{\nu_i} = (P_{\text{tot}}/P^\circ)^{\Delta\nu} K_x \tag{8.6-17}$$

where $\Delta\nu$ is the sum of the stoichiometric coefficients:

$$\Delta\nu = \sum_{i=1}^{c} \nu_i \tag{8.6-18}$$

equal to the net change in the number of moles of gas in the system if 1 mol of reaction occurs. Since the ν's are negative for reactants, this sum is the difference between the number of moles of products and the number of moles of reactants.

The quantity K_x is not a true equilibrium constant, since it depends on pressure for a gaseous reaction

$$K_x = (P_{\text{tot}}/P^\circ)^{-\Delta\nu} K_P \tag{8.6-19}$$

If the products consist of fewer moles of gas than the reactants and if the pressure on the system is increased, 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 volume (the stress) will increase the pressure by a smaller amount than if the reaction were somehow prevented from shifting.

*Exercise 8.18

For the reaction of Example 8.2, calculate the 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.

The principle of Le Châtelier can also be applied to the addition of an additional amount of a reactant or product to an equilibrium reaction mixture.

EXAMPLE 8.13

For the system of Example 8.2, find the effect of adding an additional 0.500 mol of NO_2

Solution

Let

$$n(N_2O_4) = (1.000\ \text{mol})(1.000 - \alpha)$$

$$n(NO_2) = (1.000\ \text{mol})(2.000\alpha + 0.500)$$

$$0.148 = \frac{(2.000\alpha + 0.500)^2}{1.000 - \alpha}(1.000\ \text{mol})\frac{RT}{P^\circ V}$$

$$\frac{RT}{P^\circ V} = \frac{(8.3145\ \text{J K mol}^{-1})(298.15\ \text{K})}{(100000\ \text{Pa})(0.02446\ \text{m}^3)} = 1.0135\ \text{mol}^{-1}$$

$$0.148 = \frac{(2.027\alpha + 0.5067)^2}{1.000 - \alpha}$$

which gives

$$4.0540\alpha^2 + 2.1750\alpha + 0.1054 = 0$$

Use of the quadratic formula gives

$$\alpha = -0.0539$$

where a root 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 priciple of Le Châtelier.

Exercise 8.19

Verify the result of Example 8.13 by substituting the value of α into the equilibrium constant expression.

8.7 Chemical Reactions 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. This coupling is used both in driving useful reactions and in regenerating reactants for the spontaneous reactions. The hydrolysis of adenosine triphosphate (ATP) to form adenosine diphosphate (ADP) and phosphoric acid (P) is shown in Figure 8.4. Since ATP, ADP, and phosphoric acid are all weak polyprotic acids they exist as various anions in aqueous solutions as well as in the forms shown in Figure 8.4. At neutral pH, the most abundant form of ATP is a triply negative anion with a single proton on one of the acid groups. This reaction equation is abbreviated as

$$\text{ATP} + H_2O \rightleftharpoons \text{ADP} + P_i \qquad (8.7\text{-}1)$$

where the abbreviation in Eq. (8.7-1) stand for whatever ionized and unionized forms of ATP, ADP, and phosphoric acid occur. The symbol P_i stands for "inorganic phosphate."

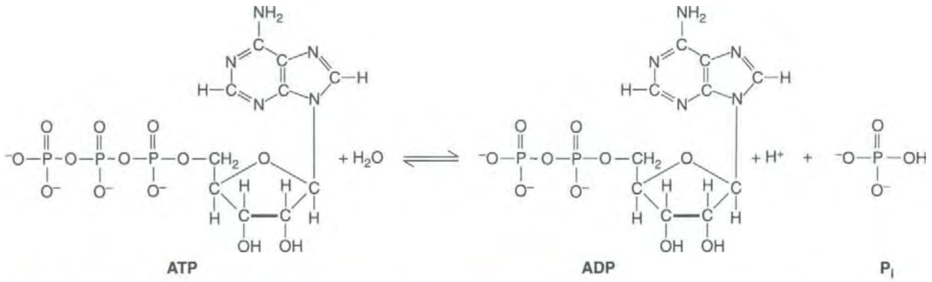


Figure 8.4. The Hydrolysis of Adenosine Triphosphate. This reaction is one of the principal energy delivery systems in biological organisms. The common abbreviation for each species is shown below its formula.

The anions of ATP and ADP have a strong tendency to form complexes with positive ions such as Mg^{2+} or 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. For the reaction of Eq. (8.7-1), using the concentration description, $\Delta G^{\circ\prime}$ is equal to $-29.3\ \mathrm{kJ\ mol^{-1}}$ at 298.15 K with pH equal to 7.00 and pMg equal to 4.00. The pMg is defined by analogy with pH:

$$\mathrm{pMg} = -\log_{10}[a(\mathrm{Mg}^{2+})] = -\log_{10}[\gamma(\mathrm{Mg}^{2+})c(\mathrm{Mg}^{2+})/c^{\circ}] \tag{8.7-2}$$

The specified value of $\Delta G^{\circ\prime}$ is for the combined reactions of whatever unionized, anionic, and complexed forms occur. For example, the standard state for ATP is the state with the sum of the concentrations of all forms of ATP equal to $1\ \mathrm{mol\ L^{-1}}$ and with all activity coefficients equal to unity.

EXAMPLE 8.14

a. Find the equilibrium constant for the reaction of Eq. (8.7-1).

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.

Solution

a.

$$K = \exp\left[\frac{2.93 \times 10^4\ \mathrm{J\ mol^{-1}}}{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})}\right] = 1.36 \times 10^5$$

b. Let $x = c_{\mathrm{eq}}(\mathrm{ATP})/c^{\circ}$

$$1.36 \times 10^5 = \frac{(0.0100 - x)^2}{x}$$

$$x = \frac{(0.0100 - x)^2}{1.36 \times 10^5} \approx \frac{(0.0100)2}{1.36 \times 10^5} \approx 7.35 \times 10^{-10}$$

$$c_{\mathrm{eq}}(\mathrm{ATP}) \approx 7.35 \times 10^{-10}\ \mathrm{mol\ L^{-1}}$$

*Exercise 8.20

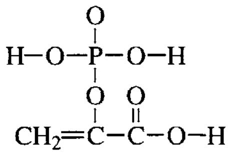
Find the value of $(\partial G/\partial \xi)_{T,P}$ for the case that $c(\mathrm{ATP}) = 0.0100\ \mathrm{mol\ L^{-1}}$ and $c(\mathrm{ADP}) = c(\mathrm{P}) = 0.0200\ \mathrm{mol\ L^{-1}}$ at pH 7.00 and pMg = 4.00. Approximate all activity coefficients by unity.

The hydrolysis of ATP is a spontaneous reaction under the conditions occurring in biological systems as well as under the modified standard-state conditions. This reaction is "coupled" to various other reactions that would otherwise not be spontaneous. That is, the spontaneous hydrolysis of ATP "drives" the nonspontaneous reactions, causing them to proceed. For example, the reaction

$$P_i + \text{glucose} \rightleftharpoons \text{glucose 6-phosphate} + H_2O \qquad (8.7\text{-}3)$$

is driven by the reaction of Eq. (8.7-1).

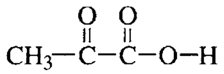
The ADP that is formed in the reaction of Eq. (8.7-1) is "recycled." That is, other substances undergo spontaneous reactions that are coupled to the reaction of Eq. (8.7-1), driving it from right to left. A reaction that drives the regeneration of ATP is the hydrolysis of phosphoenolypyruvic acid (abbreviated PEP):



The hydrolysis of PEP is sufficiently spontaneous to produce ATP from ADP. The sum of the two reactions is equivalent to a spontaneous reaction:

$$\begin{array}{lll}
\text{(A)} & PEP + H_2O \rightleftharpoons Py + P_i & \Delta G^{\circ\prime} = -53.6\ \text{kJ mol}^{-1} \\
\text{(B)} & ADP + P_i \rightleftharpoons ATP + H_2O & \Delta G^{\circ\prime} = +29.3\ \text{kJ mol}^{-1} \\
\text{(C)} & ADP + PEP \rightleftharpoons ATP + Py & \Delta G^{\circ\prime} = -24.3\ \text{kJ mol}^{-1}
\end{array}$$

where Py stands for pyruvic acid



$$CH_3\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}\overset{\overset{\displaystyle O}{\|}}{C}\text{—}O\text{—}H$$

and/or pyruvate ion. The hydrolysis of PEP produces phosphoric acid, which is a reactant in the regeneration of ATP from ADP. According to the principle of Le Châtelier the phosphoric acid would shift the equilibrium of the regeneration reaction, producing more ATP. In the next example, we show that the effect of this shift is insignificant.

EXAMPLE 8.15

Calculate the concentration of ATP produced at 298.15 K by the equilibrium shift due to 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

$$K_A = \exp\left[\frac{5.36 \times 10^4\ \text{J mol}^{-1}}{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298.15\ \text{K})}\right] = 2.46 \times 10^9$$

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. (8.7-1), or 7.35×10^{-6}. We let $x = c_{eq}(\mathrm{ATP})c^{\circ}$. The equilibrium expression gives

$$x = (7.35 \times 10^{-6})(0.0100 - x)^2 \approx (7.35 \times 10^{-6})(0.0100)^2 = 7.35 \times 10^{-10}$$

$$c_{eq}(\mathrm{ATP}) \approx 7.35 \times 10^{-10}\ \mathrm{mol\ L^{-1}}$$

To explain the coupling of reactions, there must be a mechanism that in some molecular sense makes one reaction out of two reactions. A proposed mechanism for the coupling of these two reactions involves an enzyme, pyruvate kinase, denoted by E:[4]

$$
\begin{aligned}
&(1)\quad \mathrm{E + PEP \rightleftharpoons EP + Py}\\
&(2)\quad \mathrm{EP + ADP \rightleftharpoons E + ATP}\\
&\qquad\ \ \mathrm{ADP + PEP \rightleftharpoons ATP + Py}
\end{aligned}
$$

An enzyme generally possesses an **active site**, a cavity into which a reactant molecule can fit. Once in the active site, the reactant molecule is rendered more reactive, possibly by being distorted into a conformation resembling the transition state for the reaction. 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.

*Exercise 8.21

a. Find the equilibrium constant at 298.15 K for the combined reaction

$$\mathrm{ADP + PEP \rightleftharpoons ATP + P_i}$$

b. Find the equilibrium ATP concentration for the initial concentrations of Example 8.15, treating the combined reaction as a single reaction.

Exercise 8.22

The coupling of the spontaneous hydrolysis of ATP to drive other reactions is similar to the coupling that regenerates ATP.

a. Write a possible mechanism for the coupling of the spontaneous hydrolysis of ATP to drive the phosphorylation of glucose, Eq. (8.7-3).

***b.** For the combined reaction, $\Delta G^{\circ\prime} = -9.6\ \mathrm{kJ\ mol^{-1}}$. Find $\Delta G^{\circ\prime}$ for the phosphorylation of glucose and find the equilibrium constant for the combined reaction.

Processes other than nonspontaneous chemical reactions are also coupled to the hydrolysis of ATP. Figure 8.5 depicts a proposed mechanism for the **active transport** of a hypothetical substance, A, through a biological membrane from a solution of low concentration and low chemical potential of A (on the left in the figure) to a region of high concentration and high chemical potential of A (on the right in the figure).[5] This

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[4] K. J. Laidler, *Physical Chemistry with Biological Applications*, Benjamin/Cummings, Menlo Park, CA, 1978, pp. 246ff.

[5] K. J. Laidler, *op. cit.* pp. 487ff. (Note 4).

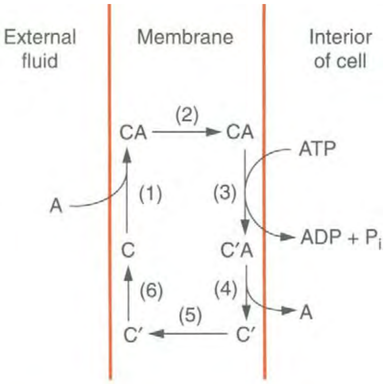

Figure 8.5. A Proposed Mechanism for Active Transport Through a Membrane. Every step of this mechanism is spontaneous, but the mechanism is able to transport the substance A from a region of lower chemical potential to a region of higher chemical potential. The ATP must be provided from outside the mechanism to make it operate.

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 and that the substance A is able to pass through the surfaces of the membrane. The first form of the carrier, denoted by C, has a tendency to form a complex with the substance A, while the second form, denoted by C′, has no such tendency. The conversion of C to C′ is nonspontaneous, and is coupled to the hydrolysis of ATP.

Step (1) of the mechanism is the combination of C with A 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 still attached to C when C is converted to C′, but A is released in step (4) as soon as the conversion to C′ is complete. Because of the dissociation of C′A, the concentration of CA is kept small on 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, the Gibbs energy of the entire system decreases due to the negative Gibbs energy change of hydrolysis of ATP.

Summary of the Chapter

For a reaction at equilibrium at constant temperature and pressure,

$$0 = \left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \sum_{i=1}^{c} \nu_i \mu_i$$

which leads to the constancy of K, the equilibrium constant:

$$K = \prod_{i=1}^{c} a_i(\text{eq})^{\nu_i}$$

where $a_i(\text{eq})$ is the equilibrium value of the activity of substance i. The equilibrium constant is related to the Gibbs energy change of the standard-state reaction:

$$K = e^{-\Delta G^\circ/RT}$$

The equilibrium constant for a reaction involving ideal gases is

$$K_P = \prod_{i=1}^{c} \left(\frac{P_i(\text{eq})}{P^\circ}\right)^{\nu_i} \quad \text{(gaseous reaction only)}$$

The equilibrium constant for a reaction in solution is

$$K = (\gamma_1 x_1)^{\nu_1} \prod_{i=2}^{c} (\gamma_i m_i(\text{eq})/m^\circ)^{\nu_i}$$

where the solvent is designated as substance number 1. For dilute solution, the solvent factor 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.

PROBLEMS

Problems for Section 8.1

8.23. A hypothetical gaseous isomerization reaction

$$A \rightleftharpoons B$$

has $\Delta G^\circ = -5.000\ \text{kJ mol}^{-1}$ at 298.15 K. Draw a 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. 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.

Problems for Section 8.2

8.24. Find the value of the equilibrium constant for the reaction of Problem 8.23 from the ΔG° value and compare it with the value found graphically in Problem 8.23.

8.25. 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. $2NO(g) + O_2(g) \rightleftharpoons N_2O_4(g)$
***c.** $S(\text{cr,rhombic}) + O_2(g) \rightleftharpoons SO_2(g)$
d. $4NO_2(g) + O_2(g) \rightleftharpoons 2N_2O_5(g)$
***e.** $2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$

8.26. Using formation values and third-law entropies, find ΔH°, ΔS°, and ΔG° for each of the following reactions. Calculate $\Delta H^\circ - T\,\Delta S^\circ$ and compare it with ΔG° to check the consistency of the data.

a. $2HgO(s) \rightleftharpoons 2Hg(l) + O_2(g)$
b. $CaCO_3(\text{calcite,cr}) + 2HCl(g) \rightleftharpoons CaCl_2(s) + H_2O(l) + CO_2(g)$
c. $2Mg(s) + O_2(g) \rightleftharpoons 2MgO(s)$
d. $CaCO_3(\text{calcite,cr}) \rightleftharpoons CaO(s) + CO_2(g)$

8.27. Find the equilibrium constant at 298.15 K for each of the reactions of the previous problem.

8.28. 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.

***8.29. 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 0.500 mol of N_2 and 1.500 mol of H_2, maintained at 298.15 K and 1.00 atm. Neglect gas nonideality.

8.30. 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_P 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.

8.31. Find ΔG° and K_P at 298.15 K for each of the gas-phase reactions:

***a.** $N_2O + O \rightleftharpoons 2NO$
b. $H_2O + \frac{7}{2}H_2S + 3NO_2 \rightleftharpoons 2NH_3 + \frac{7}{2}SO_2$
***c.** $H_2 + CO_2 \rightleftharpoons H_2O + CO$
d. $3O_2 \rightleftharpoons 2O_3$
***e.** $O_2 + O \rightleftharpoons O_3$

8.32. **a.** Find ΔG° and K_P for each of the following reactions at 298.15 K:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$
$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

b. Using the results of part (a), find ΔG° and K_P for the reaction at 298.15 K:

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$$

c. Find ΔG° and K_P for the reaction at 298.15 K:

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

8.33. 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 $(\partial \ln(K_x)/\partial n_i)_{T,P}$, 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?

Problems for Section 8.4

8.34. Find the partial vapor pressure of HCl over a 0.85 molal aqueous HCl solution at 298.15 K. State any assumptions.

***8.35.** Find ΔH°, ΔS°, and ΔG° at 298.15 K for each of the following reactions, using formation data and absolute entropy data. Compare the value of $\Delta H^\circ - T\,\Delta S^\circ$ with that of ΔG° to test the consistency of the data.

a. $Cl_2(g) + 2I^-(aq) \rightleftharpoons 2Cl^-(aq) + I_2(s)$
b. $2Ag^+(aq) + Ca(s) \rightleftharpoons 2Ag(s) + Ca^{2+}(aq)$

8.36. Find ΔH°, ΔS°, and ΔG° at 298.15 K for each of the following reactions, using formation data and absolute entropy data. Compare the value of $\Delta H^\circ - T\,\Delta S^\circ$ with that of ΔG° to test the consistency of the data.

a. $2Fe^{2+}(aq) + Sn^{4+} \rightleftharpoons 2Fe^{3+}(aq) + Sn^{2+}(aq)$
b. $Cl_2(g) + 2Br^-(aq) \rightleftharpoons 2Cl^-(aq) + Br_2(l)$

***8.37.** Find the equilibrium constant (solubility product constant) at 298.15 K for the reaction

$$AgCl(s) \rightleftharpoons Ag^+ + Cl^-$$

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.

8.38. The solubility product constant of 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.

8.39. The solubility product constant of nickel(II) hydroxide is equal to 1.7×10^{-3} 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.

8.40. The solubility of 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.

Problems for Section 8.5

8.41. 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. Chloroacetic	1.40×10^{-3}
***c.** Benzoic	6.46×10^{-5}

8.42. 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 esimate $\gamma_\pm$. In each case, 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}

***8.43.** 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 $K_2 = 1.51 \times 10^{-10}$. State any assumptions.

8.44. Calculate the pH of a solution made 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.

***8.45.** Find the molalities of H_2CO_3 and HCO_3^- in an aqueous solution at 298.15 K that has been equilibrated with gaseous CO_2 at 0.0400 atm and in which the pH is equal to 7.40.

8.46. 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 molality of citric acid and of each anion of citric acid.

***8.47.** 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? See Problem 8.44 for K.

a. Use the Henderson–Hasselbalch equation.

b. Use Eq. (8.5-3) and the Davies equation.

8.48. 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 sodium hydroxide is added.

d. Find the change in pH if 0.010 mol of sodium hydroxide is added to a solution of hydrochloric acid and sodium chloride in 1.000 kg of water, which has the same pH and ionic strength as the buffer solution in part (a).

***8.49.** A solution of ammonium benzoate is made from 0.0100 mol of ammonium benzoate and 1.000 kg of water and is maintained at 25°C. The acid ionization constant K_a for benzoic acid is equal to 6.46×10^{-5} at 25°C, and the base dissociation constant K_b for ammonia is equal to 1.774×10^{-5} at 25°C. Aguirre-Ode[6] gives an approximate formula (assuming that all activity coefficients equal unity):

$$m(\mathrm{H}^+)/m^\circ = \left(\frac{K_a K_w}{K_b}\right)^{1/2} \left(\frac{K_b + m/m^\circ}{K_a + m/m^\circ}\right)^{1/2}$$

where m is the stoichiometric modality. Find the pH using this formula.

8.50. 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.

8.51. 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, 0.100 mol of potassium hydrogen phthalate, 0.100 mol of dipotassium phthalate, and 1.000 kg of water.

Problems for Section 8.6

8.52. Multiply Eq. (8.6-9) by $d(1/T)$ and carry out an integration to obtain a formula analogous to Eq. (8.6-12). Comment on your result.

***8.53. a.** Find the equilibrium constant for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

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. Compare your answers with that of Problem 8.29.

8.54. 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. State any assumptions.

***8.55. a.** Find ΔH°, ΔG°, and K_P at 298.15 K for the reaction

$$I_2(g) \rightleftharpoons 2I(g)$$

b. Assuming that $\Delta H^\circ =$ constant, find K_P at 1000. K from the values at 298.15 K.

c. Assuming that $\Delta H^\circ =$ constant, find the temperature at which $K_P = 1.000$.

d. Assuming that $\Delta C_P^\circ =$ constant, find K_P at 1000. K.

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[6] F. Aguirre-Ode, *J. Chem. Educ.*, **64**, 957 (1987).

8.56. 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 ΔG°, ΔH°, and ΔS° at 25°C.

***8.57.** Find the value of K_P at 750 K for the reaction

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

a. Use the van't Hoff equation, Eq. (8.6-12).

b. Use the interpolated values of the $-(G^\circ_m - H^\circ_{m298})/T$ functions to find ΔG° and find K_P from that value.

8.58. a. Find ΔG° and K_P for each of the following reactions at 1000.0 K:

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$
$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$$

State any assumptions.

b. Using the results of part (a), find ΔG° and K_P for the reaction at 1000.0 K

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g)$$

c. Find ΔG° and K_P for the reaction at 1000.0 K

$$2NO_2(g) \rightleftharpoons N_2O_4(g)$$

8.59. Find the value of K_P 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. (8.6-12).

b. Use the interpolated values of the $-(G^\circ_m - H^\circ_{m298})/T$ functions to find ΔG° and find K_P from that value.

8.60. 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 $-(G^\circ - H^\circ_{m298})/T$ functions.

c. Use the Gibbs–Helmholtz equation.

8.61. Miller and Murphy[7] 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

Find the value of ΔG°, ΔH° and ΔS° for the process of transferring nicotine from water to hexane, using the concentration description.

Problems for Section 8.7

8.62. Creatine phosphate is another substance in addition to phosphoenolpyruvate that can regenerate ATP. If the temperature equals 25°C, the pH is equal to 7.00, and the pMg is equal to 4.00, the value of ΔG° for its hydrolysis is equal to $-43.1\ \text{kJ mol}^{-1}$. Assuming that a mechanism exists to couple the reactions, find the value of the equilibrium constant for the combined reaction to regenerate ATP.

***8.63.** 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.

General Problems

8.64. 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.

***8.65.** The Haber process produces gaseous ammonia directly from hydrogen gas and nitrogen gas. Since the reaction proceeds very slowly, a catalyst is used. The catalyst

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[7] D. L. C. Miller and W. R. Murphy, *Ind. Eng. Chem. Res.*, **33**, 3239 (1994).

[8] E. D. P. DeRobertis and E. M. F. DeRobertis, Jr., *Cell and Molecular Biology*, Saunders College Publishing, Philadelphia, 1980, pp. 267ff.

used in industrial manufacture is a mixture of iron oxide and potassium aluminate. The reaction is

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

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. Haber's invention made possibel the large-scale manufacture of gunpowder in Germany in World War I as well as the manufacture of synthetic fertilizers.

a. Find the value of ΔG° for this reaction at 298.15 K.

b. Find the value of K_P 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 ΔH° 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 room temperature?

g. Calculate the value of K_P at 500.°C, using values of ΔG° and ΔH° at 298.15 K and assuming that ΔH° is constant.

h. Calculate the value of K_P at 500.°C, using values of $-(G^\circ_\mathrm{m} - H^\circ_\mathrm{m298})/T$ 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.

8.66. The following reaction is known as the "water-gas reaction":

$$H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

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 ΔG° and of K_P for this reaction at 298.15 K and at 1000. K.

b. Find the value of ΔH° 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 ΔG° and of K_P at 1259 K, interpolating between values of $-(G^\circ_\mathrm{m} - H^\circ_\mathrm{m298})/T$ in Table A.8 of Appendix A. Compare your value of K_P with the accepted value of 1.60.

e. Find the value of ΔG° and of K_P for this reaction at 1259 K, using the values at 1000. K and assuming that ΔH° is constant between 1000. K and 1259 K. Compare your result with the result of part (d).

8.67. For a sparingly soluble 1–1 electrolyte, the molality at saturation is given by

$$\frac{m_\mathrm{sat}}{m^\circ} = \sqrt{K_\mathrm{sp}}$$

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.

9

The Thermodynamics of Electrical Systems

OBJECTIVES

After studying this chapter, a student should:

1. understand how the thermodynamics of a nonsimple system is applied to electrochemical cells;
2. be able to calculate cell voltages for standard conditions and other conditions using standard reduction potentials and the Nernst equation;
3. be able to solve problems relating equilibrium constants and Gibbs energy changes to electrochemically measured quantities.

PRINCIPAL FACTS AND IDEAS

1. Thermodynamic relations can be specialized to give useful 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.

9.1 The Chemical Potential and the Electric Potential

Electrochemistry exploits the fact that many chemical reactions involve the transfer of electrons and other charged particles. If a particle of charge Q has an electrostatic force $\mathbf{F}$ exerted on it, this corresponds to an **electric field** $\mathcal{E}$ such that

$$\mathbf{F} = Q\mathcal{E} \tag{9.1-1}$$

The *electric potential* φ is defined such that the electric field is equal to the negative gradient of the electric potential

$$\mathcal{E} = -\nabla\varphi \tag{9.1-2}$$

The gradient of a scalar function is defined in Eq. (B-37) of Appendix B. The x component of $\mathcal{E}$ is given by

$$\mathcal{E}_x = -\frac{\partial\varphi}{\partial x} \tag{9.1-3}$$

and the other components are similar. The electric potential is a potential energy per unit charge and the electric field is a force per unit charge. The electrostatic contribution to the potential energy of a particle of charge Q is

$$\mathcal{V}_{\text{electrostatic}} = Q\varphi \tag{9.1-4}$$

An arbitrary constant can be added to the electric potential without any physical effect, as is the case with any potential energy. It is customary to choose the value of the electric potential to be zero at a location that is infinitely distant from all charges. Electric potentials relative to this zero are sometimes 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 an ionic species i is given by

$$\mu_i = \mu_{i(\text{chem})} + N_{\text{Av}} e z_i \varphi \tag{9.1-5}$$

Faraday's constant is named for Michael Faraday, 1791–1867, a great English physicist and chemist who discovered the laws of electrolysis and who invented the first electric generator.

where e is the proton charge, N_{Av} is Avogadro's number, and z_i is the valence of the ion (the number of proton charges on the ion: it 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.**

$$F = N_{\text{Av}} e = 96485 \text{ C mol}^{-1} \tag{9.1-6}$$

Equation (9.1-5) can be written

(9.1-7)

The quantity $\mu_{i(\text{chem})}$ is the **chemical part of the chemical potential.** It is assumed to be independent of the electric potential and depends only on temperature, pressure, and composition of the system. If the substance is uncharged or if the electric potential has a zero value $\mu_{i(\text{chem})}$ is equal to the entire chemical potential. The chemical potential including the electric potential is usually called the **electrochemical potential.** It is the true chemical potential that obeys the Gibbs–Duhem relation and the fundamental fact of phase equilibrium. Unfortunaely, $\mu_{i(\text{chem})}$ has sometimes been called the "chemical potential" to distinguish it from the electrochemical potential. We will call $\mu_{i(\text{chem})}$ the chemical part of the chemical potential and will use the term chemical potential or the term electrochemical potential for the full chemical potential.

The chemical potential of a single charged species cannot be measured, since charged particles cannot easily be added without adding ions of the opposite charge at the same time. We use the analogue of Eq. (8.4-3) to write the chemical potential of a neutral electrolyte solute denoted by *i*, with the formula $M_{\nu_+}X_{\nu_-}$ and with ion valences z_+ and z_-.

$$\mu_i = \nu_+\mu_+ + \nu_-\mu_- = \nu_+\mu_{+(\text{chem})} + \nu_-\mu_{-(\text{chem})} + (\nu_+z_+ + \nu_-z_-)F\varphi \tag{9.1-8}$$

Electrical neutrality implies that $\nu_+z_+ + \nu_-z_- = 0$, so the last term in Eq. (9.1-8) vanishes and the chemical potential (electrochemical potential) of the neutral electrolyte is equal to the chemical part of the chemical potential.

$$\mu_i = \nu_+\mu_{+(\text{chem})} + \nu_-\mu_{-(\text{chem})} = \mu_{i(\text{chem})} \tag{9.1-9}$$

Exercise 9.1

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.

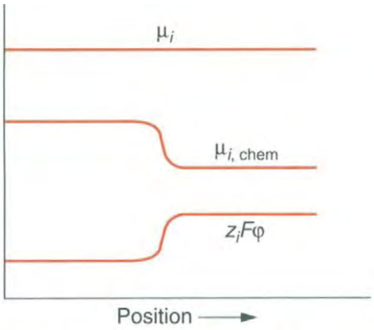

Figure 9.1. The Equilibrium Chemical Potential, the Chemical Part of the Chemical Potential, and the Electric Potential at the Interface between Two Metallic Phases (Schematic). Since the chemical potential must be uniform, if the chemical part of the chemical potential is not uniform, the electric potential is not uniform.

Electrons have a chemical potential like any other charged species:

$$\mu_e = \mu_{e(\text{chem})} - F\varphi \tag{9.1-10}$$

If two different homogeneous conducting phases are placed in close contact and allowed to come to equilibrium, the electrochemical potential of electrons will have the same value in both phases. Since the phases are of different materials, the chemical part of the electron's chemical potential can have different values in the two phases and the electric potential must also have different values in the two phases at equilibrium, as depicted in Figure 9.1. If two phases are not at equilibrium, both the chemical part of the chemical potential of electrons and the electric potential can have different values in the two phases. If electrons are used as a probe to measure a difference in the electric potential between two terminals the terminals must consist of the same material so that the chemical part of the chemical potential will have the same value in the two terminals.

9.2 Electrochemical Cells at Equilibrium

An electrochemical cell is a device in which the passage of an electric current is accompanied by the progress of a chemical reaction. There are three principal types of electrochemical cells. In an **electrolytic cell** a current is passed by an external driving force, causing an otherwise nonspontaneous chemical reaction to proceed. In a **galvanic cell** the progress of a spontaneous chemical reaction causes the electric current to flow, doing work on the surroundings.

Galvanic cells are named after Luigi Galvani, 1737–1798, 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.

An **equilibrium electrochemical cell** is at the state between being an electrolytic cell and a galvanic cell. The tendency of a spontaneous reaction to push a current through the external circuit is balanced by an external voltage (electromotive force or e.m.f.) that exactly cancels this tendency. If this **counter e.m.f.** is increased beyond the

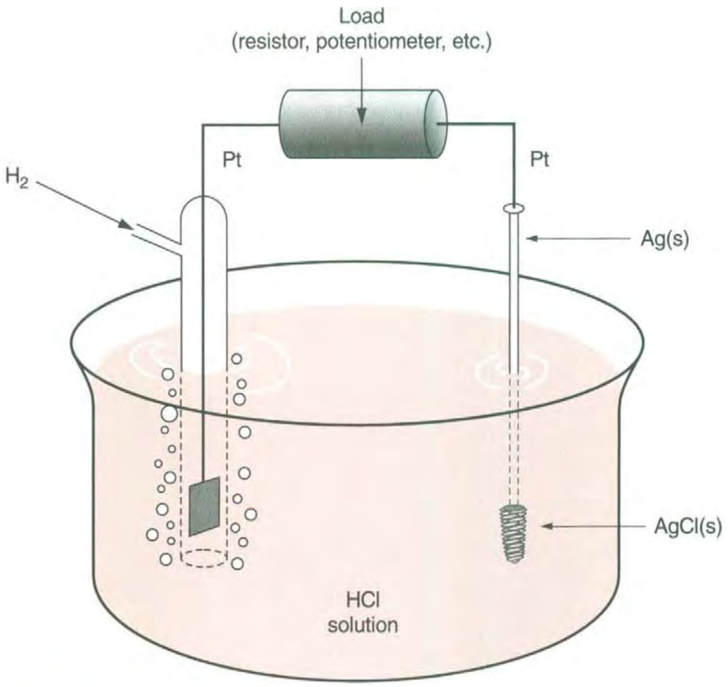

Figure 9.2. An Electrochemical Cell. An electrochemical cell always consists of several phases, and at least one phase is an ionic solution. This cell also has a gas phase, and the adsorbed gas reacts at the left electrode surface.

equilibrium value, the cell becomes an electrolytic cell, and if it is decreased below the equilibrium value, the cell becomes a galvanic cell.

Electrochemical cells always contain several phases. There are two or more **electrodes**, made of metal or graphite, that can conduct a current of electrons, and there must be at least one electrolyte solution in contact with the electrodes. 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. The zero-valent metal of a typical electrode is also insoluble in liquid solutions, and the components of a liquid solution are insoluble in the metal of the electrode. We cannot use the fundamental fact of phase equilibrium, because no substance occurs in more than one phase. However, if the material of the electrode can oxidize to form an ion that occurs in the electrolyte solution or can accept electrons from a chemical reaction in the solution, a chemical reaction can come to equilibrium at the phase boundary, and this fact will provide an equilibrium condition on the chemical potentails.

Figure 9.2 schematically depicts a particular electrochemical cell. A figure such as Figure 9.2 is called a **cell diagram** and shows the phases that occur and how they are connected. This cell is one of 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, the interface between the solutions is called a liquid junction. A cell without a liquid junction can be a reversible cell, which means that all processes in the cell can be

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[1] L. Kevan and B. Webster, eds., *Electron–Solvent and Anion–Solvent Interactions*, Elsevier, New York, 1976.

reversed by an infinitesimal adjustment of a counter e.m.f. A cell with a liquid junction is not a reversible cell.

The electrode at the left in Figure 9.2 is a **hydrogen electrode**. It has a platinum surface that has been "platinized" (plated with porous platinum) to increase its surface area. Hydrogen gas at a specified pressure is bubbled through the solution around the electrode, and is adsorbed on the platinum, where it can undergo the oxidation process:

$$H_2(g) \rightarrow 2H^+ + 2e^- \qquad (9.2\text{-}1)$$

As in this equation, we will label substances in gaseous phases by (g), those in solid phases by (s), and those in pure liquid phases (such as liquid mercury) by (l). Substances that are not labeled are understood to be in aqueous solution. The process of Eq. (9.2-1) is called a **half-reaction**, since it cannot take place without another process to accept the electrons produced. This half-reaction is an oxidation half-reaction, and the electrode for which an oxidation half-reaction is written is called an **anode**.

The electron at the right in the cell of Figure 9.2 is called the **silver–silver chloride electrode**. It is a piece of silver that is coated with solid silver chloride. The **reduction half-reaction**

$$AgCl(s) + e^- \rightarrow Ag(s) + Cl^- \qquad (9.2\text{-}2)$$

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.

can occur at this electrode. The electrode for which a reduction half-reaction is written is called a **cathode**. There is a piece of platinum attached to the silver of the right electrode so that an electric potential difference can be measured between two terminals of the same material.

We multiply the reduction half-reaction equation by 2 and add the two half-reaction equations to obtain the **cell reaction equation**:

$$H_2(g) + 2AgCl(s) + 2e^-(R) \rightarrow 2H^+ + 2Ag(s) + 2Cl^- + 2e^-(L) \qquad (9.2\text{-}3)$$

We have labeled the electrons at the right and left electrodes. In an electrochemical cell the half-reactions take place in different locations, so that the electrons must be transported from one electrode to the other through an external circuit. We use a single arrow to indicate the direction of the reaction that we are considering. This reaction is spontaneous in the direction indicated if it takes place outside of an electrochemical cell. We can rewrite the cell reaction equation using only electrons and uncharged substances:

$$H_2(g) + 2AgCl(s) + 2e^-(R) \rightarrow 2HCl + 2Ag(s) + 2e^-(L) \qquad (9.2\text{-}4)$$

Equation (9.2-3) and Eq. (9.2-4) are equivalent, but the second equation makes it easier to write the chemical potentials, since the electric potential terms of neutral electrolytes cancel, as in Eq. (9.1-10).

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.

There are several conventions that have been adopted to make the description of electrochemical cells systematic. The first 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 (or vice versa). It can happen that the spontaneous direction of the reaction is opposite to the way we write it.

A **cell symbol** communicates the same information as the 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

$$\mathrm{Pt(s)|H_2(g)|HCl|AgCl(s)|Ag(s)|Pt(s)}$$

Any substance without a phase label (such as HCl in this case) is in aqueous solution.

Since the platinum wire at the right terminal is present only to provide a phase at which to measure the potential, it is sometimes omitted from the cell symbol. The platinum at the left terminal provides a surface for the adsorbed hydrogen to react on, but it is also sometimes omitted.

The molality, concentration, or activity of the electrolyte solute involved in the reaction is usually included in the cell symbol, as is the pressure of a gas. If the molality of the HCl in solution is equal to 0.500 mol $\mathrm{kg^{-1}}$ and the pressure of the hydrogen gas is 0.990 atm, the complete cell symbol is

$$\mathrm{Pt(s)|H_2(g,\ 0.990\ atm)|HCl(0.500\ mol\ kg^{-1})|AgCl(s)|Ag(s)|Pt(s)}$$

A similar specification of composition is used for an electrode that is a solid solution or an amalgam (solution in liquid mercury).

Let us leave our galvanic cell on "open circuit" (with the two terminals not connected to a circuit) and allow the cell to stabilize at constant temperature and pressure, with a fixed partial pressure of hydrogen at the anode. The state that is reached is a metastable state, since bringing the reactants to the same location or short-circuting the terminals would permit a reaction to occur spontaneously. One way to measure the electric potential difference between its terminals is with a **potentiometer**, in which an ajustable counter e.m.f opposes the electric potential difference of the cell. The counter e.m.f. is adjusted until it is just sufficient to stop the flow of electrons in the external circuit, as indicated by a galvanometer. The state of the cell is now the same as though the cell were an open circuit, and the counter e.m.f. 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 e.m.f. 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 e.m.f. is made slightly larger, the cell functions as an electrolytic cell and a current flows in the opposite direction.

An infinitesimal amount of reaction $d\xi$ in our system at equilibrium corresponds to

$$\begin{aligned} 0 &= \left(\frac{\partial G}{\partial \xi}\right)_{T,P} d\xi \\ &= [2\mu(\mathrm{HCl}) + 2\mu(\mathrm{Ag}) - \mu(\mathrm{H_2}) - 2\mu(\mathrm{AgCl}) + 2\mu(e^-(\mathrm{L})) - 2\mu(e^-(\mathrm{R}))]\, d\xi \qquad (9.2\text{-}5) \end{aligned}$$

which can be written

$$0 = \left(\frac{\partial G_{\mathrm{chem}}}{\partial \xi}\right)_{T,P} d\xi + \left(\frac{\partial G_{\mathrm{electron}}}{\partial \xi}\right)_{T,P} d\xi \qquad (9.2\text{-}6)$$

where G_{chem} includes the chemical potentials of substances other than electrons. All of these substances are neutral, so only the chemical parts of these chemical potentials are included. If the reaction took place outside of an electrochemical cell, $(\partial G_{\mathrm{chem}}/\partial\xi)_{T,P}$ would be the rate of change of Gibbs energy for the reaction. Since all other substances were written as uncharged species, the electric potential occurs only in the chemical potential expression of the electrons. 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 cancel, we can write from Eq. (9.1-5):

$$0 = \left(\frac{\partial G_{\text{chem}}}{\partial \xi}\right)_{T,P} + 2FE \tag{9.2-7}$$

where E is the difference in electric potential between the right terminal and the left terminal. We introduce our second convention: *The potential difference of a cell (the cell voltage) is defined as the electric potential of the right electrode minus that of the left electrode:*

$$E = \Delta\varphi = \varphi(\mathrm{R}) - \varphi(\mathrm{L}) \tag{9.2-8}$$

Both electrodes must be made of the same material.

Since electrons are negatively charged, a positive value of E means that the chemical potential of the electron is larger in the left electrode, and electrons move spontaneously from the left terminal to the right terminal if a circuit is connected between the terminals. In this case oxidation occurs at the left electrode, and the cell reaction proceeds spontaneously in the direction in which we wrote it. If the cell potential difference is negative, the reverse of the cell reaction proceeds spontaneously and electrons move spontaneously from right to left in the external circuit.

The relation of Eq. (7.3-1) gives the chemical potential of each substance other than electrons in the form:

$$\mu_i = \mu_i^\circ + RT\ \ln(a_i) \tag{9.2-9}$$

We can now write

$$2FE^\circ = -\Delta G^\circ - RT\ \ln(Q) \tag{9.2-10}$$

where

$$\Delta G^\circ = 2\mu^\circ(\mathrm{HCl}) + 2\mu^\circ(\mathrm{Ag}) + \mu^\circ(\mathrm{H_2}) + 2\mu^\circ(\mathrm{AgCl}) \tag{9.2-11}$$

and where Q is the activity quotient:

$$Q = [a(\mathrm{HCl})]^2[a(\mathrm{Ag})]^2[a(\mathrm{H_2})]^{-1}[a(\mathrm{AgCl})]^{-2} = \frac{[a(\mathrm{HCl})]^2[a(\mathrm{Ag})]^2}{[a(\mathrm{H_2})][a(\mathrm{AgCl})]^2} \tag{9.2-12}$$

This quantity is the same as the activity quotient of Chapter 8, except that now Q can take on other values than its equilibrium value if there is no external circuit connecting the electrodes or if a counter e.m.f. maintains a persistent metastable state.

The standard-state potential difference E° for this cell is defined as

$$E^\circ = -\frac{\Delta G^\circ}{2F} \tag{9.2-13}$$

It is the potential difference (voltage) that would be measured if all substances were in their standard states (with unit activities). Equation (9.2-10) is now

$$\boxed{E = E^{\circ} - \frac{RT}{2F}\ln(Q)} \qquad (9.2\text{-}14)$$

The Nernst equation is named for Hermann Walther Nernst, 1864–1941, the German physical chemist who was mentioned in Chapter 4 for his work on the third law of thermodynamics.

Equation (9.2-14) is the **Nernst equation** for this cell.

Since the Ag and AgCl are both pure solids, their activities are equal to or nearly equal to unity, and can be omitted from the product Q. Treating hydrogen as an ideal gas and using Eq. (8.4-6) for the activity of HCl in terms of molalities,

$$E = E^{\circ} - \frac{RT}{2F}\ln\left[\left(\frac{\gamma(\mathrm{H}^+)^2 m(\mathrm{H}^+)^2\gamma(\mathrm{Cl}^-)^2 m(\mathrm{Cl}^-)^2}{m^{\circ 4}}\right)\left(\frac{P(\mathrm{H}_2)}{P^{\circ}}\right)^{-1}\right] \qquad (9.2\text{-}15)$$

$$= E^{\circ} - \frac{RT}{2F}\ln\left(\frac{\gamma_{\pm}^4 m^4/m^{\circ 4}}{P(\mathrm{H}_2)/P^{\circ}}\right) \qquad (9.2\text{-}16)$$

where we have assumed that $m(\mathrm{H}^+)$ and $m(\mathrm{Cl}^-)$ are equal, and have denoted them by m.

EXAMPLE 9.1

Find the potential difference of our cell at 298.15 K if the hydrogen pressure is equal to 744 torr and if the HCl is at 0.500 mol kg^{-1} with mean ionic activity coefficient equal to 0.757. The value of the standard-state potential difference is 0.2223 V.

Solution

$$E = 0.2223\ \mathrm{V} - \left(\frac{(9.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})}{(2)(96485\ \mathrm{C\ mol^{-1}})}\right)\ln\left(\frac{(0.757)^4(0.500)^4}{(744\ \mathrm{torr})/(750\ \mathrm{torr})}\right)$$

$$= 0.2223\ \mathrm{V} - (-0.0498\ \mathrm{V}) = 0.2721\ \mathrm{V}$$

Our discussion has been for a particular cell. Consider now a general cell without liquid junction and with a cell reaction that can be written with neutral substances and electrons:

$$0 = \sum_{i=1}^{c} \nu_i \mathcal{F}_i + ne^-(\mathrm{R}) - ne^-(\mathrm{L}) \qquad (9.2\text{-}17)$$

where n is the number of electrons in the reaction equation. The Nernst equation for this cell is

$$\boxed{E = E^{\circ} - \frac{RT}{nF}\ln(Q)} \qquad (9.2\text{-}18)$$

where n is the number of electrons in the cell reaction equation and where

$$Q = \prod_{i=1}^{c} a_i^{\nu_i} \qquad (9.2\text{-}19)$$

The activity quotient Q does not include the activity of the electron and contains the activities of the same substances as if the reaction took place outside of a cell.

Exercise 9.2

a. Write the cell symbol, the cell reaction equation and the Nernst equation for the cell with the half-reactions:

$$2\mathrm{Hg(l)} + 2\mathrm{Cl}^- \rightarrow \mathrm{Hg_2(Cl_2(s)} + 2e^-$$
$$\mathrm{Cl_2(g)} + 2e^- \rightarrow 2\mathrm{Cl}^-$$

***b.** Find E for the cell at 298.15 K if $P(\mathrm{Cl_2}) = 0.965\,\mathrm{atm}$ and $a(\mathrm{Cl}^-) = 0.250$. The standard cell voltage is $E^\circ = 1.091$ 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 factor in the denominator in front of $\ln(Q)$ will be increased by the same factor C, canceling the effect of the exponent C.

Exercise 9.3

Multiply the cell reaction equation in Eq. (9.2-4) by $\frac{1}{2}$. Write the Nernst equation for the new reaction equation and show that it is the same as Eq. (9.2-16).

Determination of E° Values

Since the standard states of solutes are hypothetical states, E° of any cell cannot be measured directly, but if E is measured and if the activity coefficients are known, E° can be calculated using Eq. (9.2-18). If the activity coefficients are not known, an extrapolation to zero concentration can be used since the activity coefficients approach unity in this limit. Consider the cell of Figure 9.2. We keep the pressure of the hydrogen equal to P°, and measure E at various molalities. For small enough values of m, $\gamma_\pm$ will be given by the Debye–Hückel formula. Let us use the augmented version of Eq. (7.4-14). For HCl, the ionic strength is equal to the molality m if no other electrolytes are present. If Eq. (7.4-14) is substituted into Eq. (9.2-16),

$$E = E^\circ + \frac{2RT}{F}\left(\frac{\alpha m^{1/2}}{1 + (m/m^\circ)^{1/2}} + bm - \ln\left(\frac{m}{m^\circ}\right)\right)$$

which can be rewritten

$$E + \frac{2RT}{F}\left(-\frac{\alpha m^{1/2}}{1 + (m/m^\circ)^{1/2}} - \ln\left(\frac{m}{m^\circ}\right)\right) = E^\circ - \frac{2RT}{F}\,bm \qquad (9.2\text{-}20)$$

The left-hand-side of Eq. (9.2-20) contains only measurable quantities. If this function is plotted as a function of m, the plot should be linear in the region in which Eq. (9.2-20) is valid (the region near $m = 0$), so that extrapolation to the $m = 0$ axis is straightforward. The intercept is equal to E°, and the slope of the tangent line near the axis is equal to $2RTb/F$.

An alternate method can also be used. For small values of m, not only is the $\alpha m^{1/2}$ term negligible compared to unity, but also the bm term is negligible compared to the $\alpha m^{1/2}$ term. If the bm term is omitted, Eq. (9.2-20) becomes

$$E + \frac{2RT}{F}\ln\left(\frac{m}{m^\circ}\right) = E^\circ + \frac{2RT}{F}\,\alpha m^{1/2} \qquad (9.2\text{-}21)$$

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.

9.3 Half-Cell Potentials and Cell Potentials

The cell of Figure 9.3 has a hydrogen electrode on the left side and a calomel electrode on the right side. The calomel electrode contains liquid mercury with solid calomel (mercury(I) chloride, Hg_2Cl_2) in contact with it. A platinum wire extends from the pool of mercury and acts as a terminal. The solution in this cell is an aqueous solution of hydrochloric acid, just as in the cell of Figure 9.2. The reduction half-reaction of the calomel electrode is

$$Hg_2Cl_2(s) + 2e^- \rightarrow 2Hg(l) + 2Cl^- \tag{9.3-1}$$

and the oxidation half-reaction of the hydrogen electrode is the same as in Eq. (9.2-1). $E° = 0.268$ V for this cell.

Exercise 9.4

a. Write the cell reaction equation for the cell of Figure 9.3.
b. Write the Nernst equation for the cell of Figure 9.3.
c. Write an equation analogous to Eq. (9.2-20) that could be used to determine the value of $E°$ for the cell of Figure 9.3.

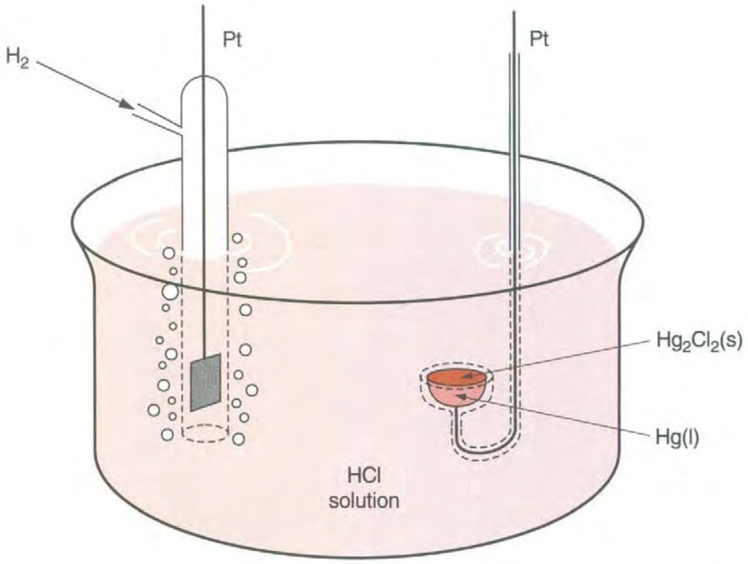

Figure 9.3. An Electrochemical Cell with a Hydrogen Electrode and a Calomel Electrode. In this cell, the half-reaction at the calomel electrode involves substances in three phases: the liquid Hg phase, the solid Hg_2Cl_2 phase, and the solution.

The cell that is obtained by interchanging the right and left half-cells of Figure 9.2 has the cell reaction equation:

$$2\mathrm{HCl} + 2\mathrm{Ag(s)} + 2e^-(\mathrm{R}) \rightarrow \mathrm{H_2(g)} + 2\mathrm{AgCl(s)} + 2e^-(\mathrm{L}) \qquad (9.3\text{-}2)$$

The standard-state cell potential difference of this cell is the negative of that of the cell of Figure 9.2, equal to -0.2223 V.

Figure 9.4 shows a cell that contains the silver–silver chloride electrode on the left and the calomel electrode on the right. It is possible to calculate the value of E° for this cell without making a measurement. We construct a double cell as depicted in Figure 9.5. This cell consists of two complete cells, one of which is the "reversed" version of

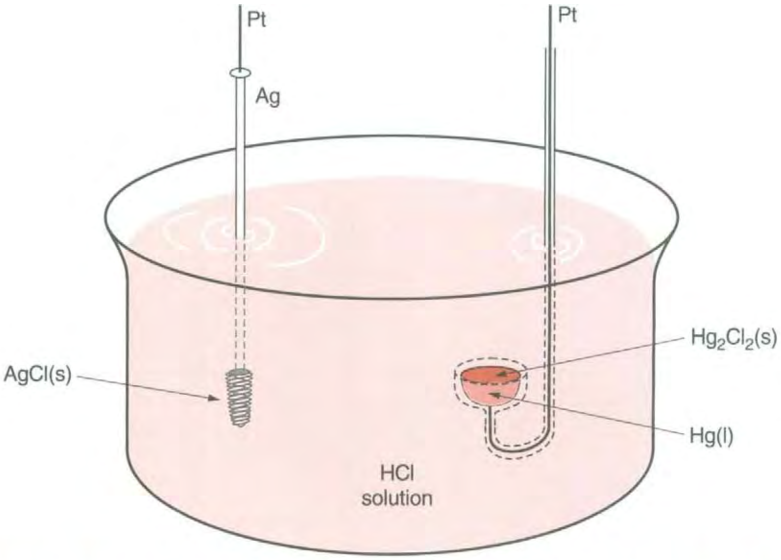

Figure 9.4. An Electrochemical Cell with a Silver–Silver Chloride Anode and a Calomel Cathode. In this cell, both half-reactions involve three phases.

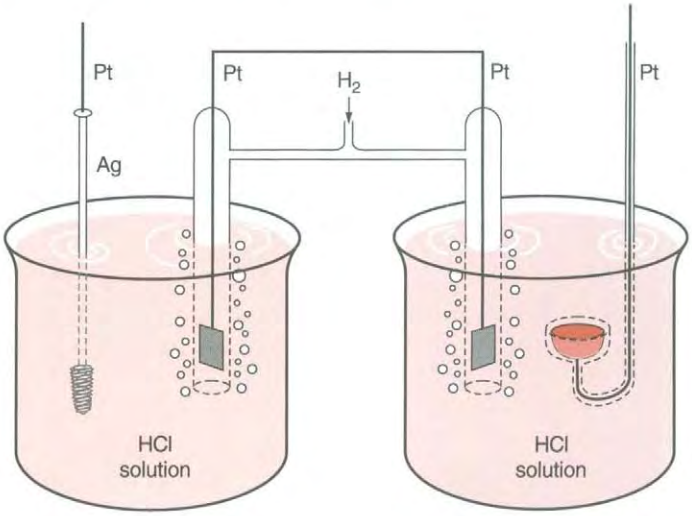

Figure 9.5. A Double Cell. This cell is used to illustrate the fact that potentials of cells with one hydrogen electrode can be used as half-cell potentials.

the cell in Figure 9.2 and one of which is the cell of Figure 9.3. Hydrogen gas at the same pressure is fed into both hydrogen electrodes and the two HCl solutions are at the same concentration (and the same activity). A wire is connected between the two hydrogen electrodes, and maintains them at the same electric potential. We can write

$$\begin{aligned} E(\text{double cell}) &= \varphi_{\mathrm{R}}(\text{right cell}) - \varphi_{\mathrm{L}}(\text{left cell}) \\ &= \varphi_{\mathrm{R}}(\text{right cell}) - \varphi_{\mathrm{L}}(\text{right cell}) + \varphi_{\mathrm{R}}(\text{left cell}) - \varphi_{\mathrm{L}}(\text{left cell}) \end{aligned}$$

The second equality follows from the fact that the two hydrogen electrodes are in the same state. The second equality is the same as

$$E(\text{double cell}) = E(\text{right cell}) + E(\text{left cell})$$

Since this relation is true for an arbitrary state, it is true for the standard state:

$$\begin{aligned} E^{\circ}(\text{double cell}) &= E^{\circ}(\text{right cell}) + E^{\circ}(\text{left cell}) \\ &= 0.268\ \mathrm{V} + (-0.2223\ \mathrm{V}) = 0.046\ \mathrm{V} \end{aligned} \tag{9.3-3}$$

The voltage of the cell in Figure 9.4 is also 0.046 V, because the state of the left electrode of the left cell in Figure 9.5 is not different from the state of the left electrode of the cell in Figure 9.2 and the state of the right electrode of the right cell in Figure 9.5 is not different from the state of the right electrode of the cell in Figure 9.4.

We adopt the following convention: *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 electrode potential.* The standard-state potential difference of the cell of Figure 9.4 can now be written

$$E^{\circ} = E^{\circ}(\text{right half-cell}) - E^{\circ}(\text{left half-cell}) \tag{9.3-4}$$

$$= 0.268\ \mathrm{V} - 0.222\ \mathrm{V} = 0.046\ \mathrm{V} \tag{9.3-5}$$

where these E° values are standard reduction potentials. The negative sign in Eq. (9.3-4) comes from the fact that the left cell in Figure 9.5 has its hydrogen electrode on the right, so that its standard-state potential difference is the negative of that conventionally assigned to its left electrode.

The procedure that led to Eq. (9.3-4) for the cell of Figure 9.4 can be applied to any pair of electrodes that can be combined to make a galvanic cell: *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 enables us to make a fairly short table of standard reduction potentials and from this table to calculate potential differences for a large number of cells.

Exercise 9.5

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.

The convention that assigns standard reduction potentials relative to the standard hydrogen electrode is an arbitrary assignment. There have been a number of theoretical approaches to the determination of the "absolute" potential of electrodes (relative to the potential at a location infinitely distant from all charges). All of them require assumptions and the use of nonthermodynamic theories. One work cites a value of

−4.43V (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. Table A.13 in the Appendix gives values for standard reduction potentials (in the molality description) for a number of half-cells. Longer versions of such tables are available in handbooks. Unfortunately, some older works use the opposite convention from the presently accepted conventions that we use, and give values that are the negative of the reduction potentials (these are called oxidation potentials). If you are not certain whether an old table gives reduction potentials or oxidation potentials, look for an active metal like sodium or potassium. If the table gives reduction potentials, the half-cell potential of such a metal will be negative.

EXAMPLE 9.2

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

$$\begin{aligned}\text{Anode:}\quad & 2\mathrm{Cl^-} \rightarrow \mathrm{Cl_2(g)} + 2e^- \\ \text{Cathode:}\quad & \mathrm{Fe^{2+}} + 2e^- \rightarrow \mathrm{Fe(s)}\end{aligned}$$

The cell reaction equation is (omitting the electrons)

$$2\mathrm{Cl^-} + \mathrm{Fe^{2+}} \rightarrow \mathrm{Cl_2(g)} + \mathrm{Fe(s)}$$

The standard-state potential difference of the cell is

$$E^\circ = -0.409\ \mathrm{V} - (+1.3583\ \mathrm{V}) = -1.767\ \mathrm{V}$$

This negative sign means that the standard-state cell reaction would spontaneously proceed in the reverse direction. A positive value of E corresponds to a reaction that is spontaneous as written.

Cells with Liquid Junctions

Some pairs of half-cells cannot be combined into a cell with a single liquid solution. A single solution in contact with both electrodes cannot contain all of the ionic species without undesired chemical reactions. Either a precipate would form or else one of the dissolved species would react directly with an electrode or another dissolved species. Such a cell must contain two different electrolyte solutions with a liquid junction between them. Consider the cell with the half-reactions

$$\begin{aligned}&\mathrm{Zn(s)} \rightarrow \mathrm{Zn^{2+}} + 2e^- \\ &\mathrm{Cu^{2+}} + 2e^- \rightarrow \mathrm{Cu(s)}\end{aligned}$$

If the $\mathrm{Cu^{2+}}$ ion were contained in the solution that contacts the zinc electrode, the oxidation and reduction half-reactions would take place at the interface between the zinc electrode and the solution, without transferring electrons through an external circuit. A galvanic cell with two compartments can be constructed to use these half-

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[2] H. Reiss and A. Heller, *J. Phys. Chem.*, **89**, 4207 (1985).

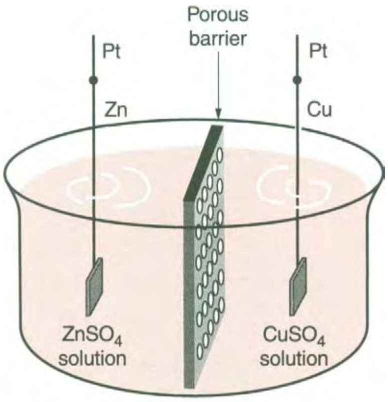

Figure 9.6. The Daniell Cell. This cell is not a reversible cell, because it contains a liquid junction between two different electrolyte solutions.

reactions as shown in Figure 9.6. This cell is known as the *Daniell cell*, and these cells were once used to power telephones and railroad signals. 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 barrier between the compartments is porous and 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.

Some Daniell cells were constructed without a porous barrier. A concentrated $CuSO_4$ solution was placed in the bottom of the cell container and a less dense dilute $ZnSO_4$ solution was layered above it. When the cell was not in use a small current was allowed to flow so that Cu^{2+} ions were moving downward toward the copper electrode in the bottom of the container. This motion overcame the tendency of the Cu^{2+} ions to diffuse upward, and the solutions did not mix appreciably.

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 of any phase boundary. The presence of the liquid junction makes it impossible to have a persistent metastable state of the cell, because ions can diffuse through the liquid junction even if the cell is on open circuit or has a counter e.m.f. to stop the flow of current. A cell with a liquid junction is not a reversible cell because reversing the current does not reverse these diffusion processes. The irreversible processes make a contribution to the potential difference of the cell, called the **liquid junction potential**.

EXAMPLE 9.3

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. Canceling the electrons, the cell reaction equation is

$$\mathrm{Zn(s)} + \mathrm{Cu}^{2+} \rightarrow \mathrm{Zn}^{2+} + \mathrm{Cu(s)}$$

and the cell symbol is

$$\mathrm{Zn(s)}|\mathrm{Zn}^{2+}|\mathrm{Cu}^{2+}|\mathrm{Cu(s)}$$

We have omitted the symbols for the platinum terminals.

b. 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 if the terminals were connected by a short circuit.

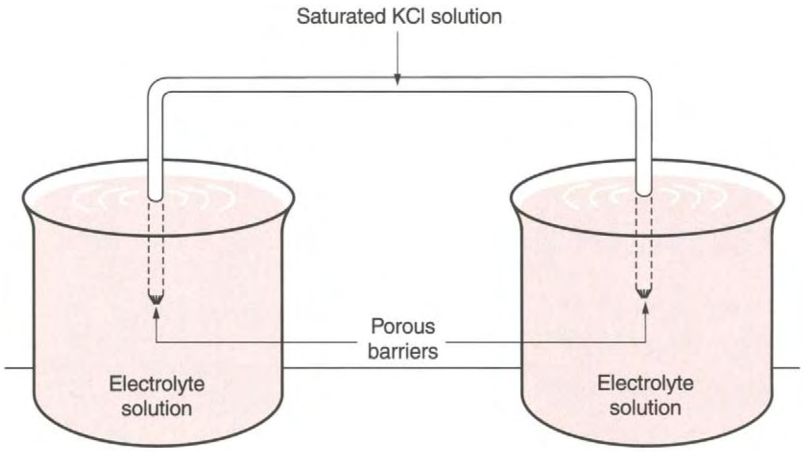

Figure 9.7. A Salt Bridge. This device is designed to minimize the liquid junction potential between two electrolyte solutions by creating two liquid junctions whose liquid junction potentials nearly cancel.

*Exercise 9.6

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 the liquid junction is not an equilibrium or metastable system, it cannot be studied thermodynamically. However, nonthermodynamic analyses have been carried out.[3] The resulting equations contain activity coefficients and transference numbers, whose values are usually not accurately known. The **transference number** of an ion is the fraction of the current that is carried by that type of ions. Those ions with the largest concentrations generally have the largest transference numbers, and can dominate in determining the liquid junction potential. A common procedure for minimizing the liquid junction potential is the use of a **salt bridge**, as shown schematically in Figure 9.7. The salt bridge contains a third electrolyte that forms a liquid junction with each cell solution. This electrolyte solution is usually very concentrated and dominates the liquid junction potential. The most common choice is saturated KCl, chosen because the potassium ions and chloride ions have nearly equal transference numbers at equal concentrations. The KCl is often suspended in an agar gel for ease of handling. For solutions that are incompatible with chloride ions, such as solutions containing silver or lead ions, ammonium nitrate can be used.

In a cell symbol, a salt bridge is represented by a double vertical line. 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. For a saturated KCl salt bridge, the transference numbers of the potassium and chloride ions are far larger than those of the ions in the cell solutions because of the large concentrations of the potassium and chloride ions. Two ions of opposite charge make opposing contributions

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[3] J. G. Kirkwood and I. Oppenheim, *Chemical Thermodynamics*, McGraw-Hill, New York, 1961, pp. 211ff.

to the liquid junction potential when diffusing in the same direction, and if their transference numbers are equal, their contributions cancel. The liquid junction potentials at the two ends of the salt bridge are of opposite signs, are fairly small, and nearly cancel. Calculations indicate that 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 30 or 40 mV.

Concentration Cells

Figure 9.8 schematically depicts a **concentration cell**, which contains two solutions of the same electrolyte with different concentrations. The cell symbol of the cell of Figure 9.8 can be written

$$\text{Pt(s)}|\text{H}_2(\text{g}, P_1)|\text{HCl}(m_1)||\text{HCl}(m_2)|\text{H}_2(\text{g}, P_2)|\text{Pt(s)}$$

where P_1 and P_2 represent two pressures of the hydrogen gas and m_1 and m_2 represent two different molalities of the HCl solutions. If the hydrogen is at the same pressure in both sides of the cell, the cell reaction for this concentration cell is

$$\text{HCl}(m_2) \rightarrow \text{HCl}(m_1) \tag{9.3-6}$$

The standard states for the half-cells are the same, so E° vanishes for any concentration cell. The Nernst equation for our concentration cell is, assuming zero liquid junction potential,

$$E = -\frac{RT}{F}\ln\left(\frac{a_1(\text{HCl})}{a_2(\text{HCl})}\right) = -\frac{RT}{F}\ln\left(\frac{[\gamma_{\pm 1}m_1/m^\circ]^2}{[\gamma_{\pm 2}m_2/m^\circ]^2}\right) = -\frac{2RT}{F}\ln\left(\frac{[\gamma_{\pm 1}m_1/m^\circ]}{[\gamma_{\pm 2}m_2/m^\circ]}\right) \tag{9.3-7}$$

where the extra subscript on $\gamma_\pm$ indicates the cell in 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.

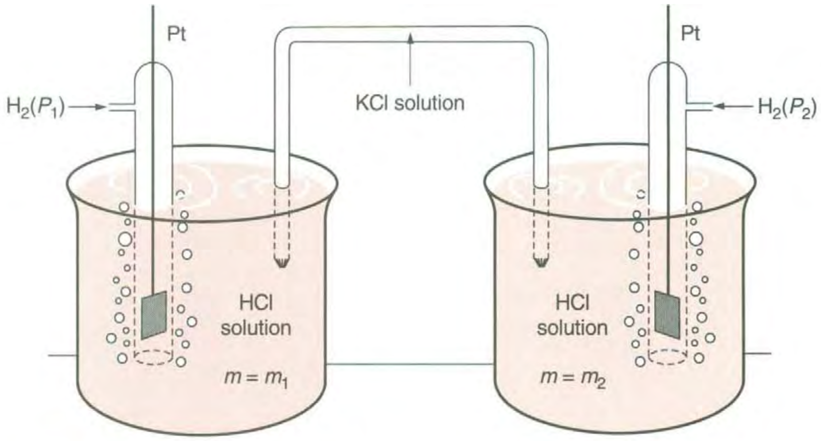

Figure 9.8. A Concentration Cell. This cell contains two parts that are identical except for the concentrations of the electrolyte solutions.

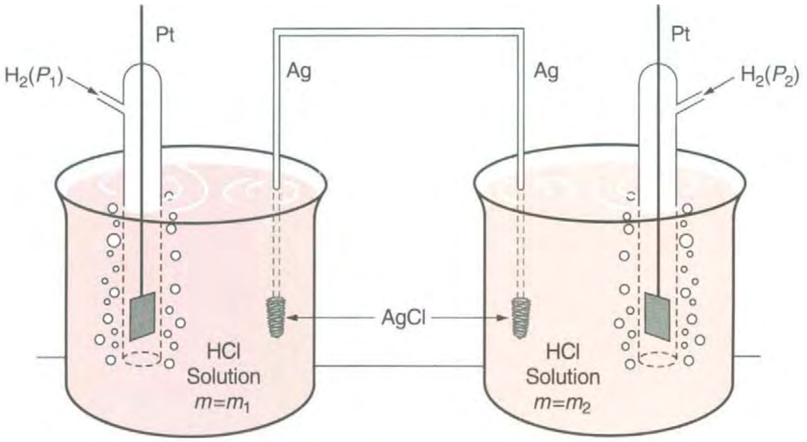

Figure 9.9. A Double Cell Equivalent to a Concentration Cell. This cell is used to replace the concentration cell with a cell having no liquid junctions.

In order to eliminate the liquid junction potential, the cell of Figure 9.8 can be replaced by the double cell of Figure 9.9, which is a reversible cell. Assuming that the pressure of hydrogen is equal to P° in both cells, the Nernst equation for the left-hand cell is

$$E(\text{left cell}) = 0.2223\ \text{V} - \frac{2RT}{F}\ \ln(\gamma_{\pm 1} m_1/m^\circ)$$

and that of the right-hand cell is

$$E(\text{right cell}) = -0.2223\ \text{V} + \frac{2RT}{F}\ \ln(\gamma_{\pm 2} m_2/m^\circ)$$

so that the potential difference of the double cell is equal to that of Eq. (9.3-7) 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 a given molality, and once when filled with a solution of another molality.

***Exercise 9.7**

Find the potential difference of the concentration cell of Figure 9.8 if in solution 1 the molality is 0.500 mol kg^{-1} with mean ionic activity coefficient equal to 0.757, and in solution 2 the molality is 0.200 mol kg^{-1} with mean ionic activity coefficient equal to 0.767.

9.4 The Determination of Activity Coefficients of Electrolytes

In the case of a volatile electrolyte such as HCl or HNO_3, the mean ionic activity coefficient can be determined for large concentrations from the partial vapor pressure, using Eq. (8.4-11).

EXAMPLE 9.4

Using information in Example 8.7, find the value of $\gamma_{\pm}$ for HCl at 10.00 mol kg^{-1} and 298.15 K, in which state the partial vapor pressure is equal to 4.20 torr.[4]

Solution

$$\gamma_{\pm}^2 = \frac{P_{\mathrm{HCl}}}{k_{\pm}^{(m)} m^2} = \frac{4.20\ (\mathrm{torr})\left(\dfrac{1\ \mathrm{atm}}{760\ \mathrm{torr}}\right)}{(4.92 \times 10^{-7}\ \mathrm{atm\ kg^2\ mol^{-2}})(10.00\ \mathrm{mol\ kg^{-1}})^2} = 112$$

$$\gamma_{\pm} = 10.6$$

Since most electrolyte solutes are not volatile, their activities cannot be determined from their vapor pressures. There are two common ways to determine these activities and activity coefficients: by electrochemical measurements and by measurement of solvent vapor pressure followed by integration of the Gibbs–Duhem equation.

Activity Coefficients of Electrolyte Solutes from Electrochemical Measurements

Consider the cell of Figure 9.2, for which the Nernst equation is

$$E = E^{\circ} - \frac{RT}{2F} \ln\left(\frac{a(\mathrm{HCl})^2}{P(\mathrm{H_2})/P^{\circ}}\right) \tag{9.4-1}$$

where $E^{\circ} = 0.2223$ V. The value of E° can be determined by use of Eq. (9.2-20) or Eq. (9.2-21) or some equivalent procedure, and the activity coefficients of HCl can then be determined from the Nernst equation. Let us maintain the pressure of hydrogen gas at P° and measure the voltage at a molality of HCl equal to m:

$$\ln[a(\mathrm{HCl})] = 2\ \ln\left(\frac{\gamma_{\pm} m}{m^{\circ}}\right) = \frac{F(E^{\circ} - E)}{RT} \tag{9.4-2}$$

EXAMPLE 9.5

In a cell such as that of Figure 9.2, a voltage of 0.3524 V was measured with a solution having a molality of HCl equal to 0.1000 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. (9.4-2)

$$\ln\left(\frac{\gamma_{\pm} m}{m^{\circ}}\right) = \frac{(96485\ \mathrm{C\ mol^{-1}})(0.2223\ \mathrm{V} - 0.3524\ \mathrm{V})}{2(9.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})} = -2.532$$

$$\gamma_{\pm} = \frac{e^{-2.532}}{0.1000} = 0.795$$

For comparison, the Davies equation gives $\gamma_{\pm} = 0.781$.

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[4] S. J. Bates and H. D. Kirschman, *J. Am. Chem. Soc.*, **41**, 1991 (1919).

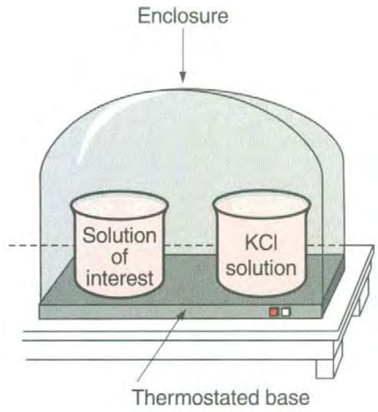

Figure 9.10. Apparatus for the Isopiestic Method of Determining Activity Coefficients. This system is allowed to equilibrate so that the chemical potential of the volatile solvent has the same value in both solutions. The activity coefficient of the solute is determined by a Gibbs–Duhem integration.

The Gibbs–Duhen Integration

For a two-component solution with a volatile solvent and a nonvolatile solute, values of the vapor pressure of the solvent can be used to obtain values of the activity coefficient of the solvent. If this is done for several values of the solvent mole fraction between unity and the composition of interest, integration of the Gibbs–Duhem relation can give the value of the activity coefficient of the solute. The vapor pressure of the solvent is usually determined using the **isopiestic method**. In this procedure, the solution of interest and a solution of a well-studied nonvolatile reference solute are placed in the same closed container at a fixed temperature, as schematically shown in Figure 9.10. For aqueous solutions, KCl is usually used as the reference solute, since accurate water activity coefficients data are available for KCl solutions. The solutions are left undisturbed at constant temperature until enough solvent has evaporated from one solution and condensed in the other solution to equilibrate the solvent in the two solutions. The solutions are then analyzed to determine the mole fractions of the solvent in both solutions. The activity of the solvent in the reference solution is then calculated from tables of values for the solvent in the reference solution, and equated to the activity of the solvent in the experimental solution.

At equilibrium, the activity of solvent (substance 1) in the solution of interest (phase II) is equal to the activity of solvent in the reference solution (phase I). Therefore

$$\gamma_{1(\mathrm{II})} = \frac{a_{1(\mathrm{I})}}{x_{1(\mathrm{II})}} = \frac{\gamma_{1(\mathrm{I})}x_{1(\mathrm{I})}}{x_{1(\mathrm{II})}} \tag{9.4-3}$$

The activity of the solvent is often expressed in terms of the **osmotic coefficient** ϕ, defined by

$$\phi = -\frac{\ln(a_1)}{M_1 \nu m_2} = \frac{\mu_1^\circ - \mu_1}{RTM_1 \nu m_2} \quad \text{(definition)} \tag{9.4-4}$$

where a_1 is the activity of the solvent, M_1 is the molar mass of the solvent, $\nu = \nu_+ + \nu_-$ for the solute, and m_2 is the stoichiometric molality of the solute (the molality that would occur if no dissociation occurred). If the solute dissociates completely, νm_2 is equal to the sum of the molalities of the ions. From Eq. (9.4-4),

$$\mu_1 = \mu_1^\circ - RTM_1 \nu m_2 \phi \tag{9.4-5}$$

The chemical potential of the solute can be written

$$\mu_2 = \mu_2^\circ + \nu RT \ \ln(\nu_\pm \gamma_2 m_2/m^\circ) \tag{9.4-6}$$

where we write γ_2 for $\gamma_\pm$.

For constant pressure and temperature, the Gibbs–Duhem relation for a two-component system is given by Eq. (5.6-11),

$$n_1\, d\mu_1 + n_2\, d\mu_2 = 0 \tag{9.4-7}$$

Since the molality m_2 is equal to the amount of substance 2 divided by the mass of substance 1,

$$n_2 = m_2 n_1 M_1 \tag{9.4-8}$$

where M_1 is the molar mass of substance 1. Use of Equations (9.4-5), (9.4-6), and (9.4-8) in Eq. (9.4-7) gives

$$-n_1 \nu RTM_1[m_2\, d\phi + \phi\, dm_2] + m_2 n_1 M_1 \nu RT[d\ln(\gamma_2) + d\ln(m_2)] = 0$$

Cancellation of the common factor and use of the identity

$$d\ \ln(m) = (1/m)\ dm$$

gives

$$-m_2\ d\phi - \phi\ dm_2 + m_2\, d\ln(\gamma_2) + dm_2 = 0 \tag{9.4-9}$$

which is the same as

$$d\ln(\gamma_2) = d\phi + \frac{\phi - 1}{m_2}\ dm_2 \tag{9.4-10}$$

Equation (9.4-10) can be integrated from $m_2 = 0$ to $m_2 = m_2'$, a particular value of m_2:

$$\int_{m_2=0}^{m_2=m_2'} d\ \ln(\gamma_2) = \int_{m_2=0}^{m_2=m_2'} d\phi + \int_0^{m_2'} \frac{\phi - 1}{m_2}\ dm_2 \tag{9.4-11}$$

The integral on the left-hand side 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

$$\ln(\gamma(m_2')) = \phi(m_2') - 1 + \int_0^{m_2'} \frac{\phi - 1}{m_2}\ dm_2 \tag{9.4-12}$$

If values of ϕ are measured over the range of molalities between 0 and m_2', numerical integration of this equation gives the value of γ_2 at m_2'.

Exercise 9.8

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.

Determination of pH

Since the activity of a single ion cannot be measured, we cannot correctly use the definition of the pH given in Eq. (8.5-1). Instead we define the pH by

$$\text{pH} = -\log_{10}[a'(\text{H}^+)] \tag{9.4-13}$$

where $a'(\text{H}^+)$ is the closest approximation to the activity of hydrogen ions that can be obtained. In Example 9.5, Eq. (9.4-2) was used to calculate the activity of HCl in a cell containing HCl in solution. We can write

$$a(\text{H}^+)a(\text{Cl}^-) = a(\text{HCl}) \tag{9.4-14}$$

If we can assume that $a(\text{H}^+)$ is approximately equal to $a(\text{Cl}^-)$, then we have a value of $a(\text{H}^+)$, and thus of the pH for this cell.

Exercise 9.9

Find the pH of the solution in the cell of Example 9.5, using the assumption stated above.

In order to measure the pH conveniently, it is customary to modify the cell of Figure 9.2 as shown in Figure 9.11. The calomel electrode is fitted with a porous plug in which

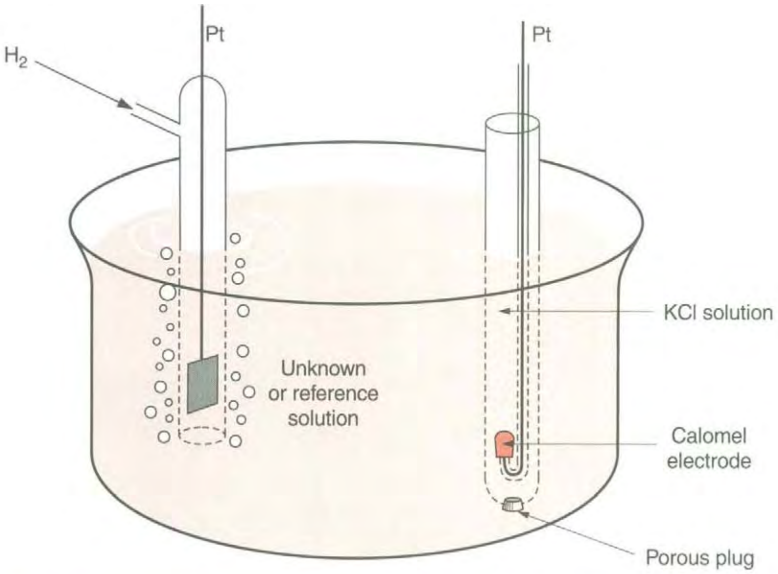

Figure 9.11. A Cell for the Measurement of pH. The potential of this cell is a well-defined function of the pH of the solution except for the liquid junction potential.

a liquid junction is formed. The solution in the container of the calomel electrode is a KCl solution that is saturated with calomel. If the concentration of the KCl is 1.000 mol L^{-1}, the electrode is called the **normal calomel electrode**. If the solution is saturated in KCl as well as in calomel, the electrode is called the **saturated calomel electrode**. The half-cell potential of the normal calomel electrode is 0.2802 V, and that of the saturated calomel electrode is 0.2415 V. We place the calomel electrode and the hydrogen electrode in the solution whose pH we wish to measure, as shown in the figure. The solution does not have to be a solution of HCl, since the chloride ions needed to react at the calomel electrode are in the solution of the calomel electrode.

The Nernst equation for the cell of Figure 9.11 is

$$E = 0.2415\ \mathrm{V} + E_{\mathrm{LJ}} - \frac{RT}{F}\ln\left(\frac{a(\mathrm{H}^+)a(\mathrm{Cl}^-)}{(P(\mathrm{H}_2)/P^\circ)^{1/2}}\right) \tag{9.4-15}$$

where $a(\mathrm{H}^+)$ is measured in one solution and $a(\mathrm{Cl}^-)$ is measured in the other solution. Since the KCl solution on the calomel electrode side of the liquid junction is presumably much more concentrated than the solution on the other side, the magnitude of the liquid junction potential should be fairly small, and should not change much when a different solution is placed in the cell.

The activity of the chloride ion is not known accurately, since it is a single-ion activity, and we cannot assume that the H^+ ions and the Cl^- ions have equal activity coefficients, so we do not try to use Eq. (9.4-15) directly. 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

$$E^{(\mathrm{II})} - E^{(\mathrm{I})} = -\frac{RT}{F}\ln[a(\mathrm{H}^+, \mathrm{II})] + \frac{RT}{F}\ln[a(\mathrm{H}^+, \mathrm{I})] \tag{9.4-16}$$

where $E^{(\mathrm{I})}$ and $E^{(\mathrm{II})}$ are the two voltages measured. Equation (9.4-16) is the same as

$$\mathrm{pH}^{(\mathrm{II})} - \mathrm{pH}^{(\mathrm{I})} = \frac{E}{RT\ \ln(10)}[E^{(\mathrm{II})} - E^{(\mathrm{I})}] \tag{9.4-17}$$

We can regard Eq. (9.4-17) as an operational definition of pH, equivalent to Eq. (9.4-13). The pH of solution I must be known in advance.

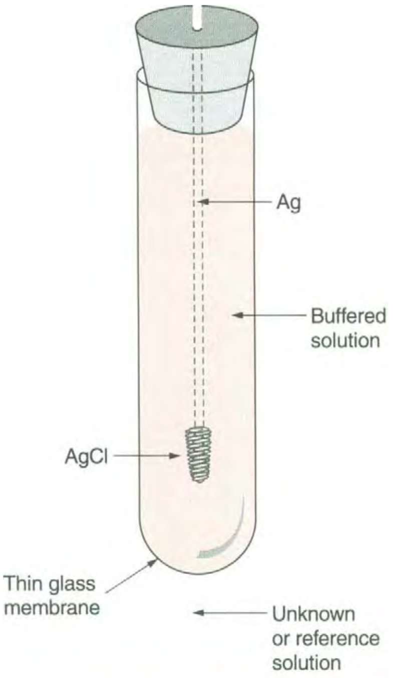

Figure 9.12. A Glass Electrode (Schematic). This electrode is used to replace a hydrogen electrode in a pH measuring device.

Exercise 9.10

Show that Eq. (9.4-17) is correct.

The **glass electrode** has come into common use to replace the hydrogen electrode, which can be dangerous. This electrode is schematically depicted in Figure 9.12. 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 immersed in the solution. The special glass of which the bulb is made allows hydrogen ions to establish an equilibrium across the membrane. Since the chemical part of the chemical potential is not the same on the two sides of the membrane, there is an electrical potential difference across the glass membrane.

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 9.11, so that Eq. (9.4-17) can be used if a reference solution is available. pH meters are found in almost every chemistry laboratory, and consist of the pair of electrodes described above, a voltage-measuring device, an analog or digital display, and a circuit that gives the pH directly without requiring the operator to substitute numbers into Eq. (9.4-17). Since the temperature occurs in Eq. (9.4-17), most pH meters have a control knob with which one can set the temperature.

The first commonly available pH meter was made possible in the late 1930s when Arnold Beckman, a chemistry professor at the California Institute of Technology, invented an amplifier that allowed the voltage-measuring device to read the cell voltage. Professor Beckman left Caltech and founded a company that sold the pH meters and the famous Beckman DU spectrophotometer, which used the same amplifier.

*Exercise 9.11

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.

9.5 Thermodynamic Information from Electrochemistry

Thermodynamic information about many chemical reactions that occur outside of electrochemical cells can be obtained from electrochemical measurements. For a general reaction written in the form of Eq. (9.2-17), the analogue of Eq. (9.2-7) is

$$-nFE = \left(\frac{\partial G_{\text{chem}}}{\partial \xi}\right)_{T,P} \tag{9.5-1}$$

where n is the number of electrons in the cell reaction equation. For the standard-state reaction,

$$-nFE^\circ = \Delta G^\circ_{\text{chem}} \tag{9.5-2}$$

The Gibbs energy change in this equation is for the reaction outside of the cell. The equilibrium constant for the reaction can be calculated using the relations shown in Eq. (8.1-20) and Eq. (9.5-2):

$$K = Q_{\text{eq}} = e^{-\Delta G^\circ_{\text{chem}}/RT} = e^{nFE^\circ/RT} \tag{9.5-3}$$

EXAMPLE 9.6

a. Find the value of K for the reaction of Eq. (9.2-4) at 298.15 K.

b. Find the equilibrium value of the hydrogen pressure when the molality of HCl is equal to 0.500 mol kg^{-1} and its mean ionic activity coefficient is equal to 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.

$$3.28 \times 10^7 = \frac{\gamma_\pm^4 m_{\text{eq}}^4/m^{\circ 4}}{P_{\text{eq}}(\text{H}_2)/P^\circ}$$

$$P(\text{H}_2)_{\text{eq}} = P^\circ\left(\frac{[(0.757)^4(0.500)^4}{3.28 \times 10^7}\right) = (6.26 \times 10^{-10})P^\circ$$

$$= 6.26 \times 10^{-10}\ \text{bar} = 4.69 \times 10^{-7}\ \text{torr}$$

*Exercise 9.12

Find the value of the equilibrium constant for the reaction of Exercise 9.2 at 298.15 K.

From Eq. (7.6-3), we can write an expression for the entropy change of a reaction outside of an electrochemical cell (we now omit the subscript "chem"):

$$\left(\frac{\partial S}{\partial \xi}\right)_{T,P} = -\left(\frac{\partial}{\partial T}\left(\frac{\partial G}{\partial \xi}\right)_{T,P}\right)_P = nF\left(\frac{\partial E}{\partial T}\right)_P \tag{9.5-4}$$

For the standard-state reaction, this equation becomes

$$\Delta S^{\circ} = -\left(\frac{\partial\, \Delta G^{\circ}}{\partial T}\right)_P = nF\left(\frac{\partial E^{\circ}}{\partial T}\right)_P \tag{9.5-5}$$

The enthalpy change of a reaction is given by

$$\left(\frac{\partial H}{\partial \xi}\right)_{T,P} = \left(\frac{\partial G}{\partial \xi}\right)_{T,P} + T\left(\frac{\partial S}{\partial \xi}\right)_{T,P} = -nFE + nFT\left(\frac{\partial E}{\partial T}\right)_P \tag{9.5-6}$$

For the standard-state reaction,

$$\Delta H^{\circ} = -nFE^{\circ} + nFT\left(\frac{\partial E^{\circ}}{\partial T}\right)_P \tag{9.5-7}$$

From Eq. (8.6-13), in the case that ΔH° can be assumed to be temperature-independent,

$$\frac{E^{\circ}(T_2)}{T_2} - \frac{E^{\circ}(T_1)}{T_1} = -\frac{\Delta H^{\circ}}{nF}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \tag{9.5-8}$$

EXAMPLE 9.7

Assuming that ΔH° is constant, find E° at 323.15 K for the Daniell cell. Neglect the liquid junction potential.

Solution

We have already found that $E^{\circ} = 1.100$ V at 298.15 K. We find from enthalpy changes of formation in Table A.8 of Appendix A that $\Delta H^{\circ} = -218.66\ \text{kJ mol}^{-1}$. From Eq. (9.5-8),

$$\begin{aligned}\frac{E^{\circ}(323.15\ \text{K})}{323.15\ \text{K}} &= \frac{1.100\ \text{V}}{298.15\ \text{K}} - \frac{-218660\ \text{J mol}^{-1}}{(2)(96485\ \text{C mol}^{-1})}\left[\frac{1}{323.15\ \text{K}} - \frac{1}{298.15\ \text{K}}\right]\\ &= 3.689 \times 10^{-3}\ \text{V K}^{-1} - 2.94 \times 10^{-4}\ \text{V K}^{-1}\\ &= 3.395 \times 10^{-3}\ \text{V K}^{-1}\end{aligned}$$

$$E(323.15\ \text{K}) = (3.395 \times 10^{-3}\ \text{V K}^{-1})(323.15\ \text{K}) = 1.097\ \text{V}$$

A chemical reaction does not have to be an oxidation–reduction reaction for us to apply Eqs. (9.5-2), (9.5-3), (9.5-5), and (9.5-8) to the reaction. It is only necessary to be able to write the reaction as the sum of an oxidation half-cell reaction and a reduction half-reaction.

EXAMPLE 9.8

Find the solubility product constant of AgI at 298.15 K from electrochemical data.

Solution

The reaction equation is

$$\text{AgI(s)} \rightarrow \text{Ag}^{+} + \text{I}^{-}$$

Even though this reaction equation is not an oxidation–reduction reaction, it can be written as the sum of the oxidation and reduction half-reaction equations:

$$\begin{array}{rl} \mathrm{AgI(s)} + e^- \rightarrow \mathrm{Ag(s)} + \mathrm{I}^- & E^\circ = -0.1519\ \mathrm{V} \\ \mathrm{Ag(s)} \rightarrow \mathrm{Ag}^+ + e^- & E^\circ = -0.7986\ \mathrm{V} \\ \hline \mathrm{AgI(s)} \rightarrow \mathrm{Ag}^+ + \mathrm{I}^- & E^\circ = -0.9505\ \mathrm{V} \end{array}$$

The solubility product constant is, from Eq. (9.5-3),

$$K_{\mathrm{sp}} = \exp\left(\frac{(1)(96485;\ \mathrm{C\ mol^{-1}})(-0.9505\ \mathrm{V})}{(9.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})}\right) = e^{-36.99} = 8.6 \times 10^{-17}$$

Summary of the Chapter

In this chapter, we have discussed the thermodynamics of electrochemical cells. An electrochemical cell can function as an electrolytic cell, in which an externally imposed voltage produces a chemical reaction, or as a galvanic cell, in which 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:

$$\mu_i = \mu_{i(\mathrm{chem})} + z_i F \varphi$$

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

$$E^\circ = E^\circ(\mathrm{right}) - E^\circ(\mathrm{left})$$

where E°(right) and E°(left) are the half-cell potentials for the two electrodes in their standard states.

Thermodynamic functions can be determined electrochemically, using the relations

$$\Delta G^\circ_{\mathrm{chem}} = -nFE^\circ$$

$$K = e^{-\Delta G^\circ_{\mathrm{chem}}/RT} = e^{nFE^\circ/RT}$$

where $\Delta G^\circ_{\mathrm{chem}}$ refers to the reaction outside of the cell.

PROBLEMS

Problems for Section 9.1

*9.13. 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 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.

9.14. Assume that the concentration of Ag^+ ions near an electrode varies from a value of zero at the electrode to a value of $0.100\ \mathrm{mol\ L^{-1}}$ at a distance of 5.0 nm from the electrode.

Estimate the electric field in this region if this concentration variation corresponds to equilibrium. Find the difference in electric potential between a location at the electrode and at a distance of 5.0 nm from the electrode.

Problems for Section 9.2

***9.15.** **a.** Find the reversible cell voltage for the cell of Figure 9.3 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 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.

9.16. **a.** Using the extrapolation of Eq. (9.2-20), find E° for the cell of Figure 9.2. The following are (contrived) data for the cell voltage at 298.15 K with $P(H_2) = P^\circ$:

m/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/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. (9.2-21), find E° for the cell of Figure 9.3.

Problems for Section 9.3

9.17. ***a.** Write the cell symbol for the cell with the half-reactions

$$Pb^{2+} + 2e^- \rightarrow Pb(s)$$
$$AgCl(s) + Cl^- \rightarrow Ag(s) + e^-$$

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 Pb^{2+} is 0.100 and that of the Cl^- is 0.200 on the molality scale. State any assumptions.

9.18. Instead of the oxidation half-reaction used in Example 9.1, use the reverse of the half-reaction

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad E^\circ = -0.8277\ \text{V}$$

to calculate the reversible cell potential. Since the OH^- ion is not in its standard state, the Nernst equation must be applied.

***9.19.** In calculating the E° value for 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

$$Fe^{3+} + 3e^- \rightarrow Fe(s)$$

from the E° values of the half-reactions

$$Fe^{2+} + 2e^- \rightarrow Fe(s)$$
$$Fe^{3+} + e^- \rightarrow Fe^{2+}$$

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 ΔG° values.) Comment on the consistency of the data in Table A.13. The measurement of these E° value has been very difficult.

9.20. 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 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 at about 13.5 V. Calculate the activity of sulfuric acid necessary to make the reversible voltage equal to 13.5 V.

***9.21.** 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 mol kg^{-1} and in the other solution the molality is equal to 0.100 mol kg^{-1}. Carry out the calculation once assuming that activity coefficients are equal to unity, and once using activity coefficient values from the graph of Figure 7.12.

Problems for Section 9.4

9.22. In a cell as pictured in Figure 9.2, a solution of HCl with molality 1.000 mol kg^{-1} and a hydrogen pressure of 0.0986 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.

***9.23.** From the data in Problem 9.16, find the value of the mean molar activity coefficient of HCl at 0.500 mol kg^{-1} and 298.15 K. State any assumptions.

9.24. Following are data on the activity of water in a calcium chloride solution at 25°C.[5]

$m(CaCl_2)$/mol kg^{-1}	$a(H_2O)$
0.1	0.99540
0.2	0.99073
0.3	0.98590
0.4	0.98086
0.5	0.97552
0.6	0.96998
0.7	0.96423
0.8	0.95818
0.9	0.95174
1.0	0.94504

Find the activity coefficient of calcium chloride at 1.000 mol kg^{-1}, using a Gibbs–Duhem integration.

***9.25.** 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.

Problems for Section 9.5

9.26. a. Using half-cell potentials, find the value of the equilibrium constant for the reaction at 298.15 K.

$$I_2(aq) + I^- \rightleftharpoons I_3^-$$

b. Find the final concentrations if 100. mL of a 0.00100 mol kg^{-1} solution of I_2 and 100. mL of a 0.00100 mol kg^{-1} solution of KI are mixed and allowed to equilibrate. Use the Davies equation to estimate activity coefficients.

9.27. a. Using half-cell potentials, find the value of the equilibrium constant for the reaction at 298.15 K.

$$Hg_2Cl_2(s) + 2Ag^+ \rightleftharpoons Hg_2^{2+} + 2AgCl(s)$$

b. Calculate ΔG° 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.

9.28. a. Using electrochemical data, find the formation constant of 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 ΔG° for the reaction.

c. If 0.200 mol of $AuCl_4^-$ is placed in 1.000 kg of water, find the equilibrium concentration of Cl^- ions.

***9.29.** Find the solubility product constants for

a. Hg_2Cl_2

b. Ag_2S

9.30. Find the solubility product constants for

a. $PbSO_4$

b. AgBr

***9.31. 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 that is formed is maintained at pressure P° and use the Davies equation to estimate activity coefficients.

9.32. Find the equilibrium constant at 298.15 K for the reaction

$$I_2(s) + 2Cl^- \rightleftharpoons 2I^- + Cl_2(g)$$

***9.33.** Find the equilibrium constant at 298.15 K for the reaction

$$AgCl(s) + Br^- \rightleftharpoons AgBr(s) + Cl^-$$

9.34. 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 2.00 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. (4.1-22), 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.

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[5] Robinson and Stokes, *Electrolyte Solutions*, 2nd ed., Butterworths, 1959, p. 478.

General Problems

*9.35. 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 minimizes 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.

9.36. Fuel cells have been used in space vehicles to provide electrical energy. A fuel cell is a galvanic cell into which reactants are brought continuously, so that no recharging 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 a 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 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}.

*9.37. A fuel cell with an acidic electrolyte using methane as a fuel has the anode half-reaction equation:

$$CH_4(g) + 2H_2O(l) \rightarrow CO_2(g) + 8H^+ + 8e^-$$

a. Write the cathode half-reaction equation and the cell reaction equation for the methane fuel cell. Calculate ΔG° 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?

10

Gas Kinetic Theory. The Molecular Theory of Dilute Gases at Equilibrium

OBJECTIVES

After studying this chapter, a student should:

1. understand the process of averaging with a probability distribution;
2. understand how a model system is used to represent a dilute gas;
3. be able to solve problems involving the use of the ideal gas velocity and speed probability distributions;
4. be able to solve problems involving wall collision rates, gas pressure, and effusion;
5. understand how intermolecular forces lead to gas nonideality;
6. be able to solve problems involving rates of collisions between hard-sphere molecules.

PRINCIPAL FACTS AND IDEAS

1. The first model system that represents a dilute gas is a system of noninteracting molecules without internal structure.
2. The first part of the kinetic theory of gases is the mathematical analysis of the behavior of this model system, and includes averages over microscopic states of the molecules of the system, using probability distributions.
3. The probability distribution for molecular velocities is the Maxwell–Boltzmann probability distribution:
$$\text{(Probability of a state of velocity } \mathbf{v}) \propto e^{-mv^2/2k_{\mathrm{B}}T}$$
4. The probability distribution for molecular speeds is
$$\text{(Probability of a speed } \mathbf{v}) \propto v^2 e^{-mv^2/2k_{\mathrm{B}}T}$$
5. Gas kinetic theory of noninteracting molecules predicts the ideal gas equation of state.
6. Gas kinetic theory 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.

10.1 The Model System for a Dilute Gas

Chapter 1 presented the two principal types of states of systems: microscopic or mechanical states, and macroscopic or thermodynamic states. A gas is a system that consists of many rapidly moving molecules moving about in a volume considerably larger than the total volume of the molecules. In previous chapters we have applied much of thermodynamic theory to the macroscopic states of gases. In this chapter we study gas kinetic theory, which explicitly averages over molecular states of a system of particles obeying classical mechanics in order to gain information about the macroscopic behavior of the gas.

Gas kinetic theory 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. It was brought to an advanced state by Joule, Maxwell, and Boltzmann. The fundamentals were worked out independently by Waterson, about 15 years prior to the work of Joule and Maxwell. Gas kinetic theory is similar in spirit to statistical mechanics, which we study in Chapter 21. However, statistical mechanics is not restricted to the study of gases, and is not restricted to the use of classical mechancs.

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.

James Prescott Joule, 1818–1889, was a great English physicist who pioneered in the thermodynamic study of work, heat, and energy while managing 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, and who killed himself when his ideas were not widely accepted.

John James Waterston, 1811–1883, was teaching in India at the time of his work on kinetic theory, and was unable to get his work published.

Definition of the Model System

The simplest model system that represents a dilute gas is depicted in Figure 10.1. It has the following properties.

1. It consists of a large number, N, of molecules, moving about randomly in a container. For the present, we assume that all of the molecules have the same mass.
2. The motions of these molecules are governed by classical (Newtonian) mechanics.
3. The molecules are point mass particles that do not exert any forces on each other. A **point mass** is an object of vanishingly small size, so that point masses cannot collide with each other.
4. The container confining the gas is a rectangular box with smooth hard walls.

We will derive the probability distributions of molecular velocities and speeds and will show that this model obeys the ideal gas law. In a later part of the chapter we will define a slightly more realistic model system.

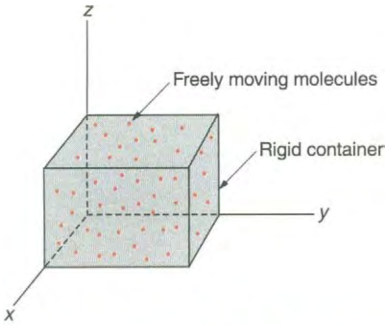


Figure 10.1. The Model System to Represent an Ideal Gas. The dots represent point mass molecules moving randomly. Only a few dots are shown, but the actual model system contains many molecules.

The Mechanical States of the Model System

According to classical mechanics, the mechanical state (microstate) of the system is specified by giving the position and velocity of every particle. Let us number the particles from 1 to N. The position of particle number i in three dimensions can be specified by its cartesian coordinates x_i, y_i, and z_i, equivalent to a **position vector** $\mathbf{r}_i$ that has its tail at the origin of the coordinate system and its head at the particle's location. The **components** of the position vector are the cartesian coordinates x_i, y_i, and z_i. The unit vectors **i**, **j**, and **k** (vectors of unit length) are defined such that **i** points in the direction of the positive x axis, **j** points in the direction of the positive y axis, and **k** points in the direction of the positive z axis. The position vector can be written in terms of the unit vectors and components:

$$\mathbf{r}_i = \mathbf{i}x_i + \mathbf{j}y_i + \mathbf{k}z_i \qquad (10.1\text{-}1)$$

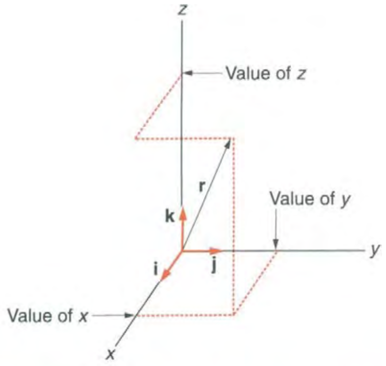


Figure 10.2. A Position Vector r in Three-Dimensional Space. The vector **r** specifies the position of the particle when its tail is at the origin. The unit vectors **i**, **j**, and **k** are also shown.

A vector is denoted by a letter in boldface type. Since it is difficult to write in boldface, you can also represent a vector by a letter with an arrow above it, as in $\vec{v}$. A vector is also denoted by its three cartesian components listed within parentheses, as in $\mathbf{r}_i = (x_i, y_i, z_i)$. Appendix B contains a brief introduction to vectors.

Figure 10.2 shows the vector **r**, the cartesian axes, the unit vectors, and the cartesian components of the vector. Each term in Eq. (10.1-1) is a product of a scalar (the component) and a unit vector. Such a product is a second vector with the same direction as the unit vector if the scalar is positive. If the scalar is negative, the product is in the opposite direction from the unit vector. The position vector equals the sum of three vectors. The sum of two vectors can be represented geometrically by moving the second vector so its tail is at the head of the first vector, and drawing the sum vector from the tail of the first to the head of the second. Figure 10.3 shows how its three components times their unit vectors add to equal the position vector $\mathbf{r}_i$.

The velocity of particle number i is specified by the **velocity vector**

$$\mathbf{v}_i = \mathbf{i}v_{ix} + \mathbf{j}v_{iy} + \mathbf{k}v_{iz} \tag{10.1-2}$$

The components of the velocity are the rates of change of x_i, y_i, and z_i:

$$v_{ix} = \frac{dx_i}{dt}, \qquad v_{iy} = \frac{dy_i}{dt}, \qquad v_{iz} = \frac{dz_i}{dt} \tag{10.1-3}$$

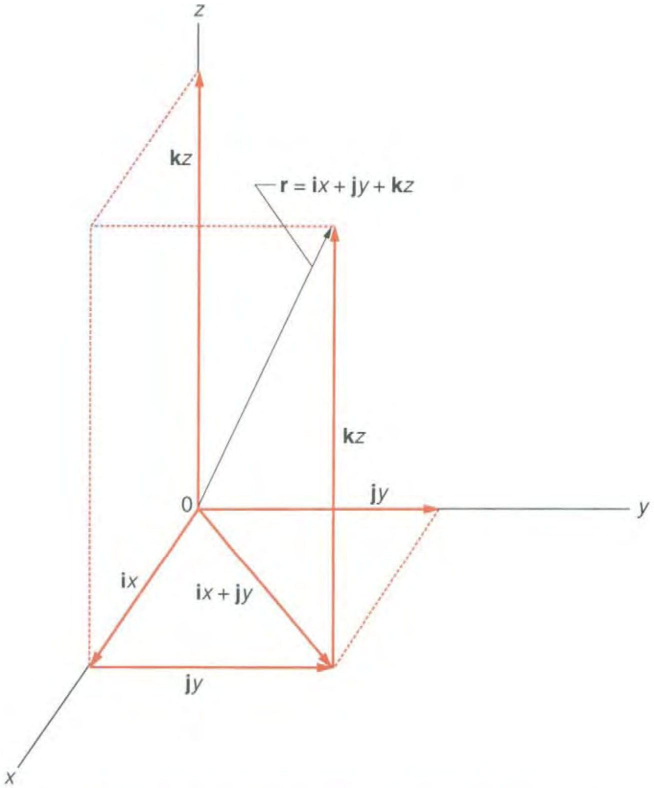


Figure 10.3. The Addition of the Components of a Position Vector. To use the geometric recipe for adding vectors: translate **j***y* so that its tail is at the head of the **i***x* vector; draw the sum vector **i***x* + **j***y* from the origin to the head of the **j***y* vector. Then translate the **k***z* vector so that its tail is at the head of the **i***x* + **j***y* vector and draw the **r** vector from the origin to the head of the translated **k***z* vector.

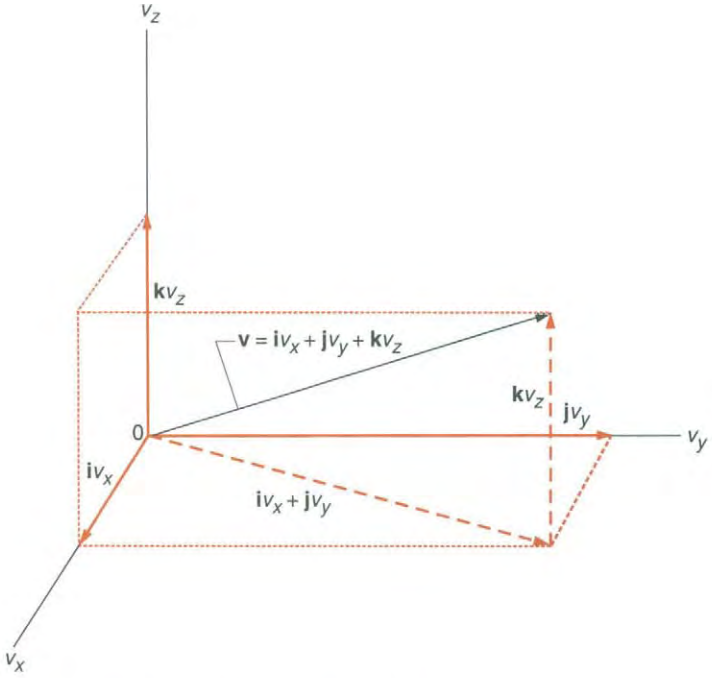


Figure 10.4. A Velocity Vector in Velocity Space. The velocity vector has a magnitude equal to the speed of the particle, and a direction that is the instantaneous direction of the motion of the particle. The space of this figure is not a physical (coordinate) space, but a graph in which distances on the axes represent velocity components. Cartesian components are shown, and these can be handled in the same way as components in ordinary space.

The velocity vector can be represented geometrically in much the same way as the position vector, as in Figure 10.4. The space of this figure is called **velocity space**. It is not a physical space, but is a graph of rates of motion. However, many of the mathematical properties of ordinary space apply to velocity and we will treat it much like ordinary space.

The direction of the velocity vector is the direction of motion of the particle and its magnitude is the **speed**:

$$|\mathbf{v}_i| = v_i = (v_{ix}^2 + v_{iy}^2 + v_{iz}^2)^{1/2} \tag{10.1-4}$$

We use either of the two notations in Eq. (10.1-4) to denote the magnitude of a vector: the boldface letter within vertical bars, and the letter in plain type. The magnitude of a vector is always nonnegative, although a vector's components can be positive, negative, or equal to zero.

Exercise 10.1

a. Use the theorem of Pythagoras to verify Eq. (10.1-4). (It must be used twice.)

***b.** Find the speed of a particle with the velocity components:

$$v_x = 400 \text{ m s}^{-1}, \qquad v_y = -600 \text{ m s}^{-1}, \qquad v_z = 750 \text{ m s}^{-1}$$

***c.** If this particle is a neon atom, find its kinetic energy.

The instantaneous microstate of the model system is specified by giving the values of three coordinates and three velocity components for each of the N particles, a total of $6N$ numbers. Note the vast difference between the amount of information in the specification of the microscopic state and the specification of the macroscopic state of our gas. Specification of the microscopic state requires approximately 3600,000,000,000,000,000,000,000 values for a system containing one mole. It is impossible to determine this many values, especially since molecules are too small to be observed directly.

Specification of the equilibrium macroscopic state requires the values of only three variables, such as T, V, and n. This vast difference in amount of information indicates that many microscopic states must correspond to the same macroscopic state. In Chapter 1 we asserted that an average of these many microscopic states corresponds to the single macroscopic state. Gas kinetic theory provides a way to carry out this average without information about the states of the individual molecules.

The Mechanical Behavior of the System—Newton's Laws of Motion

Newton's second law is the most important formula of classical mechanics:

$$\mathbf{F}_i = m_i \mathbf{a}_i = m_i \frac{d\mathbf{v}_i}{dt} = m_i \frac{d^2\mathbf{r}_i}{dt^2} \tag{10.1-5}$$

where $\mathbf{F}_i$ is the force on the ith particle, m_i is its mass, and $\mathbf{a}_i$ is its acceleration, or rate of change of its velocity. Since the velocity is a vector, $\mathbf{a}_i$ is also a vector. Equation (10.1-5) is a vector equation, so it is equivalent to three scalar equations, one of which is

$$F_{ix} = m_i\left(\frac{dv_{ix}}{dt}\right) = m_i\left(\frac{d^2x_i}{dt^2}\right) \tag{10.1-6}$$

Since the particles in our model system do not interact with each other, the only forces on them are the forces due to interactions at the walls of the container holding the gas. Away from the walls, the particles move in straight lines at constant speeds.

Mean Values over Molecular States

Just as we recognized state functions of macroscopic states, we recognize state functions of microscopic states. All mechanical properties of the system are functions of the positions and velocities of the particles, and therefore are state functions depending only on the microscopic state of the system. The mechanical energy is the sum of the kinetic and the potential energy:

$$E = \mathcal{K} + \mathcal{V} \tag{10.1-7}$$

The kinetic energy of the system, $\mathcal{K}$, is a microscopic state function that depends only on the velocities of the particles. It is given by

$$\begin{aligned}\mathcal{K} &= \mathscr{k}_1 + \mathscr{k}_2 + \mathscr{k}_3 + \cdots + \mathscr{k}_N = \frac{m}{2}(v_1^2 + v_2^2 + v_3^2 + \cdots + v_N^2)\\ &= \frac{m}{2}\sum_{i=1}^{N} v_i^2 \end{aligned} \tag{10.1-8}$$

where $\mathscr{k}_i$ represents the kinetic energy of particle number i and where we have assumed that all of the particles of our model system have the same mass.

Forces that are velocity-independent can be derived from a potential energy (see Appendix D). The potential energy, $\mathcal{V}$, is a microscopic state function that depends only on the positions of the particles:

$$\mathcal{V} = \mathcal{V}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) \tag{10.1-9}$$

For the present, we will ignore the effects of gravity, which are insignificant unless the gas is confined in a very tall container. The molecules of our system have no forces exerted on them except by the walls enclosing the system, so their potential energy is constant so long as they remain within these walls, and we can set this potential energy equal to zero inside the container. (No physical effect is ever produced by adding a constant to a potential energy.) In order to represent the confinement of the particles in the container, we assign an infinite value to the potential energy if any particle is outside of the box.

Since the potential energy is zero for possible states of the system, the energy of the system is equal to the sum of the molecular kinetic energies:

$$E = \varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \cdots + \varepsilon_N = \mathscr{k}_1 + \mathscr{k}_2 + \mathscr{k}_3 + \cdots + \mathscr{k}_N = \mathscr{K} \tag{10.1-10}$$

where we use the symbol ε_i for the energy of particle number i, which is now equal to the kinetic energy of the particle, denoted by $\mathscr{k}_i$. The **mean molecular kinetic energy** is given by the sum of the molecular kinetic energies divided by the number of molecules:

$$\langle \varepsilon \rangle = \frac{1}{N}(\varepsilon_1 + \varepsilon_2 + \varepsilon_3 + \cdots + \varepsilon_N) = \frac{\mathscr{K}}{N} = \frac{E}{N} \tag{10.1-11}$$

We now seek a means of determining this mean value without knowledge of the many individual terms making it up. If p_j is the fraction of the molecules in state j with energy equal to ε_j,

$$p_j = \frac{N_j}{N} \tag{10.1-12}$$

then we can write the mean molecular energy as in Eq. (1.5-4):

$$\langle \varepsilon \rangle = \sum_j p_j \varepsilon_j \tag{10.1-13}$$

where this sum is a sum over the possible molecular states, not over the molecules. The set of fractions $p_2, p_2, p_3, \ldots$ is a **probability distribution**, since the probability that a particular state will be observed if a molecule is chosen randomly is equal to the fraction of the molecules that are in this state. If we can obtain an expression for the p's, we can carry out the average without knowledge of the energies of the individual molecules.

10.2 The Velocity Probability Distribution

Since we describe our system with classical mechanics, averaging over molecular energies is equivalent to 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. (10.1-13).

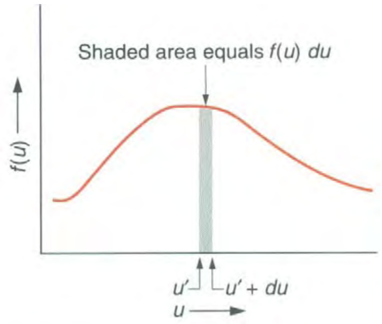


Figure 10.5. An Example Probability Density (Probability Distribution). The function $f(u)$ is defined such that the probability that the variable u lies in a range du is equal to $f(u)\,du$.

Probability Distributions for Continously Varying Quantities

Consider some continuously varying quantity u that can take on values in some range. We define a probability distribution $f(u)$ such that

$$\begin{pmatrix}\text{The probability that } u \text{ lies} \\ \text{between } u' \text{ and } u' + du\end{pmatrix} = f(u)\,du \tag{10.2-1}$$

where du is a small (infinitesimal) range of values of u. The probability distribution $f(u)$ is independent of the size of du and is a probability per unit length on the u axis, so that it is also called a **probability density**. Figure 10.5 schematically depicts a probability density. The probability of a small interval of width du is given by the product $f(u)\,du$, which is equal to the area that is shaded in the figure.

If u_1 is the smallest possible value of u and u_2 is the largest possible value, the total probability is equal to the integral

$$\text{Total probability} = \int_{u_1}^{u_2} f(u)\,du \tag{10.2-2}$$

which is equal to the area under the curve representing the probability density. In some cases $u_1 = -\infty$ and $u_2 = +\infty$. To **normalize** the probability density, we multiply the probability density by a constant so that the total probability equals unity. If the probability density is normalized, the mean value of u is given by an equation that is analogous to Eq. (1.5-4) and Eq. (10.1-13):

$$\langle u\rangle = \int_{u_1}^{u_2} uf(u)\,du \tag{10.2-3}$$

We can calculate the mean of a function of the independent variable u:

$$\langle h(u)\rangle = \int_{u_1}^{u_2} h(u)f(u)\,du \tag{10.2-4}$$

Velocity Probability Distributions

We now seek a formula that represents the probability distribution for the velocities of molecules in our model system. Such a formula will enable us to write an integral representing the mean kinetic energy of the molecules of our system, among other things. We begin with a reasonable (but unproved) assumption: *The probability density of each velocity component is independent of the other velocity components.* This assumption is sufficient to determine the mathematical form of the probability distribution. Consider the velocity of a representative particle, with components v_x, v_y, and v_z. Let $f(v_x)$ be the probability density for v_x. The probability that v_x will lie between v'_x (a particular value of v_x) and $v'_x + dv_x$ is given by

$$(\text{Probability}) = f(v'_x)\,dv_x \tag{10.2-5}$$

The probability density in the other two dimensions is similar. Now consider the joint probability in three dimensions. Let v'_x, v'_y, and v'_z be particular values of v_x, v_y, and v_z. Let the probability that v_x lies between v'_x and $v'_x + dv_x$, and that v_y is in the range between v'_y and $v'_y + dv_y$, and that v_z lies between v'_z and $v'_z + dv_z$ be given by

$$(\text{Probability}) = g(v'_x, v'_y, v'_z)\,dv_x\,dv_y\,dv_z = g(\mathbf{v}')\,d^3\mathbf{v} \tag{10.2-6}$$

where we abbreviate the product of the three differentials $dv_x\, dv_y\, dv_z$ by the symbol $d^3\mathbf{v}$ and write the dependence on the vector components as dependence on the vector $\mathbf{v}$.

The probability density $g(\mathbf{v})$ is a probability per unit volume in velocity space. That is, the probability for an infinitesimal region in velocity space is equal to the probability density evaluated for the location of the region times the volume of the infinitesimal region (a **volume element**), which is equal to $dv_x\, dv_y\, dv_z$. The probability for a finite region is the integral of the probability density over that region. Figure 10.6 shows the velocity space with a volume element, which unfortunately must be drawn with finite size.

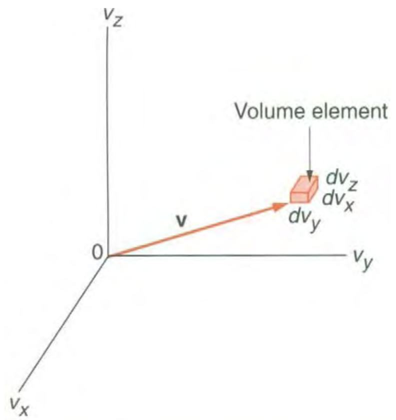


Figure 10.6. A Velocity Vector in Velocity Space, With a Cartesian Volume Element. The volume element is a rectangular box that is taken to be infinitesimal, although in the figure it must be drawn with finite size.

If the effects of gravity are negligible, there is no physical difference between any two directions. Therefore, g can depend only on the magnitude of $\mathbf{v}$ (the speed v), and not on its direciton. Furthermore, the probability distributions for v_y and v_z must be the same function as that for v_x. We have assumed that the probability densities for v_x, v_y, and v_z are independent of each other. It is a fact of probability theory that the joint probability of three independent events is the product of the probabilities of the three events. Therefore,

$$g(\mathbf{v}) = g(v) = f(v_x)f(v_y)f(v_z) \tag{10.2-7}$$

The assumptions made to obtain Eq. (10.2-7) are sufficient to determine the mathematical forms of the probability distributions f and g, as follows.

We first differentiate g with respect to v_x. By the chain rule, Eq. (B-9) of Appendix B,

$$\begin{aligned}\frac{\partial g}{\partial v_x} &= \frac{dg}{dv}\frac{\partial v}{\partial v_x} = \frac{dg}{dv}\frac{\partial}{\partial v_x}[(v_x^2+v_y^2+v_z^2)^{1/2}] \\ &= \frac{dg}{dv}\frac{1}{2}(v_x^2+v_y^2+v_z^2)^{-1/2}(2v_x) = \frac{dg}{dv}\frac{v_x}{v}\end{aligned} \tag{10.2-8}$$

We divide this equation by v_x to get

$$\frac{1}{v_x}\frac{\partial g}{\partial v_x} = \frac{1}{v}\frac{dg}{dv} \tag{10.2-9}$$

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 will be the same except for having v_y or v_z in place of v_x. The right-hand side of each equation will be the same, so that

$$\frac{1}{v_x}\frac{\partial g}{\partial v_x} = \frac{1}{v_y}\frac{\partial g}{\partial v_y} = \frac{1}{v_z}\frac{\partial g}{\partial v_z} = \frac{1}{v}\frac{dg}{dv} \tag{10.2-10}$$

We extract three ordinary differential equations for this partial differential equation by **separation of variables**. The first step in this technique is to manipulate the equation into a set of terms such that each term depends on only one variable. Since v_y and v_z are treated as constants in the v_x differentiation

$$\frac{\partial g}{\partial v_x} = f(v_y)f(v_z)\frac{df}{dv_x} \tag{10.2-11}$$

Similar equations for $(\partial g/\partial v_y)$ and $(\partial g/\partial v_z)$ can be written, so that Eq. (10.2-10) becomes

$$\frac{1}{v_x}f(v_y)f(v_z)\left(\frac{df}{dv_x}\right) = \frac{1}{v_y}f(v_x)f(v_z)\left(\frac{df}{dv_y}\right) = \frac{1}{v_z}f(v_x)f(v_y)\left(\frac{df}{dv_z}\right) \tag{10.2-12}$$

Division of this equation by $f(v_x)f(v_y)f(v_z)$ gives

$$\frac{1}{v_x f(v_x)}\left(\frac{df}{dv_x}\right) = \frac{1}{v_y f(v_y)}\left(\frac{df}{dv_y}\right) = \frac{1}{v_z f(v_z)}\left(\frac{df}{dv_z}\right) \tag{10.2-13}$$

In this equation we have separated the variables v_x, v_y, and v_z. That is, we have an equation in which each of these variables occurs in only one term. Since these variables are independent, it is possible to keep v_y and v_z constant while allowing v_x to range. Therefore, the first term must 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 of the equation equals the same constant, denoted by C. Setting the first term equal to C and multiplying by $v_x f(v_x)$, we obtain:

$$\frac{df}{dv_x} = Cv_x f(v_x) \tag{10.2-14}$$

We will use this technique of separation of variables several times in our study of quantum mechanics. The basic procedure is to manipulate the expression into a set of terms such that each depends on a single independent variable and set each term equal to a constant.

Equation (10.2-14) is an ordinary differential equation that can be solved by a second version of separation of variables. In Eq. (10.2-13) we separated three independent variables from each other. We now separate a dependent variable from an independent variable. We multiply Eq. (10.2-14) by dv_x and divide it by $f(v_x)$.

$$\frac{1}{f}\frac{df}{dv_x}\,dv_x = Cv_x\,dv_x \tag{10.2-15}$$

We recognize $(df/dv_x)\,dv_x$ as the differential of the dependent variable, df, and write

$$\frac{1}{f}\,df = Cv_x\,dv_x \tag{10.2-16}$$

The variables are separated: the left-hand side of this equation contains only f, the dependent variable, and the right-hand side contains only v_x, the independent variable. This equation can be solved by carrying out an integration. An indefinite integration of both sides of Eq. (10.2-16) gives

$$\ln(f) = \frac{Cv_x^2}{2} + A \tag{10.2-17}$$

where A is a constant of integration. We take the exponential of each side to obtain the formula for our probability distribution,

$$f(v_x) = e^A e^{Cv_x^2/2} \tag{10.2-18}$$

We will require that f is **normalized**, which means that the integral of f over all possible values of v_x is equal to unity:

$$\int_{-\infty}^{\infty} f(v_x)\,dv_x = 1 \tag{10.2-19}$$

Since we are using nonrelativistic mechanics, speeds greater then the speed of light are not excluded.

The constant C must be negative, since otherwise the integrand in Eq. (10.2-19) would grow without bound for large magnitudes of v_x, and the integral would diverge.

We let $b = -C$, so that b is positive. We eliminate the parameter A by the normalization condition:

$$1 = e^A \int_{-\infty}^{\infty} e^{-bv_x^2/2}\, dv_x = e^A \sqrt{\frac{2\pi}{b}} \tag{10.2-20}$$

where we have looked up the definite integral in Appendix C. Solving Eq. (10.2-20) for e^A, we have

$$e^A = \left(\frac{b}{2\pi}\right)^{1/2} \tag{10.2-21}$$

and Eq. (10.2-18) becomes

$$f(v_x) = \left(\frac{b}{2\pi}\right)^{1/2} e^{-bv_x^2/2} \tag{10.2-22}$$

The probability distribution for all three components is

$$\begin{aligned} g(v) &= f(v_x)f(v_y)f(v_z) = \left(\frac{b}{2\pi}\right)^{3/2} e^{-bv_x^2/2}e^{-bv_y^2/2}e^{-bv_z^2/2} \\ &= \left(\frac{b}{2\pi}\right)^{3/2} e^{-b(v_x^2+v_y^2+v_z^2)/2} \end{aligned} \tag{10.2-23}$$

The exponent in the probability distribution function is proportional to the kinetic energy of the particle, ε, so that we can also write

$$g(v) = \left(\frac{b}{2\pi}\right)^{3/2} e^{-b\varepsilon/m} \tag{10.2-24}$$

To finish our derivation, we must identify the parameter b. The total energy of a system is the sum of kinetic and potential energy. We have set the potential energy of the system equal to zero, so that the energy is all kinetic energy:

$$E = \mathcal{K} = N\langle\varepsilon\rangle = N\frac{M}{2}\langle v^2\rangle \tag{10.2-25}$$

The mean molecular kinetic energy is

$$\begin{aligned} \langle\varepsilon\rangle &= \frac{m}{2}\langle v^2\rangle = \frac{m}{2}\langle v_x^2 + v_y^2 + v_z^2\rangle \\ &= \frac{m}{2}(\langle v_x^2\rangle + \langle v_y^2\rangle + \langle v_z^2\rangle) \end{aligned} \tag{10.2-26}$$

Because the x, y, and z velocity component probability distributions are the same function, the three terms in Eq. (10.2-26) will be equal to each other after integration, and

$$\langle\varepsilon\rangle = \frac{3m}{2}\langle v_x^2\rangle = \left(\frac{3m}{2}\right)\left(\frac{b}{2\pi}\right)^{3/2} \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} v_x^2 e^{-bv_x^2/2}e^{-bv_y^2/2}e^{-bv_z^2/2}\, dv_x\, dv_y\, dv_z \tag{10.2-27}$$

where we have written g in its original factored form. We can factor the multiple integral in Eq. (10.2-27), since our limits are constants and the integrand can be factored:

$$\langle\varepsilon\rangle = \left(\frac{3m}{2}\right)\left(\frac{b}{2\pi}\right)^{3/2} \int_{-\infty}^{\infty} v_x^2 e^{bv_x^2/2}\, dv_x \int_{-\infty}^{\infty} e^{-bv_y^2/2}\, dv_y \int_{-\infty}^{\infty} e^{-bv_z^2/2}\, dv_z \tag{10.2-28}$$

The integrals over v_y and v_z in Eq. (10.2-28) are the same as in Eq. (10.2-20), so they produce factors of $(2\pi/b)^{1/2}$. The integration over v_x gives

$$\begin{aligned}\langle \varepsilon \rangle &= \left(\frac{3m}{2}\right)\left(\frac{b}{2\pi}\right)^{1/2}\int_{-\infty}^{\infty} v_x^2 e^{-bv_x^2/2}\,dv_x \\ &= \left(\frac{3m}{2}\right)\left(\frac{b}{2\pi}\right)^{1/2}(2\pi)^{1/2}b^{-3/2} = \frac{3m}{2b}\end{aligned} \tag{10.2-29}$$

where we have looked the integral up in Appendix C.

In order to complete our identification of the parameter b, we must invoke some experimental information. In Chapter 3, we asserted as an experimental fact that the thermodynamic energy of a monatomic gas is very nearly given by Eq. (3.3-6):

$$U = \frac{3}{2}nRT = \frac{3}{2}Nk_BT \tag{10.2-30}$$

where k_B is Boltzmann's constant, already introduced in Eq. (1.3-13), and equal to R/N_{Av}, the ideal gas constant divided by Avogadro's constant. We assume that we can identify the thermodynamic energy with the mechanical energy of the system:

$$U = E = N\langle \varepsilon \rangle \tag{10.2-31}$$

The mean molecular kinetic energy is now

$$\langle \varepsilon \rangle = \frac{3}{2}k_BT \tag{10.2-32}$$

Comparison of Eqs. (10.2-29) and (10.2-32) allows us to identify the parameter b:

$$b = m/k_BT \tag{10.2-33}$$

Equation (10.2-23) becomes

$$g(v) = \left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-m(v_x^2+v_y^2+v_z^2)/2k_BT} \tag{10.2-34}$$

This function is called the **Maxwell probability distribution** or the **Maxwell–Boltzmann probability distribution**. In terms of the molecular kinetic energy,

$$g(\mathbf{v}) = \left(\frac{m}{2\pi k_BT}\right)^{3/2} e^{-\varepsilon/k_BT} \tag{10.2-35}$$

which is the same as the Boltzmann probability distribution of Eq. (1.5-17) in normalized form.

The important qualitative physical facts about the Boltzmann probability distribution were presented in Chapter 1:

1. At a fixed temperature, molecular states of higher energy are less probable than states of lower energy. States with energy much larger than k_BT are quite improbable.
2. A molecular state of high energy will be more probable at a high temperature than at a low temperature. As the temperature approaches infinity, all states approach equal probability.

EXAMPLE 10.1

Find the ratio of the probabilities of the following two velocities of neon atoms at 300 K:

First velocity: $v_x = 500\ \mathrm{m\ s^{-1}}$, $v_y = -400\ \mathrm{m\ s^{-1}}$, $v_z = 250\ \mathrm{m\ s^{-1}}$
Second velocity: $v_x = 200\ \mathrm{m\ s^{-1}}$, $v_y = 350\ \mathrm{m\ s^{-1}}$, $v_z = -275\ \mathrm{m\ s^{-1}}$

Solution

Neon has several isotopes. We use the average molecular mass:

$$m = \frac{0.020183\ \mathrm{kg\ mol^{-1}}}{6.022 \times 10^{23}\ \mathrm{mol^{-1}}} = 3.35 \times 10^{-26}\ \mathrm{kg}$$

First velocity:

$$v^2 = (500\ \mathrm{m\ s^{-1}})^2 + (-400\ \mathrm{m\ s^{-1}})^2 + (250\ \mathrm{m\ s^{-1}})^2 = 472500\ \mathrm{m^2\ s^{-2}}$$

$$\frac{\varepsilon}{k_B T} = \frac{mv^2}{2k_B T} = \frac{(3.35 \times 10^{-26}\ \mathrm{kg})(472500\ \mathrm{m^2\ s^{-2}})}{(2)(1.3807 \times 10^{-23}\ \mathrm{J\ K^{-1}})(300\ \mathrm{K})} = 1.91$$

Second velocity:

$$\frac{\varepsilon}{k_B T} = 0.963 \text{ (calculation similar to first velocity)}$$

$$\text{Probability ratio} = \frac{e^{-1.91}}{e^{-0.963}} = 0.388$$

*Exercise 10.2

Find the ratio of the probabilities of the following two velocities of argon atoms at 300 K:

First velocity: $v_x = 650\ \mathrm{m\ s^{-1}}$, $v_y = 780\ \mathrm{m\ s^{-1}}$, $v_z = 990\ \mathrm{m\ s^{-1}}$
Second velocity: $v_x = 300\ \mathrm{m\ s^{-1}}$, $v_y = 290\ \mathrm{m\ s^{-1}}$, $v_z = 430\ \mathrm{m\ s^{-1}}$

The probability density for the x component of the velocity is

$$f(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mv_x^2/2k_B T} \tag{10.2-36}$$

This probability distribution is represented in Figure 10.7 for oxygen molecules at 298 K. It is an example of a **gaussian distribution**, also called a **normal distribution**. A gaussian probability distribution is sometimes called a "bell-curve" or a "bell-shaped curve" because of the shape of the graph representing it. It is represented by the formula

$$\boxed{f(u) = \frac{1}{\sqrt{2\pi}\sigma} e^{-(u-\mu)^2/2\sigma^2}} \tag{10.2-37}$$

where u stands for the independent variable, or random variable, where σ is the **standard deviation**, and where μ is the mean value of u. The independent variable u is assumed to range over all real values from $-\infty$ to $+\infty$. A graph of this probability distribution is shown in Figure 10.8a.

The standard deviation of an arbitrary probability distribution for the variable u is defined by

$$\boxed{\sigma_u = [\langle u^2 \rangle - \langle u \rangle^2]^{1/2} \quad \text{(definition)}} \tag{10.2-38}$$

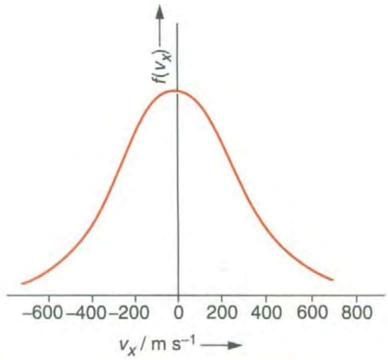
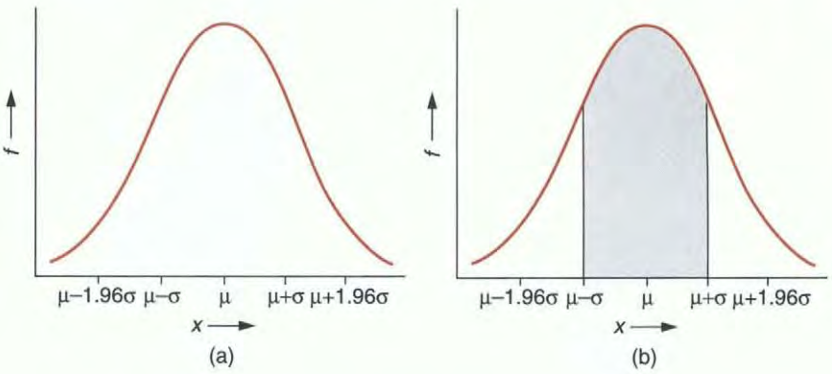


Figure 10.7. The Probability Distribution for a Velocity Component of Oxygen Molecules at 298 K. The most probable value of the velocity component is zero, and most of the molecules have values of the velocity component between $-400\ \mathrm{m\ s^{-1}}$ and $400\ \mathrm{m\ s^{-1}}$.



(a)

(b)

Figure 10.8. 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 shaded area represents this probability, given that the total area under the curve equals unity (normalization).

where u stands for the independent variable. The standard deviation is a convenient measure of the width of a probability distribution.

Exercise 10.3

Show that the definition in Eq. (10.2-38) when applied to the gaussian probability distribution leads to $\sigma_u = \sigma$.

*Exercise 10.4

a. By comparison with Eq. (10.2-37), find a formula for the standard deviation σ of the probability distribution of Eq. (10.2-36).

b. Find the value of the standard deviation for oxygen molecules at 298 K.

If $h(u)$ is a function of u, the mean value of $h(u)$ can be calculated as in Eq. (10.2-4) and the mean value of $h(u)^2$ can be calculated in a similar way. The standard deviation of h is defined as follows:

$$\sigma_h = [\langle h(u)^2\rangle - \langle h(u)\rangle^2]^{1/2} \quad \text{(definition)} \qquad (10.2\text{-}39)$$

*Exercise 10.5

a. Obtain a formula for the standard deviation of the v_x contribution to the kinetic energy.

b. Evaluate this standard deviation for oxygen molecules at 298 K.

Since the probability that a variable u has a value between u' and $u' + du$ equals $f(u')\,du$, the probability that u lies between a and b is

$$(\text{Probability that } a < u < b) = \int_a^b f(u)\,du \qquad (10.2\text{-}40)$$

Unfortunately, the gaussian probability distribution is an integrand function for which no antiderivative can be found, so that a probability integral such as in Eq. (10.2-40) for a gaussian distribution must be carried out numerically or looked up in a table of values.

In a gaussian probability distribution, 68.3% of the members of the statistical population lie within one standard deviation of the mean. This probability is represented in Figure 10.8b as a shaded area. For most ordinary distributions other than the gaussian distribution, the probability that the random variable lies within one standard deviation of the mean is approximately equal to two-thirds.

EXAMPLE 10.2

Find the probability that v_x lies between 0 and 500 m s^{-1} for neon atoms at 300 K.

Solution

$$(\text{Probability}) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} \int_0^{500} e^{-mv_x^2/2k_B T}\, dv_x$$

This is an integral that cannot be worked out in closed form. We change variables to get it into the form of the **error function**, defined in Appendix C by[1]

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-t^2}\, dt \qquad (10.2\text{-}41)$$

We let

$$t = \left(\frac{mv_x^2}{2k_B T}\right)^{1/2}; \qquad dt = \left(\frac{m}{2k_B T}\right)^{1/2} dv_x$$

At the upper limit, we have

$$t = \sqrt{\frac{(3.35 \times 10^{-26}\ \text{kg})(500\ \text{m s}^{-1})^2}{(2)(1.3807 \times 10^{-23}\ \text{J K}^{-1})(300\ K)}} = 1.0055$$

so that

$$(\text{Probability}) = \frac{1}{\sqrt{\pi}} \int_0^{1.0055} e^{-t^2}\, dt = \frac{1}{2}\operatorname{erf}(1.0055)$$
$$= 0.4225 = 42.25\%$$

where the numerical value was obtained from the table of the error function in Appendix C. If we are interested in a small finite range Δv_x, we can obtain an approximate value of the probability by replacing the infinitesimal interval dv_x in Eq. (10.2-5) by Δv_x.

$$(\text{Probability}) \approx f(v_x')\, \Delta v_x \quad (\text{for small } \Delta v_x) \qquad (10.2\text{-}42)$$

where v_x' is a value of v_x within the range Δv_x.

*Exercise 10.6

a. Find the probability that v_x for an argon atom in a system at 273.15 K is in the range 650 m s^{-1} $< v_x <$ 651 m s^{-1}. Use Eq. (10.2-42).

b. Find the probability that v_x for an argon atom in a system at 273.15 K is in the range 650 m s^{-1} $< v_x <$ 652 m s^{-1}.

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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, D.C., 1964, pp. 297ff.

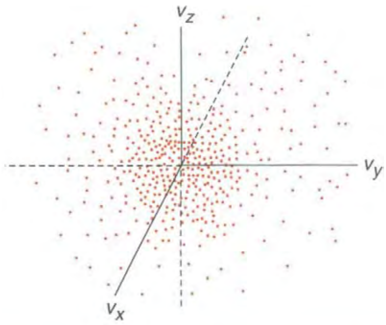

Figure 10.9. Points Representing the Velocity States of Molecules in a System. There is one point for each molecule. Instead of the several hundred points shown here, there might be Avogadro's number of points for an actual system.

***Exercise 10.7**

a. What fraction of the molecules have x-components of the velocity between $-\sigma$ and $+\sigma$?

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.

c. Repeat this calculation for 1000.0 K.

Equation (10.2-34) represents the probability density in the three-dimensional velocity space of Figure 10.4. Every point in the velocity space represents a possible velocity of a molecule. We say that there is a one-to-one correspondence between the points of the space and the possible velocity states of a molecule. If we have N molecules, we can represent their velocities by a set of N points, one for each molecule. The density (number of points per unit volume) of this swarm of points at some location, say $\mathbf{v}'$, is proportional to $g(v')$, the probability density for the velocity evaluated at that point. Figure 10.9 schematically represents the swarm of points for a system of a few hundred molecules.

10.3 The Distribution of Molecular Speeds

The speed is the magnitude of the velocity, so that it is a nonnegative quantity represented by the length of the directed line segment in Figure 10.4. All velocity vectors that have the same magnitude but differ in direction correspond to the same speed, so that the probability distribution of speeds is different from the distribution of velocities. We change to spherical polar coordinates in velocity space, analogous to the spherical polar coordinates in coordinate space usually studied in mathematics courses. One of the coordinates is the speed v. The second coordinate is θ, the angle between the positive z axis and the velocity vector. The third coordinate is ϕ, the angle between the positive x axis and line segment in the x–y plane that lies directly under the head of the position vector. These angles specify the direction of the velocity vector in velocity space and the speed v specifies its magnitude.

An infinitesimal volume element corresponding to an infinitesimal increment in each coordinate is shown crudely in Figure 10.10. The volume element is a little "box" with length in the v direction equal to dv, length in the θ direction equal to $v\,d\theta$, and length in the ϕ direction equal to $v\sin(\theta)\,d\phi$. If the increments were finite, the sides of this volume element would not all be planes and all pairs of opposite sides would not be parallel. However, an infinitesimal volume element is a rectangular parallelepiped, and the volume of this element is equal to $v^2\sin(\theta)\,dv\,d\theta\,d\phi$. We denote the volume element by the symbol

$$d^3\mathbf{v} = v^2\sin(\theta)\,dv\,d\theta\,d\phi \tag{10.3-1}$$

Using the symbol $d^3\mathbf{v}$ both for the volume element in cartesian coordinates and for the volume element in spherical polar coordinates enables us to write some equations so that they apply to either set of coordinates.

The probability that the velocity of a randomly chosen molecule lies in the volume element $v^2\sin(\theta)\,dv\,d\theta\,d\phi$ is

$$(\text{Probability}) = g(v)\,d^3\mathbf{v} = g(v)v^2\sin(\theta)\,dv\,d\theta\,d\phi \tag{10.3-2}$$

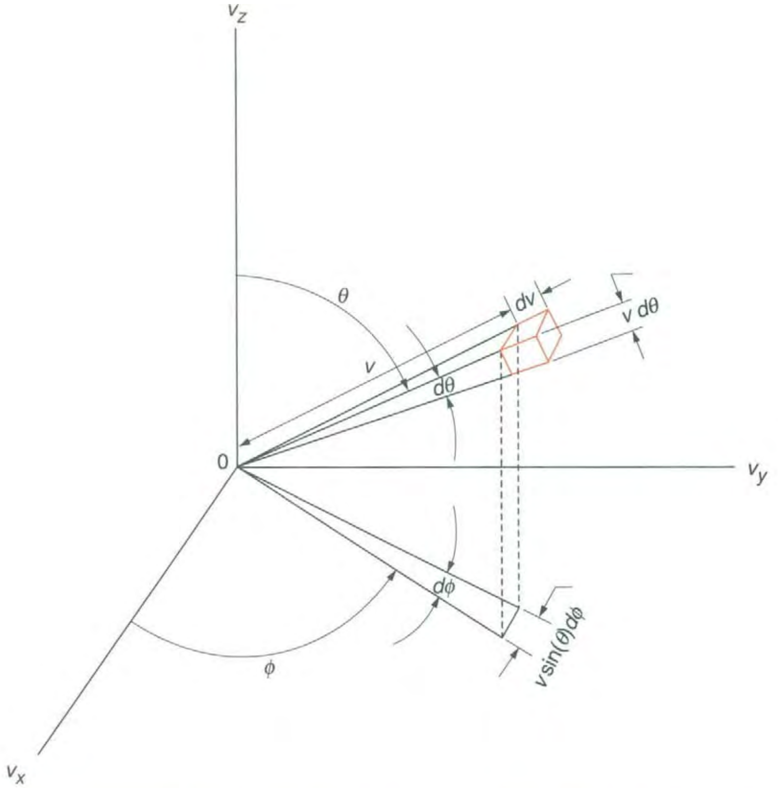

Figure 10.10. Spherical Polar Coordinates in Velocity Space, with a Volume Element. We can choose to specify the location of a point in velocity space and the size of a volume element in velocity space with cartesian coordinates or spherical polar coordinates, or any other coordinate system. The volume element can be considered to be a rectangular box, since it is infinitesimal in size.

To get the probability density for molecular speeds, we integrate (sum) this probability over all points in velocity space corresponding to speeds in an infinitesimal range dv, making up a spherical shell of thickness dv as shown in Figure 10.11. We integrate the probability shown in Eq. (10.3-2) over all values of θ and ϕ for a fixed value of v. Since $g(v)$ depends only on the speed, it factors out of the integral:

$$(\text{Probability} = g(v)v^2\,dv \int_0^{\pi} \sin(\theta)\,d\theta \int_0^{2\pi} d\phi \tag{10.3-3}$$

$$= 4\pi v^2 g(v)\,dv \tag{10.3-4}$$

The factor $4\pi v^2$ is the area of one surface of the spherical shell in Figure 10.11, and $4\pi v^2\,dv$ is the volume of the shell. The probability in Eq. (10.3-4) is therefore a probability density (probability per unit volume in velocity space) times the volume of the shell.

Exercise 10.8

Show that the integrals in Eq. (10.3-3) lead to the factor 4π in Eq. (10.3-4).

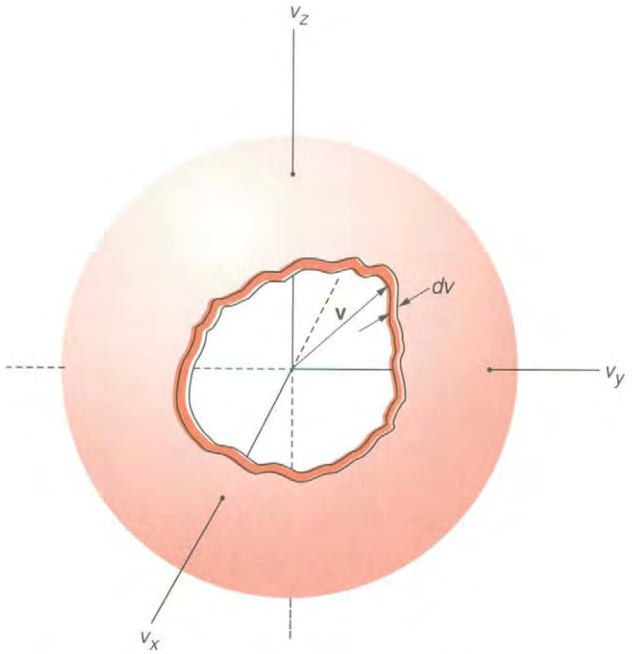

Figure 10.11. A Spherical Shell of Thickness dv in Velocity Space. This shell contains all of the points in velocity space that represent velocities with magnitudes (speeds) between v and $v + dv$.

The probability in Eq. (10.3-4) is a probability density times an infinitesimal interval dv, so the probability density f_v for molecular speeds is

$$f_v(v) = 4\pi v^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mv^2/2k_B T} \tag{10.3-5}$$

Figure 10.12 shows this probability density for oxygen molecules at 298 K. Compare this figure with Figure 10.7. The most probable value of any 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 probability density of a speed is proportional 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. The area of the spherical shell vanishes for zero speed.

A formula for the **most probable speed**, v_p, is obtained by finding the value of the speed at which the first derivative of the probability density in Eq. (10.3-5) vanishes. The result is

$$v_p = \sqrt{\frac{2k_B T}{m}} \quad \text{(most probable speed)} \tag{10.3-6}$$

The derivative also vanishes at $v = 0$ and $v = \infty$. These points correspond to minimum values of the probability.

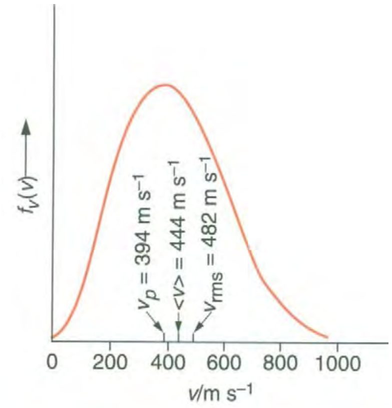

Figure 10.12. The Probability Distribution of Molecular Speeds for Oxygen Molecules at 298 K. The most probable speed, the mean speed, and the root-mean-square speed are labeled on the axis.

Exercise 10.9

a. Verify Eq. (10.3-6) by setting the derivative of f_v equal to zero and solving for v.

***b.** Find the most probable speed of oxygen molecules at 298 K.

***c.** Find the most probable speed of helium atoms at 298 K.

The **mean speed** is given by

$$\langle v\rangle = \int_0^\infty v f_v(v)\, dv = 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\int_0^\infty v^3 e^{-mv^2/2k_B T}\, dv$$

$$\langle v\rangle = \sqrt{\frac{8k_B T}{\pi m}} \tag{10.3-7a}$$

where we have looked up the integral in the table of Appendix C. The mean speed can also be written in terms of the molar mass, M, since k_B is equal to R/N_{Av}:

$$\langle v\rangle = \sqrt{\frac{8RT}{\pi M}} \tag{10.3-7b}$$

EXAMPLE 10.3

Find the mean speed of oxygen molecules at 298 K.

Solution

$$\langle v\rangle = \sqrt{\frac{(8)(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298\ \mathrm{K})}{(\pi)(0.0320\ \mathrm{kg\ mol^{-1}})}} = 444\ \mathrm{m\ s^{-1}}$$

The most probable value (called the **mode**) and the **mean value** are two different types of average. A third kind of average is the **root-mean-square value**, which for the speed is the square root of the mean-square speed: $v_{rms} = \langle v^2\rangle^{1/2}$:

$$\begin{aligned}\langle v^2\rangle &= \int_0^\infty v^2 f_v(v)\, dv\\ &= 4\pi\left(\frac{m}{2\pi k_B T}\right)^{3/2}\int_0^\infty v^4 e^{-mv^2/2k_B T}\, dv = \frac{3k_B T}{m} = \frac{3RT}{M}\end{aligned} \tag{10.3-8}$$

where we have looked up the integral in the table of Appendix C. The root-mean-square speed is given by

$$v_{rms} = \langle v^2\rangle^{1/2} = \sqrt{\frac{3k_B T}{m}} = \sqrt{\frac{3RT}{M}} \tag{10.3-9}$$

The word "average" is ambiguous. Here are three different quantities (the mean, the mode, and the root-mean-square) that are all called averages. The median is another kind of average. It is a value such that half of the members of a set lie above it and half lie below it.

EXAMPLE 10.4

Find the value of the root-mean-square speed of oxygen molecules at 298 K.

Solution

$$v_{rms} = \left(\frac{(3)(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298\ \mathrm{K})}{0.0320\ \mathrm{kg\ mol^{-1}}}\right)^{1/2} = 482\ \mathrm{m\ s^{-1}}$$

The most probable speed, the mean speed, and the root-mean-square speed are all indicated in Figure 10.12.

*Exercise 10.10

Find the most probable speed, the mean speed, and the root-mean-square speed of helium atoms at 298 K.

*Exercise 10.11

Show that the two ratios $\langle v\rangle/v_{\mathrm{p}}$ and $v_{\mathrm{rms}}/v_{\mathrm{p}}$ have the same two values for all gases at all temperatures and find those values.

*Exercise 10.12

Find the ratio of the probability densities for each of the following pairs of speeds:

a. v_{p} and $\langle v\rangle$ for O_2 gas at 298.15 K.
b. v_{p} and $\langle v\rangle$ for O_2 gas at 500.0 K.
c. v_{p} and $\langle v\rangle$ for He gas at 298.15 K.
d. v_{p} and v_{rms} for O_2 gas at 298.15 K.
e. v_{p} and v_{rms} for O_2 gas at 500.0 K.
f. v_{p} and v_{rms} for He gas at 298.15 K.

10.4 The Pressure of an Ideal Gas

Our model gas is an ideal gas. To show this, we will derive an equation for the pressure of our model gas by computing the force exerted on the walls of the container by individual molecules and adding these forces up. We assume that our model system of N noninteracting molecules is confined in a rectangular box the edges of which are parallel to our coordinate axes and the walls of which are smooth, slick, flat, and impenetrable. Since the walls are smooth and slick, the molecules will collide specularly with them. A **specular collision** has the properties: (1) It is elastic. That is, the kinetic energy of the molecule is the same before and after the collision. (2) No force parallel to the wall is exerted on the particle.

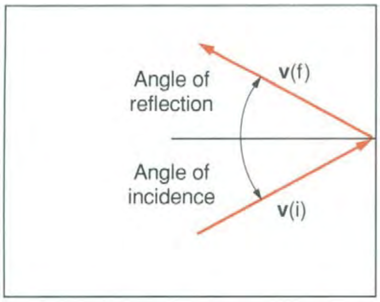

Figure 10.13. The Trajectory of a Particle Colliding Specularly with a Wall. The angle of incidence and the angle of reflection are equal, because of the fact that the wall puts a force on the molecule only in a direction perpendicular to the wall.

The trajectory of a particle striking the wall at the right end of the box is shown in Figure 10.13. The values of v_x and v_y do not change since no force is exerted in these directions. Since the kinetic energy does not change and since v_x^2 and v_z^2 do not change, v_y^2 cannot 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:

$$v_x(f)=v_x(i), \qquad v_y(f)=-v_y(i), \qquad v_z(f)=v_z(i) \tag{10.4-1}$$

As the particle strikes the wall, the magnitude of the force exerted on the wall rises suddenly and drops just as suddenly. Any measuring instrument used to measure the force on the wall requires a period of time, called the **response time**, to adjust to a sudden change in the force. The reading of the instrument is a time average over the response time, which we denote by τ. The time average of the y component of the force on the particle over a period of time from 0 to τ is defined by

$$\langle F_y \rangle = \frac{1}{\tau_0}\int_0^{\tau} F_y(t)\, dt \quad \text{(definition of time average)} \tag{10.4-2}$$

The $\langle\ \rangle$ symbol denotes either a time average or a mean value computed with a probability distribution. One must determine from the context which type of average is meant in a particular case.

From Newton's second law, Eq. (10.1-5), the force component equals the mass times the acceleration component:

$$\langle F_y \rangle = \frac{1}{\tau_0}\int_0^{\tau} ma_y\, dt = \frac{1}{\tau}\int_0^{\tau} m\,\frac{d^2y}{dt^2}\, dt = \frac{1}{\tau}\int_0^{\tau} m\frac{dv_y}{dt}\, dt \tag{10.4-3}$$

The differential dv_y is equal to $(dv_y/dt)\, dt$, so that

$$\langle F_y \rangle = \frac{m}{\tau}\int_0^{\tau} dv_y = \frac{m}{\tau}[v_y(\tau) - v_y(0)] = \frac{m}{\tau}[v_y(\mathrm{f}) - v_y(\mathrm{i})] \tag{10.4-4}$$

Equation (10.4-1) can be used to replace $v_y(\mathrm{f})$ by $-v_y(\mathrm{i})$, so that

$$\langle F_y \rangle = -\frac{2mv_y(\mathrm{i})}{\tau} \tag{10.4-5}$$

By Newton's third law, the force on the wall, $\mathbf{F}_{\mathrm{w}}$, is equal in magnitude to $\mathbf{F}$ and opposite in direction, so that

$$\langle F_{\mathrm{w}y} \rangle = -\langle F_y \rangle = \frac{2mv_y}{\tau} \tag{10.4-6}$$

We use only initial velocities from now on and omit the (i) label on our velocity component.

The total force on the wall is the sum of the contributions to the force from all of the particles in the system. Consider first the particles whose velocities lie in the infinitesimal volume element in velocity space $dv_x\, dv_y\, dv_z$. The fraction of all particles whose velocities lie in this volume element is

$$(\text{fraction}) = g(\mathbf{v})\, dv_x\, dv_y\, dv_z \tag{10.4-7}$$

All of the particles with velocities in this infinitesimal range are moving in the same direction with the same speed. Those particles in this set that will strike an area $\mathscr{A}$ on the wall are contained in a prism whose sides are parallel to the direction of motion of the particles, as shown in Figure 10.14.

The particles that are no farther from the wall in the y direction than a distance equal to τv_y will strike the wall during the time interval τ (due to 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 the y component of the velocity, not the speed. We assume that our system is uniform. The **number density**, $\mathcal{N}$, 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 volume of the prism is equal to the area of its base times its altitude:

$$V_{\mathrm{prism}} = \mathscr{A} v_y \tau \tag{10.4-8}$$

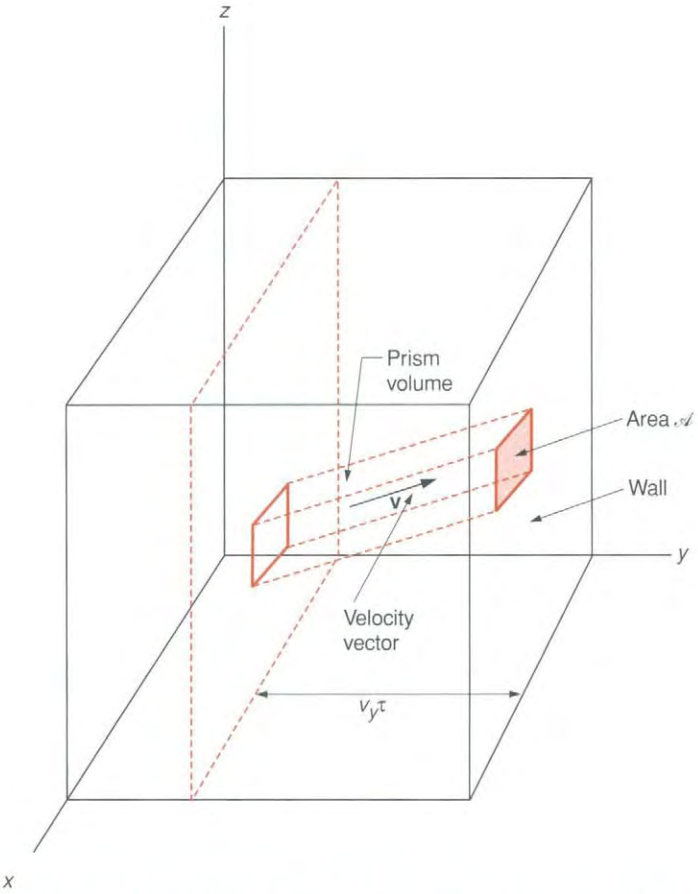

Figure 10.14. The Prism That Contains Molecules of a Certain Velocity That Will Strike Area $\mathcal{A}$ in time τ. Molecules with velocities not equal to the given velocity lie in different prisms.

The number of particles in the prism is

$$\text{(Number in prism)} = \mathcal{N}\mathcal{A}v_y\tau = \frac{N}{V}\mathcal{A}v_y\tau \tag{10.4-9}$$

so that

$$\begin{pmatrix}\text{Number with velocities in}\\ \text{the given volume element}\\ \text{striking } \mathcal{A} \text{ in time } \tau\end{pmatrix} = \mathcal{N}\mathcal{A}v_y\tau g(v)\,dv_x\,dv_y\,dv_z \tag{10.4-10}$$

Let the total force on $\mathcal{A}$ be denoted by $\langle F_{\mathcal{A}}\rangle$. Each particle makes a contribution to this force that is given by Eq. (10.4-6):

$$\begin{aligned}\begin{pmatrix}\text{Contribution to } \langle F_{\mathcal{A}}\rangle \text{ due}\\ \text{to particles with velocities}\\ \text{in the given range}\end{pmatrix} &= (2mv_y/\tau)\mathcal{N}\mathcal{A}v_y\tau g(v)\,dv_x\,dv_y\,dv_z\\ &= 2m\mathcal{N}\mathcal{A}v_y^2 g(v)\,dv_x\,dv_y\,dv_z\\ &= 2m\frac{N}{V}\mathcal{A}v_y^2 g(v)\,dv_x\,dv_y\,dv_z\end{aligned} \tag{10.4-11}$$

Notice that τ cancels out of this equation.

We not 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, while the components parallel to the wall can be positive or negative. The total time-average force on $\mathscr{A}$ is

$$\langle F_{\mathscr{A}} \rangle = \frac{2mN\mathscr{A}}{V} \int_{-\infty}^{\infty} \int_{0}^{\infty} \int_{-\infty}^{\infty} v_y^2 g(v)\, dv_x\, dv_y\, dv_z \tag{10.4-12}$$

The integral in this equation is the same as one of the terms in Eq. (10.2-26) except that the lower limit of the v_y integration is 0 instead $-\infty$. Since the integrand is an even function of v_y, the value of the integral will be half of that of the integral obtained by changing the lower limit to $-\infty$.

$$\begin{aligned} \langle F_{\mathscr{A}} \rangle &= 2m\frac{N}{V}\mathscr{A}\frac{1}{2}\langle v_y^2 \rangle = 2m\frac{N}{V}\mathscr{A}\frac{1}{6}\langle v^2 \rangle \\ &= \frac{1}{3}m\frac{N}{V}\mathscr{A}\frac{3k_BT}{m} = \frac{N\mathscr{A}k_BT}{V} = \mathscr{N}\mathscr{A}k_BT \end{aligned} \tag{10.4-13}$$

where we have used the relation shown in Eq. (10.3-8) for $\langle v^2 \rangle$ and have used the fact that $2\langle v_y^2 \rangle = \langle v^2 \rangle$.

The pressure, P, is the force per unit area so that

$$P = \frac{\langle F_{\mathscr{A}} \rangle}{\mathscr{A}} = \mathscr{N}k_BT = \frac{Nk_BT}{V} = \frac{nRT}{V} \tag{10.4-14}$$

where

$$k_B = \frac{nR}{N} = \frac{R}{N_{Av}} \tag{10.4-15}$$

and where N_{Av} is Avogadro's number. We do not label P as a time average, since it is a time-independent equilibrium quantity.

We have taken a model system whose states and processes are described mechanically on the molecular scale. An average over microscopic states has given a macroscopic pressure of the model system that is the same as that of an ideal gas. This analysis depended on the use of Eq. (10.2-30), which gave the energy of the gas as proportional to the temperature. It is also possible to assume that the gas obeys the ideal gas equation of state and then to derive Eq. (10.2-30).

EXAMPLE 10.5

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.

Solution

$$\begin{aligned} \langle F_y \rangle \tau = 2mv_y(\mathrm{i}) &= \frac{(2)(0.0320\ \mathrm{kg\ mol^{-1}})(444\ \mathrm{m\ s^{-1}})}{6.0221 \times 10^{23}\ \mathrm{mol^{-1}}} \\ &= 4.72 \times 10^{-23}\ \mathrm{kg\ m\ s^{-1}} = 4.72 \times 10^{-23}\ \mathrm{N\ s} \end{aligned}$$

*Exercise 10.13

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 101,325 N to be exerted on the area.

The Pressure of a Mixture of Gases

We now change our model system so that it contains a mixture of different gaseous substances but continue to assume that the molecules do not exert forces on each other. The molecules of each substance will move just as though the other substances were not present. The total pressure is the sum of the pressure exerted by each set of molecules:

$$P = P_1 + P_2 + P_3 + \cdots + P_c \tag{10.4-16}$$

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. Equation (10.4-16) is **Dalton's law of partial pressures**. Since each gas obeys Eq. (10.4-14),

$$P = \frac{n_1RT}{V} + \frac{n_2RT}{V} + \cdots + \frac{n_cRT}{V} = \frac{nRT}{V} \tag{10.4-17}$$

where

$$n = n_1 + n_2 + \cdots + n_c \tag{10.4-18}$$

Our model system conforms to the ideal gas law and to Dalton's law of partial pressures. Real gases conform approximately to these laws and conform more closely at lower pressures. This supports the belief that a real dilute gas consists of moving molecules that do not collide with each other frequently enough to make it much different from our model system.

10.5 Wall Collisions and Effusion

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. **Graham's law of effusion** is an empirical law, asserting that at a given temperature and a given pressure the rates of effusion of different gases are inversely proportional to the square roots of the densities of the gases, and thus to the square roots of the molecular masses or molar masses.

Graham's law is named for Thomas Graham, 1805–1869, a British chemist who not only studied diffusion and effusion, but also determined the formulas of the various species formed from phosphoric acid in aqueous solution.

Refer again to Figure 10.14. Our analysis of effusion will be similar to that of Section 10.4, except that we will now compute the number of molecules striking an area $\mathcal{A}$ instead of the force exerted on the wall. If this area is a section of the wall, we obtain the rate of wall collisions. If the area is a hole in the wall, we obtain the rate of effusion.

The number of molecules whose velocities lie in the velocity interval $dv_x\, dv_y\, dv_z$ and which will strike the area $\mathcal{A}$ in time τ is given by Eq. (10.4-10):

$$(\text{Number striking } \mathcal{A} \text{ in time } \tau) = \mathcal{N}\mathcal{A}v_y\tau g(v)\, dv_x\, dv_y\, dv_z \tag{10.5-1}$$

The total number of molecules striking the area $\mathcal{A}$ in the time interval τ is

$$\begin{pmatrix}\text{Total number} \\ \text{striking area} \\ \mathcal{A} \text{ in time } \tau\end{pmatrix} = \mathcal{N}\mathcal{A}\tau \int_{-\infty}^{\infty}\int_0^{\infty}\int_{-\infty}^{\infty} v_y g(v)\, dv_x\, dv_y\, dv_z$$
$$= \mathcal{N}\mathcal{A}\left(\frac{m}{2\pi k_B T}\right)^{3/2} \tau \int_{-\infty}^{\infty}\int_0^{\infty}\int_{-\infty}^{\infty} v_y e^{-mv^2/2k_BT}\, dv_x\, dv_y\, dv_z \tag{10.5-2}$$

This equation is factored as was Eq. (10.2-28) and the integrations over v_x and v_z are carried out as with that equation:

$$\begin{pmatrix}\text{Total number}\\ \text{striking area}\\ \mathscr{A}\text{ in time }\tau\end{pmatrix} = \mathscr{N}\mathscr{A}\left(\frac{m}{2\pi k_{\mathrm{B}}T}\right)^{1/2}\tau\int_0^\infty v_y e^{-mv_y^2/2k_{\mathrm{B}}T}\,dv_y \tag{10.5-3}$$

The integral in this equation can be performed by the method of substitution. We let $w = v_y^2$, so that the integral becomes

$$\begin{aligned}\int_0^\infty v_y e^{-mv_y^2/2k_{\mathrm{B}}T}\,dv_y &= \frac{1}{2}\int_0^\infty e^{-mw/2k_{\mathrm{B}}T}\,dw\\ &= \frac{1}{2}\frac{2k_{\mathrm{B}}T}{m}\left(-e^{-mw/2k_{\mathrm{B}}T}\right)\Big|_0^\infty = -\frac{1}{2}\frac{2k_{\mathrm{B}}T}{m}(0-1) = \frac{k_{\mathrm{B}}T}{m}\end{aligned} \tag{10.5-4}$$

Therefore,

$$\begin{pmatrix}\text{Total number}\\ \text{striking area}\\ \mathscr{A}\text{ in time }\tau\end{pmatrix} = \mathscr{N}\mathscr{A}\tau\left(\frac{k_{\mathrm{B}}T}{2\pi m}\right)^{1/2} = \frac{1}{4}\mathscr{N}\mathscr{A}\tau\left(\frac{8k_{\mathrm{B}}T}{\pi m}\right)^{1/2} = \frac{1}{4}\mathscr{N}\mathscr{A}\tau\langle v\rangle \tag{10.5-5}$$

Notice how physically reasonable this result is. 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 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:

$$\nu = \frac{1}{4}\mathscr{N}\langle v\rangle = \frac{\mathscr{N}}{4}\left(\frac{8k_{\mathrm{B}}T}{\pi m}\right)^{1/2} \tag{10.5-6}$$

EXAMPLE 10.6

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, and assume that the area of the eardrum is 0.50 cm^2.

Solution

$$\begin{aligned}\langle v(\mathrm{O})_2)\rangle &= 444\ \mathrm{m\ s^{-1}} &&\text{from Example 10.3}\\ \langle v(\mathrm{N}_2)\rangle &= 475\ \mathrm{m\ s^{-1}} &&\text{by a similar calculation}\\ \mathscr{N}(\mathrm{N}_2) &= N(\mathrm{N}_2)/V = P(\mathrm{N}_2)/k_{\mathrm{B}}T\\ &= \frac{(101325\ \mathrm{N\ m^{-2}\ atm^{-1}})(0.79\ \mathrm{atm})}{(1.3807\times10^{-23}\ \mathrm{J\ K^{-1}})(298\ \mathrm{K})} = 1.9\times10^{25}\ \mathrm{m^{-3}}\end{aligned}$$

where $P(\mathrm{N}_2)$ is the partial pressure of N_2, $N(\mathrm{N}_2)$ is the number of N_2 molecules and $\mathscr{N}(\mathrm{N}_2)$ is the number density of N_2 (number of molecules per unit volume).

$$\begin{aligned}\mathscr{N}(\mathrm{O}_2) &= N(\mathrm{O}_2)/V = 5.2\times10^{24}\ \mathrm{m^{-3}} &&\text{by a similar calculation}\\ \nu(\mathrm{N}_2) &= \frac{1}{4}(1.9\times10^{25}\ \mathrm{m^{-3}})(475\ \mathrm{m\ s^{-1}}) = 2.3\times10^{27}\ \mathrm{m^{-2}\ s^{-1}}\\ \nu(\mathrm{O}_2) &= 5.7\times10^{26}\ \mathrm{m^{-2}\ s^{-1}} &&\text{by a similar calculation}\end{aligned}$$

$$(\text{Number per second}) = [\nu(\mathrm{N}_2)+\nu(\mathrm{O}_2)](5.0\times10^{-5}\ \mathrm{m^2}) = 1.4\times10^{23}\ \mathrm{s^{-1}}$$

***Exercise 10.14**

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 containing 0.5 mol% carbon monoxide passes over the catalyst at 350 K and 1.00 atm. Find the amount of CO in moles striking 1 g of the catalyst per second.

Equation (10.5-6) also gives the rate of effusion per unit area through a small hole, since nothing in the derivation depended on the fate of the molecules after they struck the area $\mathscr{A}$. The effusion rate predicted by Eq. (10.5-6) is inversely proportional to the square root of the mass of the particles, in agreement with Graham's law of effusion. The model system defined in this chapter conforms to Graham's law of effusion, and to the ideal gas law.

10.6 The Model System with Potential Energy

We now define two model systems with molecules that have variable potential energy as well as kinetic energy. We first consider a system in which the potential energy of each particle is independent of the positions of the other particles. This case excludes intermolecular forces but includes gravitational potential energy. Let the potential energy of particle number i be denoted by

$$\varphi = \varphi(x_i, y_i, z_i) \tag{10.6-1}$$

(Do not confuse this potential energy with the electric potential denoted by the same symbol in Chapter 9. There are not enough letters in the alphabet to use one letter for only one quantity.) The total energy of the molecule is

$$\varepsilon_i = \frac{m}{2}(v_{ix}^2 + v_{iy}^2 + v_{iz}^2) + \varphi(x_i, y_i, z_i) \tag{10.6-2}$$

The Boltzmann probability distribution applies. From Eqs. (1.5-17) and (10.2-35), the probability of the state with energy of Eq. (10.6-2) is given by the proportionality

$$\text{Probability} \propto e^{-m(v_x^2+v_y^2+v_z^2)/2k_\mathrm{B}T} e^{-\varphi(x,y,z),k_\mathrm{B}T} \tag{10.6-3}$$

We now normalize this probability distribution in order to write it as an equality instead of a proportionality. Let the probability that the position of a randomly chosen particle lies in the coordinate volume element $dx\,dy\,dz$ and that its velocity lies in the velocity space volume element $dv_x\,dv_y\,dv_z$ be given by

$$\begin{aligned}(\text{Probability}) &= G(x', y', z', v_x', v_y', v_z')\,dx\,dy\,dz\,dv_x\,dv_y\,dv_z \\ &= G(\mathbf{r}', \mathbf{v}')\,d^3\mathbf{r}\,d^3\mathbf{v}\end{aligned} \tag{10.6-4}$$

where x', y', and z' are coordinates lying in the volume element $dx\,dy\,dz$ and where v_x', v_y', and v_z' are velocity coordinates lying in the volume element $dv_x\,dv_y\,dv_z$. From Eq. (10.6-3), this probability density is the product of a velocity factor and a coordinate factor:

$$G = g(v_x, v_y, v_z)g_c(x, y, z) = g(\mathbf{v})g_c(\mathbf{r}) \tag{10.6-5}$$

where $g(\mathbf{v})$ is the same function as in Eq. (10.2-34) and where

$$g_c(\mathbf{r}) \propto e^{-\varphi/k_\mathrm{B}T} \tag{10.6-6}$$

The probability that a particle is in the coordinate volume element $dx\,dy\,dz$, irrespective of its velocity is

$$\begin{aligned}(\text{Probability}) &= \left[\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} g_{\mathrm{c}}(\mathbf{r})g(\mathbf{v})\,dv_x\,dv_y\,dv_z\right]dx\,dy\,dz \\ &= g_{\mathrm{c}}(\mathbf{r})\,dx\,dy\,dz \end{aligned} \qquad (10.6\text{-}7)$$

The second equality follows from the fact that the velocity probability distribution of Eq. (10.2-34) is separately normalized.

We assume that the system is enclosed in a rectangular box of dimensions a by b by c, and require that g_{c} be normalized

$$\int_0^c\int_0^b\int_0^a g_{\mathrm{c}}(\mathbf{r})\,dx\,dy\,dx = \int_V g_{\mathrm{c}}(\mathbf{r})\,d^3\mathbf{r} = 1 \qquad (10.6\text{-}8)$$

where the second version of the integral is an abbreviation for the first version. We define the **configuration integral** ζ:

$$\zeta = \int_V e^{-\varphi/k_{\mathrm{B}}T}\,d^3\mathbf{r} \qquad (10.6\text{-}9)$$

where the label on the integral indicates that the integration is over the volume of the box containing the gas. The normalized coordinate distribution function is

$$g_{\mathrm{c}} = \frac{1}{\zeta}e^{-\varphi/k_{\mathrm{B}}T} \qquad (10.6\text{-}10)$$

The barometric distribution can be obtained from this distribution, since the pressure is proportional to the number of molecules per unit volume and since the gravitational potential energy is given by

$$\varphi = mgz$$

The barometric distribution for an atmosphere of constant temperature is

$$\frac{P}{P_0} = e^{-mgh/k_{\mathrm{B}}T} = e^{-Mgh/RT} \qquad (10.6\text{-}11)$$

where h is the altitude, P_0 is the pressure at altitude $h = 0$, g is the acceleration due to gravity, and M is the molar mass of the gas (sometimes taken as an average value for the atmosphere). We do not normalize the barometric distribution in Eq. (10.6-11) because the system is not confined in a convenient box.

Exercise 10.15

a. Show that for a system confined in a box with potential energy $\mathcal{V} = 0$ inside the box, the configuration integral is given by

$$\zeta = V$$

where V is the volume of the box.

***b.** Find an expression for ζ if $\varphi = mgz$, where z is the vertical coordinate and where g is the acceleration due to gravity, 9.80 m s^{-2}. Assume the system to be confined in a box of dimensions a by b by c with z ranging from 0 to c.

Inclusion of Intermolecular Forces

In order to represent a nonideal gas, a model system must include intermolecular forces. Two uncharged molecules attract each other at moderate intermolecular distances and repel each other at smaller intermolecular distances. The attractive forces are called **London dispersion forces**[2] or **van der Waals forces**. A classical picture used to visualize the attractive force between neutral molecules is that electron motion produces temporary fluctuating electric dipoles in two molecules, which can become synchronized and attract each other. Intermolecular repulsions are also visualized in a relatively simple way. One repulsive effect arises from the fact that according to quantum mechanics the kinetic energy of a moving object rises when it is confined to a smaller region, as happens to the electrons in two molecules that are pushed close together. Another repulsive effect arises from the fact that the electrons move primarily in the outer regions of a molecule or atom, and repel the electrons in a nearby atom or molecule.

Forces that are independent of velocities can be derived from a potential energy function (see Appendix D). The potential energy u of a pair of argon atoms is shown in Figure 10.15 as a function of the distance between the centers of the molecules. The behavior in this figure is typical of pairs of atoms that do not react chemically. Diatomic and polyatomic molecules exhibit a similar intermolecular potential energy with additional dependence on molecular orientations. A force is the negative of the derivative of the potential energy function, so that at any intermolecular distance the force points in the direction in which the potential energy function decreases. There is repulsion at small distances and attraction at somewhat larger distances. A minimum in a potential energy corresponds to a **mechanical equilibrium**, with repulsive forces balancing attractive forces. In a condensed phase (liquid or solid) the average separation of the molecules from their nearest neighbors is approximately equal to the intermolecular distance at the minimum. Since mechanical work must be done either to expand or compress the system, solids and liquids have nearly fixed volumes.

A simple model system with intermolecular forces is defined to have potential energies of pairs of molecules similar to that in Figure 10.15:

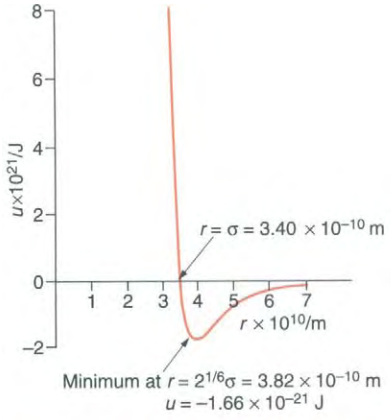

Figure 10.15. The Lennard-Jones Representation of the Intermolecular Potential of a Pair of Argon Atoms. This representation is only qualitatively correct, but is widely used as a convenient approximation.

1. The system consists of a number, N, of particles, which move according to classical mechanics.
2. The intermolecular forces are independent of the particles' velocities.
3. The force on particle 1 due to particle 2 is unaffected by the positions of particle 3, particle 4, etc., and similarly for the other pairs of particles. This is a good approximation for gases, although only a fairly good assumption for liquids.[3]
4. The magnitudes of the intermolecular forces depend only on the distances between the particles, and not on their orientations.
5. The force on one particle due to a second particle is in the direction of the second particle.

For this model system, the intermolecular potential energy $\mathscr{V}$ is a sum of one-body and two-body contributions:

$$\mathscr{V}=\sum_{i=1}^{N-1}\sum_{j=i+1}^{N}u(r_{ij}) \tag{10.6-12}$$

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[2] F. London, *Z. physik. Chem.*, **B11**, 222 (1930); *Trans. Faraday Soc.*, **33**, 8 (1937).

[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 (1944) for a three-body potential for helium atoms.

The function u is the **pair potential energy function** of the pair of particles i and j and is a function such as shown in Figure 10.15. The limits on the double sum in Eq. (10.6-12) are chosen so that the contribution of a single pair of particles is not counted twice. A common approximate representation for the pair potential function is the **Lennard-Jones 6–12 potential**, which was used to draw Figure 10.15:

$$u_{\mathrm{LJ}}(r) = 4\varepsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \tag{10.6-13}$$

The values of the parameters σ and ε are chosen to match experimental data for each substance. Table A.14 of Appendix A gives values for a few substances.[4] The parameter σ is equal to the intermolecular separation at which the potential energy is equal to zero, and the parameter ε is equal to the depth of the minimum in the curve. The designation 6–12 denotes the choice of the exponents in the formula. Other choices for the exponents are also used, but the Lennard-Jones 6–12 potential is the most common choice, and is usually called simply "the Lennard-Jones potential." Other, more accurate potentials have been obtained.[5]

The Lennard-Jones potential is named for J. E. Lennard-Jones, 1894–1954, a prominent British theoretical chemist.

Exercise 10.16

a. Show that for the Lennard-Jones potential,

$$u_{\mathrm{LJ}}(\sigma) = 0 \tag{10.6-14}$$

b. Show that the value of r at the minimum in the Lennard-Jones potential is

$$r_{\mathrm{min}} = 2^{1/6}\sigma = (1.12246)\sigma \tag{10.6-15}$$

c. Show that

$$u_{\mathrm{LJ}}(r_{\mathrm{min}}) = -\varepsilon \tag{10.6-16}$$

d. 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

$$F_r = 4\varepsilon\left(12\frac{\sigma^{12}}{r^{13}} - 6\frac{\sigma^{6}}{r^{7}}\right) \tag{10.6-17}$$

e. Show that $F_r = 0$ if $r = 2^{1/6}\sigma$.

A simpler but less realistic representation of the pair potential function is the **square well potential**

$$u(r) = \begin{cases} +\infty & \text{if } r < d \\ -\varepsilon & \text{if } d < r < c \\ 0 & \text{if } r > c \end{cases} \tag{10.6-18}$$

This potential function is shown in Figure 10.16. A still simpler representation of the pair potential is the **hard-sphere potential**

$$u(r) = \begin{cases} +\infty & \text{if } r < d \\ 0 & \text{if } r > d \end{cases} \tag{10.6-19}$$

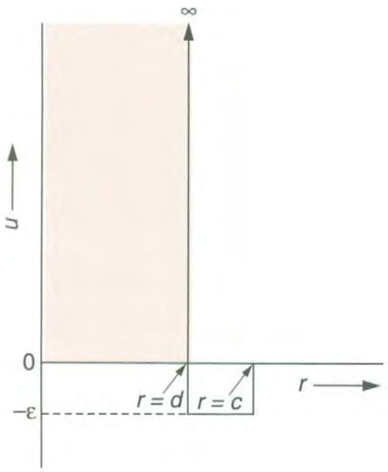

Figure 10.16. The Square-Well Representation of the Intermolecular Potential of a Pair of Atoms. This representation is the crudest representation that contains an attraction.

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[4] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1954, pp. 1110ff.

[5] See, for example, D. E. Moon, *J. Chem. Phys.*, **100**, 2838 (1994).

which is depicted in Figure 10.17. The parameter d is the distance of closest approach of the centers of the two spheres, and is thus equal to the sum of their radii. If the two spheres have equal radii, this is twice the radius of one of them and is equal to the diameter of each.

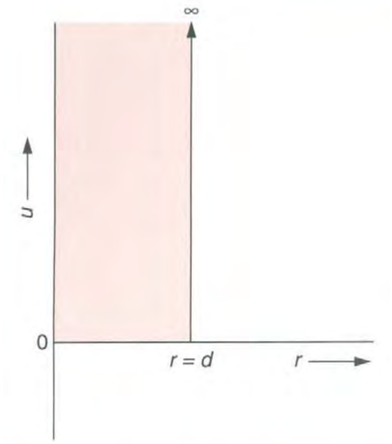

Figure 10.17. The Hard-Sphere Representation of the Intermolecular Potential of a Pair of Atoms. This representation is the crudest of all possible representations of intermolecular potential energy, but does a surprisingly good qualitative job in describing actual gas behavior.

10.7 The Hard-Sphere Gas

The hard-sphere potential is the crudest possible representation of intermolecular potential energy. It completely disregards the attractive forces that are responsible for condensation and cannot be used in a realistic description of liquids or solids, but when the appropriate size of the spheres is taken, many of the properties of a real gas can be simulated by a model gas of hard spheres. Table A.15 gives the value of the effective hard-sphere diameter for several gases.

The centers of two molecules in a hard-sphere gas cannot approach any closer than a distance d. To obtain an approximate equation of state for a hard-sphere gas, 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, due to the presence of the other particles. Figure 10.18 shows the volume due to particle 2 into which the center of particle 1 cannot penetrate. This excluded volume is spherical, with radius equal to d, the diameter of one particle. If the gas contains N molecules, the total volume from which particle 1 is excluded is $N - 1$ times the volume in Figure 10.18:

$$V_{\text{exc}} = (N-1)\left(\frac{4}{3}\pi d^3\right) \approx N\frac{4}{3}\pi d^3 \tag{10.7-1}$$

where we neglect unity compared with N.

If all of the particles are moving, the excluded volume in Figure 10.18 represents not only the volume from which particle 1 is excluded because of particle 2, but also the

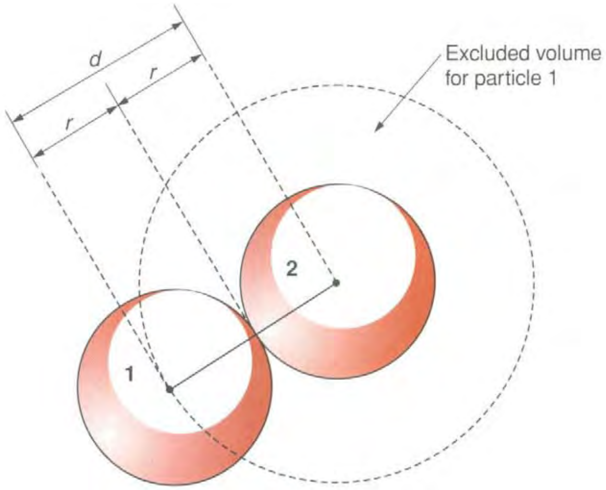

Figure 10.18. The Excluded Value of a Pair of Hard Spheres. The important fact about this excluded volume is that its radius is the sum of the radii of the two molecules.

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

$$V_{\mathrm{exc}} = \frac{N}{2}\left(\frac{4}{3}\pi d^3\right) = N\frac{2}{3}\pi d^3 \tag{10.7-2}$$

We take as our approximate equation of state that of an ideal gas in a container whose volume is equal to the volume in which each particle can move,

$$P(V - V_{\mathrm{exc}}) = Nk_{\mathrm{B}}T = nRT \tag{10.7-3}$$

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. (10.7-3) by n and obtain

$$P(V_{\mathrm{m}} - b) = RT \tag{10.7-4}$$

where $V_{\mathrm{m}} = V/n$, the molar volume, where we define the constant b,

$$b = \frac{N}{n}\frac{2}{3}\pi d^3 = N_{\mathrm{Av}}\frac{2}{3}\pi d^3 \tag{10.7-5}$$

and where N_{Av} is Avogadro's number. Equation (10.7-4) resembles the van der Waals equation of state of Eq. (2.3-1) except for the absence of the term containing the parameter a.

If we write Eq. (10.7-4) in the form

$$P = \frac{RT}{V_{\mathrm{m}} - b} \tag{10.7-6}$$

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 present system has only repulsive forces, we assert that repulsive forces generally make a positive contribution to the pressure. The parameter b in the van der Waals equation has the same relationship to the effective size of the molecules as in Eq. (10.7-5). Attractive forces make a negative contribution to the pressure, so that the parameter a in the van der Waals equation represents the effect of attractive forces. The argument has been advanced that attractive forces must slow a particle down just before it strikes a wall since other molecules will be only on the side of the molecule away from the wall as it strikes the wall. Similarly, repulsive forces accelerate a particle as it strikes the wall.

*Exercise 10.17

Calculate the radius of an argon atom from the value of the van der Waals parameter b in Table A.3. Compare your result with argon's radius in Table A.15. Why might the two values differ?

Equation (10.7-4) is only an approximation because of our assumption that the excluded volumes of the different molecules simply add together. It ignores the effect of finding two particles close enough together so that the volumes which they exclude for a third particle partially overlap.

The virial equation of state of Eq. (2.3-3) is a widely used equation of state for nonideal gases. Classical statistical mechanics, which is introduced briefly in Chapter 22, provides formulas for calculating all of the virial coefficients of a nonideal monatomic gas. The formulas for the higher virial coefficients contain numerous terms, but the formula for the second virial coefficient contains a single term:

$$B_2 = -\frac{N_{\mathrm{Av}}}{2}\int_0^\infty [e^{-u(r)/k_{\mathrm{B}}T} - 1]4\pi r^2\, dr \tag{10.7-7}$$

where r is the intermolecular distance and $u(r)$ is the pair potential energy function. This equation is valid for any pairwise additive potential that depends only on the distance between the molecules.

Exercise 10.18

***a.** Obtain a formula for the second virial coefficient of a hard-sphere gas.

b. Write Eq. (10.7-6) in the form

$$\frac{PV_{\mathrm{m}}}{RT} = \frac{1}{1 - b/V_{\mathrm{m}}}$$

and use the identity

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

to transform Eq. (10.7-6) into the form of the virial equation of state. Show that the same formula results for the second virial coefficient as in part (a).

The equation of state of a hard-sphere fluid has been the subject of considerable research, and far better approximate equations than Eq. (10.7-4) have been obtained.[6] One such equation of state is found in Problem 10.61. Much of this research has used the technique of molecular dynamics, in which solutions to the equations of motion (Newton's second law in appropriate forms) for a system of several hundred particles are numerically simulated by a computer program. Energies, pressures, etc., are then calculated as a function of time from the particles' positions and velocities. The molecular dynamics technique has also been used for other model systems, including those with Lennard-Jones potentials, and has also been used to compute nonequilibrium properties.

The results of molecular dynamics calculations indicate that there is no gas–liquid condensation in the hard-sphere system, and we would expect no such condensation since there are no attractive intermolecular forces. However, there is considerable evidence from these results that a gas–solid phase transition occurs.[7] This result was originally somewhat surprising.

Molecular Collisions in a Hard-Sphere Gas

In the hard-sphere model system at fairly low density, a molecule will undergo a number of collisions, moving at a constant velocity between collisions. Study of these collisions will help us to understand transport processes (diffusion, viscous flow, and thermal conduction) and chemical reaction rates in gases. For fairly small pressures, the probability that three molecules will collide is small, so we neglect three-body collisions.

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[6] R. Hoste and W. Van Dael, *J. Chem. Soc. Faraday Trans. 2*, **80**, 477 (1984).

[7] H. Reiss and A. D. Hammerich, *J. Phys. Chem.*, **90**, 6252 (1986).

For a first approximate analysis of molecular collisions, we assume 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

$$\frac{N-1}{V} \approx \frac{N}{V} = \mathcal{N} \tag{10.7-8}$$

where we neglect unity compared with N. The mean number N' of particles in a given portion of the system with volume V' is given by

$$N' = \mathcal{N}V' \tag{10.7-9}$$

As the moving particle travels along, it "sweeps out" a cylindrical volume as shown in Figure 10.19. The radius of this **collision cylinder** is equal to d, the sum of the radii of two particles, which is called the **collision diameter**. Any molecule whose center is within the cylinder will be struck by the moving particle. The length of the cylinder that contains on the average one stationary particle is equal to the mean distance between collisions, called the **mean free path** and denoted by λ. The cross-sectional area of the collision cylinder is called the **collision cross section**

$$(\text{Collision cross section}) = \pi d^2 \tag{10.7-10}$$

The volume containing on the average one stationary particle is

$$(\text{Volume containing one particle}) = \lambda\pi d^2 \tag{10.7-11}$$

This must equal V/N, the mean volume per molecule:

$$\frac{V}{N} = \frac{1}{\mathcal{N}} = \lambda\pi d^2 \tag{10.7-12}$$

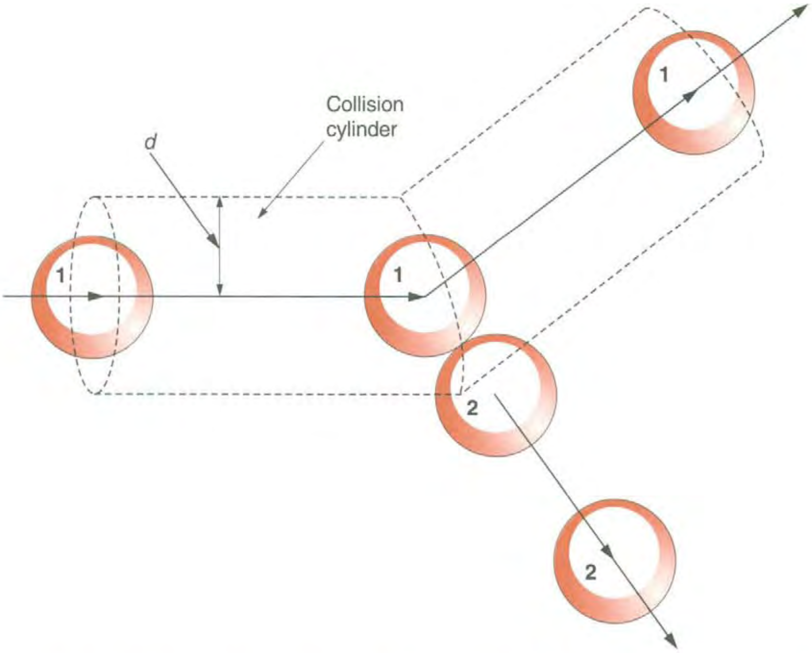

Figure 10.19. A Portion of the Collision Cylinder of Particle 1. Like the excluded volume, the collision cylinder has a radius that is the sum of the radii of the two molecules.

The mean free path is therefore given by

$$\lambda = \frac{1}{\pi d^2 \mathcal{N}} \quad \text{(approximate equation)} \tag{10.7-13}$$

We assume that our moving particle has a speed equal to the mean molecular speed given by Eq. (10.3-7):

$$v_1 = \langle v \rangle = \sqrt{\frac{8k_B T}{\pi m}} \tag{10.7-14}$$

From the simple relationship, distance = rate × time, the mean time between collisions is equal to the mean free path divided by the speed. We denote this time by τ_{coll}.

$$\tau_{\text{coll}} \approx \frac{\lambda}{\langle v \rangle} = \frac{1}{\langle v \rangle \pi d^2 \mathcal{N}} = \sqrt{\frac{\pi m}{8k_B T}} \frac{1}{\pi d^2 \mathcal{N}} \quad \begin{pmatrix} \text{approximate} \\ \text{equation} \end{pmatrix} \tag{10.7-15}$$

The rate of collisions (number of collisions per unit time) for our moving particle is denoted by z_1,

$$z_1 = \frac{1}{\tau_{\text{coll}}} \approx \pi d^2 N \sqrt{\frac{8k_B T}{\pi m}} \quad \text{(approximate equation)} \tag{10.7-16}$$

These equations are crude approximations 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 10.20, and that both particles are moving at the mean speed. If, prior to the collision, x is the

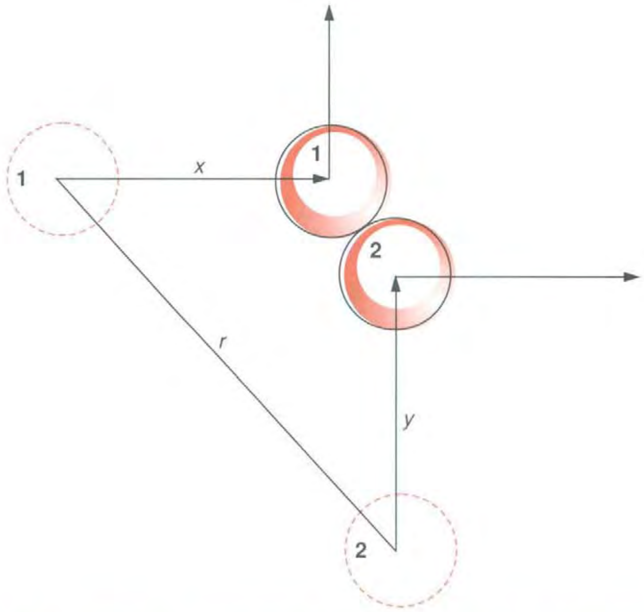

Figure 10.20. An "Average" (Right-Angle) Collision of Two Hard Spheres of the Same Type. Our analysis based on assuming that this kind of collision is an average that can represent all collision leads to the correct formula for the mean relative speed, in spite of its crudity.

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

$$r = (x^2 + y^2)^{1/2} \tag{10.7-17}$$

The **relative speed** is defined as $|dr/dt|$.

If the particles are moving at the same speed, x and y must be equal to each other in order for the collision to occur. Therefore, by the theorem of Pythagoras

$$r = \sqrt{2}x \tag{10.7-18}$$

The relative speed is larger than the speed of each particle by a factor of $\sqrt{2}$:

$$v_{\text{rel}} = \left|\frac{dr}{dt}\right| = \sqrt{2}\left|\frac{dx}{dt}\right| \tag{10.7-19}$$

If both particles are moving at the mean speed, we identify their relative speed as the mean relative speed:

$$\langle v_{\text{rel}}\rangle = \sqrt{2}\langle v\rangle = \sqrt{2}\sqrt{\frac{8k_{\text{B}}T}{\pi m}} = \sqrt{\frac{16k_{\text{B}}T}{\pi m}} \tag{10.7-20}$$

Our analysis is approximate, but Eq. (10.7-20) 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 $\langle v\rangle$ it will meet the other particle in a time that is shorter by a factor of $\sqrt{2}$, so that the mean collision time becomes

$$\tau_{\text{coll}} = \sqrt{\frac{\pi m}{16k_{\text{B}}T}}\frac{1}{\pi d^2\mathcal{N}} \tag{10.7-21}$$

and the mean molecular collision rate becomes

$$z_1 = \frac{1}{\tau_{\text{coll}}} = \pi d^2\mathcal{N}\sqrt{\frac{16k_{\text{B}}T}{\pi m}} \tag{10.7-22}$$

where we use the subscript 1 to indicate that this is the mean collision rate for substance 1, the only substance present. The mean free path is also shorter by a factor of $2^{-1/2}$:

$$\lambda_1 = \frac{1}{\sqrt{2}\pi d^2\mathcal{N}} \tag{10.7-23}$$

EXAMPLE 10.7

For nitrogen gas at 298 K and a molar volume of 24.45 L (approximately corresponding to 1.00 atmosphere pressure):

a. Find the mean free path.

b. Find the mean collision time and the mean molecular collision rate.

Solution

$$\mathcal{N} = \frac{N}{V} = \frac{6.022 \times 10^{23}\ \mathrm{mol^{-1}}}{0.02445\ \mathrm{m^3\ mol^{-1}}} = 2.463 \times 10^{25}\ \mathrm{m^{-3}}$$

$$\langle v \rangle = \left(\frac{8(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298.15\ \mathrm{K})}{\pi(0.0280\ \mathrm{kg\ mol^{-1}})}\right)^{1/2} = 475\ \mathrm{m\ s^{-1}}$$

$$\langle v_{\mathrm{rel}} \rangle = \sqrt{2}\langle v \rangle = 671\ \mathrm{m\ s^{-1}}$$

a.

$$\lambda = \frac{1}{\sqrt{2}\pi(3.7 \times 10^{-10}\ \mathrm{m^3})^2(2.463 \times 10^{25}\ \mathrm{m^{-3}})} = 6.7 \times 10^{-8}\ \mathrm{m}$$

b.

$$\tau_{\mathrm{coll}} = \frac{\lambda}{\langle v \rangle} = \frac{6.7 \times 10^{-8}\ \mathrm{m}}{475\ \mathrm{m\ s^{-1}}} = 1.4 \times 10^{-10}\ \mathrm{s}$$

$$z_1 = \frac{1}{1.4 \times 10^{-10}\ \mathrm{s}} = 7.1 \times 10^{9}\ \mathrm{s^{-1}}$$

*Exercise 10.19

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)?

The total rate of collisions per unit volume is not equal to the mean molecular collision rate multiplied by the number of molecules per unit volume because 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:

$$Z_{11} = \frac{1}{2} z_1 \mathcal{N} = \frac{1}{2}\pi d^2 \langle v \rangle \mathcal{N}^2 = \pi d^2 \sqrt{\frac{4k_{\mathrm{B}}T}{\pi m}}\mathcal{N}^2 \qquad (10.7\text{-}24)$$

where Z_{11} stands for the total collision rate per unit volume of molecules of substance 1 with other molecules of substance 1.

We 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 temperature. For example, doubling the number density quadruples Z_{11}, while doubling the absolute temperature raises the Z_{11} by a factor $\sqrt{2}$. These facts will aid in analyzing the rates of chemical reactions in gases.

EXAMPLE 10.8

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 10.7,

$$Z_{11} = \frac{1}{2} z_1 \mathcal{N}_1 = \frac{1}{2}(7.1 \times 10^9\ \mathrm{s}^{-1})(2.463 \times 10^{25}\ \mathrm{m}^{-3}) = 8.7 \times 10^{34}\ \mathrm{m}^{-3}\ \mathrm{s}^{-1}$$

$$(\text{Total rate}) = (8.7 \times 10^{34}\ \mathrm{m}^{-3}\ \mathrm{s}^{-1})(0.02445\ \mathrm{m}^3) = 2.1 \times 10^{33}\ \mathrm{s}^{-1}$$

The total number of collisions per second is about a billion times larger than Avogadro's number, since each molecule collides about a billion times per second.

Collisions and Free Paths in a Multicomponent Hard-Sphere Gas

If other substances are present, a molecule might have collided with other types of molecules between the two collisions with others of its own kind. The effect of such collisions will be to put bends in the collision cylinder. So long as there are not too many such bends, the volume of the cylinder will be nearly the same as if it were straight, so that the results for a one-component gas can be applied to the collisions between like particles in a multicomponent gas.

The radius of the collision cylinder (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:

$$d_{12} = \tfrac{1}{2}(d_1 + d_2) \tag{10.7-25}$$

where d_1 and d_2 are the collision diameters for collisions of like molecules.

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 $\langle v_2 \rangle$, the mean speed of molecules of type 2. Assume again that the average collision takes place at right angles. Figure 10.20 must be modified, as shown in Figure 10.21. In order for the molecules to collide, the distances from the site of the collision must be

$$x = t_c \langle v_1 \rangle, \qquad y = t_c \langle v_2 \rangle \tag{10.7-26}$$

where t_c is the time yet to elapse before the collision occurs. The molecular separation is given by the theorem of Pythagoras:

$$r = t_c[\langle v_1 \rangle^2 + \langle v_2 \rangle^2]^{1/2} \tag{10.7-27}$$

and the mean relative speed is given by

$$\langle v_{\mathrm{rel}} \rangle = \langle v_{12} \rangle = \sqrt{\langle v_1 \rangle^2 + \langle v_2 \rangle^2} = \sqrt{\frac{8k_{\mathrm{B}}T}{\pi m_1} + \frac{8k_{\mathrm{B}}T}{\pi m_2}}$$

$$\boxed{\langle v_{\mathrm{rel}} \rangle = \sqrt{\frac{8k_{\mathrm{B}}T}{\pi \mu_{12}}}} \tag{10.7-28}$$

where m_1 and m_2 are two molecular masses, and where μ_{12} is the **reduced mass** of particles 1 and 2:

$$\boxed{\mu_{12} = \frac{m_1 m_2}{m_1 + m_2} \quad \text{(definition of the reduced mass)}} \tag{10.7-29a}$$

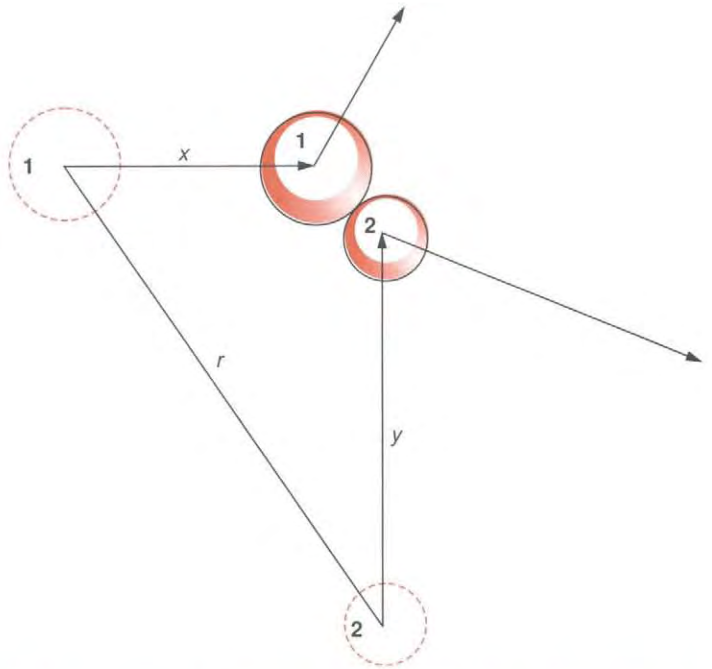

Figure 10.21. An "Average" (Right-Angle) Collision of Two Hard Spheres of Different Types. This diagram is similar to that of Figure 10.19, except that the particles are moving with different speeds, and must approach the collision site from different distances.

One can also write

$$\boxed{\frac{1}{\mu_{12}} = \frac{1}{m_1} + \frac{1}{m_2}} \tag{10.7-29b}$$

For a pair of identical particles, μ is equal to $m/2$, so that Eq. (10.7-28) is valid for that case as well as for two different substances.

EXAMPLE 10.9

Calculate the mean relative speed of nitrogen and oxygen molecules at 298 K.

Solution

Let nitrogen be substance 1 and oxygen be substance 2,

$$\langle v_{12}\rangle = \sqrt{\frac{8k_BT}{\pi\mu_{12}}} = \sqrt{\frac{8RT}{\pi N_{Av}\mu_{12}}} \tag{10.7-30}$$

$$N_{Av}\mu_{12} = \frac{(0.0280\ \text{kg mol}^{-1})(0.0320\ \text{kg mol}^{-1})}{0.0280\ \text{kg mol}^{-1} + 0.0320\ \text{kg mol}^{-1}} = 0.0149\ \text{kg mol}^{-1}$$

$$\langle v_{12}\rangle = \sqrt{\frac{8(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298\ \text{K})}{\pi(0.0149\ \text{kg mol}^{-1})}} = 650\ \text{m s}^{-1}$$

When we take account of the fact that the molecules of substance 2 are moving, we obtain the mean free path between collisions of a single particle of substance 1 with particles of substance 2:

$$\lambda_{1(2)} = \frac{\langle v_1 \rangle}{\langle v_{12} \rangle} \frac{1}{\pi d_{12}^2 \mathcal{N}_2} = \sqrt{\frac{m_2}{m_1 + m_2}} \frac{1}{\pi d_{12}^2 \mathcal{N}_2} \tag{10.7-31}$$

This is not necessarily an average straight-line path length. Collisions with other molecules of substances other than substance 2 can intervene between the two collisions with molecules of substance 2. 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. (10.7-31). It 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. (10.7-22):

$$z_{1(2)} = \frac{1}{\tau_{1(2)}} = \sqrt{\frac{8k_{\mathrm{B}}T}{\pi \mu_{12}}} \pi d_{12}^2 \mathcal{N}_2 \tag{10.7-32}$$

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. (10.7-32).

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. (10.7-32) times the number density of molecules of substance 1, and vice versa:

$$Z_{12} = z_{1(2)} \mathcal{N}_2 = z_{2(1)} \mathcal{N}_1 = \sqrt{\frac{8k_{\mathrm{B}}T}{\pi \mu_{12}}} \pi d_{12}^2 \mathcal{N}_1 \mathcal{N}_2 \tag{10.7-33}$$

There is no need to divide by 2, as in Eq. (10.7-24). The two molecules in a given collision are of different substances, so there is no double counting. The important physical fact shown in Eq. (10.7-33) is: *The total rate of collisions between molecules of two substances is proportional to the number density of each substance.* This fact, like that of Eq. (10.7-24), will aid us in discussing the rates of chemical reactions in gaseous systems.

***Exercise 10.20**

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 $z_{1(2)}$, $z_{2(1)}$, $z_{1(1)}$, and $z_{2(2)}$.
b. Find Z_{11}, Z_{22}, and Z_{12}.
c. Find the total number of collisions per second.

10.8 The Molecular Structure of Liquids

The model system of noninteracting particles is a usable model system for the pressure of a dilute gas because of the large average distances between molecules in a gas. Similarly, the hard sphere gas is a usable model for collisions in a dilute gas. Since liquid molecules are close together, it is more difficult to construct a simple model system for liquids. A great deal of theoretical research has been carried out on the properties of liquids, but a single comprehensive theory for the liquid state does not now exist. The theories that do exist are much more complicated than gas kinetic theory, and we are not prepared to discuss them.

We present a few elementary comments about the equilibrium structure of liquids, based on a simple but important fact: *The structure and properties of a liquid are primarily determined by the potential energy of the system, not its kinetic energy.* For example, consider liquid argon. The Lennard-Jones representation of the intermolecular potential function for argon was shown in Figure 10.15. If two argon atoms are separated by about 3.8×10^{-10} m (380 pm or 3.8 Å), they are at a stable equilibrium position, and the potential energy of the pair of atoms must be increased either to separate them or to push them closer together. Therefore, the atoms in solid argon or liquid argon tend to be about 380 pm from their nearest neighbors.

Substances such as argon consist of spherical atoms. In a solid lattice of spherical particles, 12 "nearest-neighbor" spheres can surround a given sphere. Each of these nearest neighbors touches the central sphere and four of the other 11 nearest neighbors. In solid argon, the nearest-neighbor distance is equal to 3.72×10^{10} m, nearly equal to the equilibrium separation of the Lennard-Jones potential of Figure 10.15. The volume of the solid is nearly fixed, because considerable energy is required either to increase or to decrease the nearest-neighbor distance.

In liquid argon, although the density is smaller than in the solid, the nearest neighbors are at very nearly the same distance as in the solid. On the average there are fewer nearest neighbors, because the nearest neighbors are disordered and voids exist between them. In a liquid of spherical molecules, the average number of nearest neighbors is approximately 10 or 11, in accordance with the fact that the liquid is less dense than the solid.

*Exercise 10.21

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 nearest neighbors at nearly the same distance as in a solid, their motions are very different from those of gaseous atoms. The nearest-neighbor molecules form a sort of "cage" in which a given molecule is confined by the repulsive intermolecular forces of the neighbors. Instead of moving considerable distances in nearly straight trajectories between occasional collisions, a molecule of a liquid is almost constantly involved in collisions as it undergoes a kind of zig-zag rattling motion.

Intermolecular forces do not depend on velocities, so the velocity distribution of Section 10.2 is valid for a liquid or solid as well as for a gas. The mean speed of molecules of mass m in a liquid at temperature T is given by Eq. (10.3-7):

$$\langle v \rangle = \sqrt{\frac{8k_BT}{\pi m}} \tag{10.8-1}$$

Since the molecules in a liquid are much closer together than in a gas, and since they are moving just as rapidly 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 the definition of 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.[8]

EXAMPLE 10.10

Estimate the collision frequency of an argon atom in liquid argon at its normal boiling temperature, 85 K. Assume that the molecule is moving at the mean speed of gaseous argon molecules at 85 K. Find the time required to travel twice the distance from the minimum in the potential function of Figure 10.15 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.

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 corresponding to 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

$$1.49 \times 10^{-21}\ \mathrm{J} = 4\varepsilon\left[\left(\frac{\sigma}{r'}\right)^{12} - \left(\frac{\sigma}{r'}\right)^{6}\right]$$

where r' is the value of r that we seek. This equation must be solved by numerical approximation. 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 m $\mathrm{s^{-1}}$ is equal to 4.7×10^{-13} s, giving a collision rate of $2.1 \times 10^{12}\ \mathrm{s^{-1}}$. The rough approximate calculation in this example is based on a web of assumptions, but it illustrates the rapid collision rates in a liquid.

As seen in Example 10.10, collision rates of a molecule in a typical liquid are roughly several hundred times larger than in a typical gas.

Summary of the Chapter

We have deduced the macroscopic properties of a model system of noninteracting point mass molecules by averaging over molecular states, using the Maxwell probability

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[8] P. K. Davies, *J. Chem. Phys.*, **57**, 517 (1972).

distribution of molecular velocities:

$$g(v) = \left(\frac{m}{2k_{\mathrm{B}}T}\right)^{3/2} e^{-mv^2/2k_{\mathrm{B}}T}$$

The probability distribution for molecular speeds is

$$f_v(v) = 4\pi\left(\frac{m}{2k_{\mathrm{B}}T}\right)^{3/2} v^2 e^{-mv^2/2k_{\mathrm{B}}T}$$

We derived formulas for the mean speed, the most probable speed, and the root-mean-square speed.

It was found that the model system obeyed the ideal gas law and Dalton's law of partial pressures. The rate of wall collisions per unit area per unit time was also derived:

$$\nu = \frac{1}{4}\frac{N}{V}\langle v\rangle = \frac{1}{4}\mathcal{N}\langle v\rangle$$

Beginning with Section 10.6, we discussed a model system with interacting molecules. The hard-sphere gas is a special case of this system. 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 one-component and for 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.

In Section 10.8, we presented a few elementary ideas about the molecular structure of liquids. 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 a hundred times as many collisions per second as does a molecule in a typical gas.

PROBLEMS

Problems for Section 10.1

10.22. A group of people has the following distribution of annual income:

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. The **median** of a set of numbers is a kind of average value 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 our set of people.

b. Find the mean income.

c. Find the root-mean-square income.

d. Find the mode.

e. Explain any differences between these average values.

*10.23. Find the mean value and the root-mean-square value of $\sin(x)$ for $0 < x < 2\pi$ radians, assuming a uniform probability distribution.

10.24. Find the mean value and the root-mean-square value of $\sin(x)$ for $-\infty < x < \infty$, assuming the standard normal (gaussian) probability distribution

$$f(x) = \frac{1}{\sqrt{2\pi}} e^{-x^2/2}$$

Problems for Section 10.2

*10.25. For nitrogen molecules at 300 K, estimate the error in the normalization integral of Eq. (10.2-20) that is produced by neglecting relativity. The following asymptotic formula[9] gives values of the error function for large arguments:

$$\mathrm{erf}(z) = 1 - \frac{e^{-z^2}}{\sqrt{\pi}z}\left(1 + \sum_{m=1}^{\infty} \frac{(1)(3)\cdots(2m-1)}{(2z^2)^m}\right)$$

10.26. **a.** Use Eq. (10.2-42) 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 m s^{-1}.

b. Find the correct value of the probability and compare it with your result from part (a).

*10.27. Find the fraction of the molecules in a gas which have

$$v_x^2 > \frac{k_B T}{m}$$

Show that this fraction is the same for all gases at all temperatures.

10.28. 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

$$v_{\mathrm{esc}} = 1.12 \times 10^4 \text{ m s}^{-1} = 2.5 \times 10^4 \text{ miles per hour}$$

a. Find the fraction of N_2 molecules at 298 K having an upward vertical velocity component exceeding v_{esc}.

b. Find the fraction of helium atoms at 298 K having an upward vertical velocity component exceeding v_{esc}. The asymptotic formula in Problem 10.25 can be used.

c. Find the fraction of helium atoms at 298 K having a speed exceeding v_{esc}. Note: You will need the identity in Problem 10.29 or a numerical approximation to an integral here.[10]

d. Find the temperature at which the mean speed of helium atoms equals the escape velocity.

Problems for Section 10.3

*10.29. **a.** Find the fraction of molecules that have speeds greater than $k_B T/m$. Explain the relationship of this fraction to the fraction computed in Problem 10.27. You can use the identity

$$\int_0^x t^2 e^{-at^2}\, dt = \frac{\sqrt{\pi}}{4a^{3/2}} \mathrm{erf}(\sqrt{a}x) - \frac{x}{2a} e^{-ax^2}$$

b. Find the fraction of molecules that have kinetic energies greater than $k_B T/2$. Explain the relationship of this fraction to that part (a).

10.30. Find the fraction of molecules in a gas that have:

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

Explain why these fractions are independent of the temperature and of the mass of the molecules.

Note: You will need the identity in Problem 10.29 or numerical approximations to integrals for this problem.[11]

10.31. The speed of sound in air and in other gases is somewhat less (about 20% 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 will depend on the temperature?

c. How do you think that the speed of sound in helium gas will compare with its speed in air? Why do you think a person's voice sounds different after a breath of helium?

10.32. Find the fraction of molecules in a gas that have speeds greater than 80% of the mean speed.

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[9] M. Abramowitz and I. A. Stegun, *op. cit.*, p. 298 (Note 1).

[10] See R. G. Mortimer, *Mathematics for Physical Chemistry*, 2nd ed, Academic Press, New York, 1999, pp. 105ff.

[11] R. G. Mortimer, 1999, *loc. cit* (Note 10).

10.33. **a.** The **standard deviation** of an arbitrary probability distribution for the variable x is defined by Eq. (10.2-38):

$$\sigma_x = [\langle x^2 \rangle - \langle x \rangle^2]^{1/2} \quad \text{(definition)}$$

where x stands for the independent variable. 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.

10.34. Find the ratio of the mean speeds of O_2 and O_3 molecules

a. at 298 K
b. at 1000 K

*10.35. If oxygen molecules had mass 32 g instead of 32 amu, what would their mean speed be at 298 K?

10.36. **a.** Find a general expression for the median speed of molecules in a dilute gas. Hint: See the identity in Problem 10.29. Your expressions will contain a constant that you will have to evaluate numerically.

b. Find the median speed for oxygen molecules at 298 K.

Problems for Section 10.4

10.37. In Section 10.4, 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.

10.38. 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.

*10.39. Estimate the mass (in pounds and in kilograms) whose gravitational force at the surface of the earth is equal to the force of the atmosphere on your entire body. State any assumptions.

10.40. Derive the ideal gas equation of state without using the velocity distribution function. (Hint: Start with Eq. (10.2-29) and (10.5-12).)

Problems for Section 10.5

*10.41. 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 h.

10.42. 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 container per second.

*10.43. 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.

10.44. 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 K

Comment on the temperature dependence.

*10.45. 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 μm 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.)

10.46. Estimate the time required for a bicyle tire to go flat due to a circular hole of 50 μm diameter. State your assumptions.

Problems for Section 10.6

*10.47. **a.** Find the probability of drawing the ace of spades from one 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.

10.48. Compute the odds for each of the possible values of the sum of the two numbers showing when two dice are thrown.

*10.49. 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}.

10.50. 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.

*10.51. Estimate the difference in barometric pressure between the ground floor of a building and the forty-first floor, assumed to be 400 ft (122 m) higher. State any assumptions.

10.52. A 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).

Problems for Section 10.7

*10.53. Write an expression for the excluded volume of a pair of hard-sphere molecules of different sizes.

10.54. Calculate the pressure of carbon dioxide gas at 298.15 K and a molar volume of 24.00 L, assuming (a) the ideal gas equation of state, (b) the van der Waals equation of state, and (c) Eq. (10.7-6), taking the same value of the parameter b as for the van der Waals equation of state.

*10.55. 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.

b. Using the value of molecular diameter calculated from the value of the van der Waals parameter b.

10.56. 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.

*10.57. Another approximate representation for intermolecular pair potentials is the **exponential-6 potential**

$$u(r) = be^{-ar} - cr^{-6}$$

where a, b, 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 exponential-6 representation of the interatomic potential of argon 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.

10.58. 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 rough 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.

*10.59. 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.

10.60. The intermolecular potential of argon can be represented as a square well with $d = 3.162 \times 10^{-10}$ m, $c = 5.850 \times 10^{-10}$ m, and $u_0 = 9.58 \times 10^{-22}$ J. Evaluate the second virial coefficient of argon at 70 K, 140 K, and 300 K. Compare your values with those in Table A.4 of Appendix A. Find the temperature at which the second virial coefficient is equal to zero.

10.61. A good 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

$$y = \frac{\pi N d^3}{6V}$$

*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 10.18.

10.62. Explain why, after the correction for relative motion was made, the formula for the collision time is still

$$\tau_{\text{coll}} = \frac{\lambda}{\langle v \rangle} \quad \text{(correct)}$$

instead of

$$\tau_{\text{coll}} = \frac{\lambda}{\langle v_{\text{rel}} \rangle} \quad \text{(wrong)}$$

***10.63.** For a mixture of 2.000 mol of CO and 1.000 mol of O_2 at 292 K and 1.000 atm, calculate the following.

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.

10.64. 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.

10.65. Estimate the mean free path for hydrogen atoms under the conditions of the previous problem.

Problems for Section 10.8

10.66. The density of ice is 0.917 g mL^{-1} at 0°C, and that of liquid water is 1.000 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.

***10.67.** **a.** Calculate the density of solid xenon from the Lennard-Jones parameters.

b. The density of liquid xenon is 3.52 g mL^{-1}. Estimate the number of nearest-neighbor atoms in the liquid.

10.68. **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 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.

General Problems

10.69. Assume that a certain sample of air maintained at 25°C contains dust particles all of which are the same size. The diameter of the dust particles is 5.0 μm and their density is 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 giant 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.

10.70. 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.

***10.71.** 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.

10.72. Assume that a certain sample of polluted air has the following composition by moles: nitrogen, 76.08%; oxygen, 20.41%; water vapor, 2.63%; 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.

*10.73. Label each of the following statements as either true or false. If a statement is true only under special circumstances, label is 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 ten times as great as the distance betweeen 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. Since 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.

11

Transport Processes

OBJECTIVES

After studying this chapter, a student should:

1. understand qualitatively the behavior of a rate of a process governed by a linear law;
2. be able to solve a variety of problems relating to transport processes in fluids;
3. understand the gas kinetic theory of transport processes in dilute gases;
4. understand qualitatively the relation of molecular motions in liquids to transport processes and electrical conduction in liquids.

PRINCIPAL FACTS AND IDEAS

1. If there is any tendency for a process to occur in a system, that system is not at equilibrium.
2. The macroscopic description of nonequilibrium states of fluid systems requires two classes of variables that do not occur in equilibrium thermodynamics: variables to specify the extent to which the system deviates from equilibrium and variables to express the rates of processes.
3. The three principal transport processes are heat conduction, diffusion, and viscous flow.
4. Each transport process is described macroscopically by an empirical linear law.
5. Molecular theories of transport processes in dilute gases are based on gas kinetic theory.
6. The electrical conductivity of solutions of ions can be understood on the basis of ionic motion in an electric field.

11.1 The Macroscopic Description of Nonequilibrium States

In a one-phase simple system at equilibrium, the intensive macroscopic state is specified by $s+1$ variables, where s is the number of independent chemical substances. These variables could be T, P, and $s-1$ concentrations or mole fractions. (We use the letter s now rather than the letter c for the number of substances because we will use c for concentrations.) Nonequilibrium states are more complicated than equilibrium states and require more variables to specify them. The discussion of this chapter is limited to a one-phase simple system containing several substances in which no chemical reactions can occur and in which the deviation from equilibrium is not very large. Processes that take place far from equilibrium, including such things as explosions and turbulent flow, are difficult to describe mathematically, and we do not attempt to describe them.

The thermodynamic variables of a nonequilibrium system can depend on position, although the definitions of these variables require measurements at equilibrium. In order to define these variables in a nonequilibrium system, we visualize the following process: A small portion of the system (a subsystem) is suddenly removed from the system and allowed to relax adiabatically to equilibrium at fixed volume. Once equilibrium is reached, variables such as the temperature, pressure, density, and concentrations in this subsystem are measured. These measured values are assigned to a point inside the volume originally occupied by the subsystem and to the time at which the subsystem was removed. This procedure is performed repeatedly at different times and different locations in the system, and interpolation procedures are carried out to obtain smooth functions of position and time to represent the temperature, concentrations, etc.

$$T = T(x, y, z, t) = T(\mathbf{r}, t) \tag{11.1-1a}$$

$$P = P(x, y, z, t) = P(\mathbf{r}, t) \tag{11.1-1b}$$

$$c_i = c_i(x, y, z, t) = c_i(\mathbf{r}, t) \qquad (i = 1, 2, \ldots, s) \tag{11.1-1c}$$

where c_i is the concentration of substance i, measured in mol m^{-3} or mol L^{-1}. The symbol $\mathbf{r}$ stands for the position vector with components x, y, and z.

The intensive variables are measured after each subsystem comes to equilibrium, so they obey the same relations among themselves as they would in an equilibrium system. At any point in a nonflowing system, $s+1$ intensive variables are independent variables, and all other intensive variables are dependent variables. If the system is flowing, a specification of the flow velocity as a function of position and time is also needed. We also need a specification of the dependence of the independent variables on position. We will consider only the near-equilibrium case, in which the deviation from equilibrium is not very large. In this case, we assume that the intensive state at a point is adequately described by $s+1$ independent intensive variables and the flow velocity plus the gradients of these quantities.

The **gradient** of a scalar function f is defined by Eq. (B-37) of Appendix B. It is a vector 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. For example, the temperature gradient is denoted by ∇T and is given in cartesian coordinates by

$$\nabla T = \mathbf{i}\,\frac{\partial T}{\partial x} + \mathbf{j}\,\frac{\partial T}{\partial y} + \mathbf{k}\,\frac{\partial T}{\partial z} \tag{11.1-2}$$

where **i**, **j**, and **k** are unit vectors in the directions of the x, y and z axes. The concentration gradient of substance number i is

$$\nabla c_i = \mathbf{i}\,\frac{\partial c_i}{\partial x} + \mathbf{j}\,\frac{\partial c_i}{\partial y} + \mathbf{k}\,\frac{\partial c_i}{\partial z} \tag{11.1-3}$$

The time derivatives of the temperature, concentrations, etc., are not required to specify the state of the system. They are dependent variables.

*Exercise 11.1

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 $\partial c_2/\partial t$.

The flow velocity **u** can also be written as a function of position and time:

$$\mathbf{u} = \mathbf{u}(x, y, z, t) = \mathbf{u}(r, t) = \mathbf{i}u_x(\mathbf{r}, t) + \mathbf{j}u_y(\mathbf{r}, t) + \mathbf{k}u_z(\mathbf{r}, t) \tag{11.1-4}$$

Each of the three components of the velocity has a gradient with three components. The gradient of the flow velocity vector thus has nine components. Such a nine-component quantity is called a **dyadic**, or **cartesian tensor**. Fortunately, we will be able to avoid using more than one component of it at a time. For example, consider

$$(\nabla\mathbf{u})_{zy} = \frac{\partial u_y}{\partial z} \tag{11.1-5}$$

which is the derivative of the y component of the velocity with respect to z, giving the rate of change of u_y in the z direction. This quantity specifies the **rate of shear**, or the rate at which one layer of the fluid is sliding (shearing) past an adjacent layer.

Gradients can also be expressed in other coordinate systems. In cylindrical polar coordinates the three coordinates are z, as in cartesian coordinates, ϕ as in spherical polar coordinates, and ρ, equal to $\sqrt{x^2 + y^2}$. The gradient of a scalar function f is given by

$$\nabla f = \mathbf{e}_\rho\,\frac{\partial f}{\partial \rho} + \mathbf{e}_\phi\,\frac{1}{\rho}\frac{\partial f}{\partial \phi} + \mathbf{k}\,\frac{\partial f}{\partial z} \tag{11.1-6}$$

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.

EXAMPLE 11.1

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

$$\mathbf{u} = \mathbf{k}u_z(\rho) = \mathbf{k}A(\rho^2 - R^2)$$

where A is a constant. Find the gradient of this velocity.

Solution

All of the nine components will vanish except for $\partial u_z/\partial \rho$:

$$\nabla u_z = \mathbf{e}_\rho\,\frac{\partial u_z}{\partial \rho} = \mathbf{e}_\rho 2A\rho$$

The gradient of the flow velocity points at right angles to the velocity.

The gradient of a function f expressed in spherical polar coordinates is

$$\nabla f = \mathbf{e}_r \frac{\partial f}{\partial r} + \mathbf{e}_\theta \frac{1}{r} \frac{\partial f}{\partial \theta} + \mathbf{e}_\phi \frac{1}{r \sin(\theta)} \frac{\partial f}{\partial \phi} \qquad (11.1\text{-}7)$$

where the unit vectors $\mathbf{e}_r$, $\mathbf{e}_\theta$, and $\mathbf{e}_\phi$ point in the directions in which infinitesimal changes in the respective coordinates move a point in space.

In the near-equilibrium case all of the gradients of the intensive variables and of the flow velocity are assumed to be small. We do not attempt a description of turbulent flow and other processes involving states far from equilibrium, in which case the gradients might be large and chaotic.

11.2 Transport Processes

In the absence of chemical reactions, the principal nonequilibrium processes that can occur in a simple system are heat conduction, diffusion, and viscous flow. These processes are called **transport processes** because in each process some quantity is transported from one location to another. In heat conduction, energy in the form of heat is transported; in diffusion, substances are transported; and in viscous flow, momentum is transported. These three processes are important in the chemical process industry, in biological organisms, and in many activities of everyday life.

Variables to Specify the Rates of Transport Processes

In addition to variables needed to specify the nonequilibrium state of the system, dependent variables are needed to specify the rates of heat flow, diffusion, and viscous flow. The rate of heat flow is specified by the **heat flux**, which is a vector $\mathbf{q}$ that has the direction of the flow of heat and has 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.

Specification of the rate of viscous flow is not quite so straightforward as that of heat flow and diffusion. Figure 11.1 shows an idealized experimental apparatus for the measurement of viscosity, which is the resistance of a fluid to shearing flow. The fluid is confined between two very large parallel plates perpendicular to the z direction. The top plate is dragged along parallel to its surface in the y direction, and the lower plate is fixed to a stationary object (assumed to have infinite mass). The moving plate drags a layer of fluid along, transferring momentum to it, and this layer of fluid drags another layer along, transferring momentum to it, and so on. The momentum is eventually transferred to the stationary object, which has an infinitesimal acceleration due to its infinite mass. Because of frictional losses the speed of each layer is a little smaller than the speed of the layer above it, giving a nonzero value to the rate of shear defined in Eq. (11.1-5). In Figure 11.1, 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**.

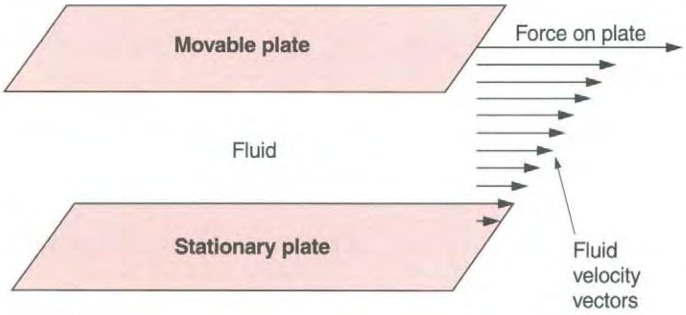

Figure 11.1. An Idealized Viscosity Experiment. The lower plate is stationary, and the upper plate is pulled at a constant speed relative to the lower plate. The fluid between the plates exhibits laminar flow, with a velocity that depends smoothly on the height above the lower plane.

In order to make our discussion of viscous flow similar to that of heat flow and diffusion, the **momentum flux** could be used as a rate variable. However, it is customary to use as a rate variable (dependent variable) the **force per unit area** that must be exerted on the moving plate by an external agent in order to keep it at a steady state. Since Newton's second law relates force to the rate of change of momentum, this variable gives the same information in a different form. A force per unit area is a pressure if the force is exerted perpendicular to the area. The force exerted on the upper plate is parallel to the area so this force per unit area is not a pressure.

Driving Forces and Linear Laws

To a first approximation each rate variable depends on a single state variable that we will 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 velocity gradient (rate of shear) is the driving force for viscous flow. Each rate variable is a dependent variable whose value is determined by the value of the driving force of that process. 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.[1]

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.

There are three well-known empirical laws that give the dependence of the rates on the driving forces for our three transport processes. The first is **Fourier's law of heat conduction**.

$$\mathbf{q} = -\kappa\,\nabla T \quad \text{(Fourier's law)} \tag{11.2-1}$$

where κ is called the **thermal conductivity**. If the temperature varies only in the z direction, this equation is

$$q_z = -\kappa\,\frac{\partial T}{\partial z} \tag{11.2-2}$$

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[1] See, for example, R. G. Mortimer and H. Eyring, *Proc. Natl. Acad. Sci. USA*, **77**, 1828 (1980) and R. L. Rowley and F. H. Horne, *J. Chem. Phys.*, **68**, 325 (1978).

Fourier's law is an example of a **linear law**. It is called linear because the rate is directly proportional to (linearly dependent on) the driving force. The thermal conductivity κ is the proportionality constant. It is not a true constant and depends on the composition, the temperature, the pressure, and the identities of the substances present, but does not depend on the gradients of temperature, concentrations, or velocity. Although gaseous systems, liquid systems, and solid systems are very different from each other on the molecular level, Fourier's law holds quite accurately for all three. Table A.16 in Appendix A gives the values of the thermal conductivity for several pure substances.

In some cases transport processes are studied by measuring the rate at which an isolated system originally in a nonequilibrium state relaxes toward equilibrium. In other cases a system is maintained in a time-independent nonequilibrium state (a **steady state**). A time-independent temperature gradient might be maintained by keeping one end of a system at one temperature and the other end at another temperature while heat flows through the system as in Figure 4.8. A steady state is not an equilibrium state, although it is time-independent, since an external agent must maintain the steady state.

EXAMPLE 11.2

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. Calculate the amount of heat flowing through the benzene per hour after a steady state is achieved, neglecting convection.

Solution

The thermal conductivity of pure benzene at 26°C and 1.00 atm pressure is equal to $0.151\ \mathrm{J\ m^{-1}\ s^{-1}\ K^{-1}}$. 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 $\Delta T/\Delta z$. In a steady state, the temperature gradient must be uniform in a system with uniform thermal conductivity and uniform cross-sectional area, and the gradient at any point must equal the average gradient. If the temperature gradient in such a uniform system were not uniform, heat would accumulate in some region and we would not have a steady state. Fourier's law now gives the result

$$q_z = -\kappa(\Delta T/\Delta z) = -(0.151\ \mathrm{J\ m^{-1}\ s^{-1}\ K^{-1}})(100\ \mathrm{K\ m^{-1}}) = -15.1\ \mathrm{J\ m^{-2}\ s^{-1}}$$

The cross-sectional area is $0.0100\ \mathrm{m^2}$, so the total amount of heat flowing in 1.00 h is

$$|-(15.1\ \mathrm{J\ m^{-2}\ s^{-1}})(0.0100\ \mathrm{m^2})(3600\ \mathrm{s})| = 544\ \mathrm{J}$$

Fick's law is named for Adolf Fick, 1829–1901, a German physiologist.

The second linear law is **Fick's law of diffusion**:

$$\mathbf{J}_i = -D_i \nabla c_i \quad \text{(Fick's law)} \tag{11.2-3}$$

If the concentration varies only in the z direction, Fick's law becomes

$$J_{iz} = -D_i\left(\frac{\partial c_i}{\partial z}\right) \tag{11.2-4}$$

The quantity D_i is 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. Fick's law is a very good approximation for most gaseous, liquid and solid systems. Table A.17 gives the value of several diffusion coefficients near room temperature. It is remarkable that 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.

***Exercise 11.2**

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 mol $\mathrm{L^{-1}}$ and at the bottom of the cell is maintained at 0.0300 mol $\mathrm{L^{-1}}$.

Fick's law expressed in Eq. (11.3-3) is sometimes called **Fick's first law**. **Fick's second law** is obtained by combining Fick's first law with the **equation of continuity**. We now derive a one-dimensional version of the equation of continuity. Consider a small 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 11.2. The area of the large face of the slab is $\mathscr{A}$ and the thickness of the slab is Δz. A diffusion flux is present in the upward direction. The diffusion flux is the amount passing unit are per unit time and the net amount of substance i entering the slab per second from below is

$$\text{Influx} = \mathscr{A} J_{iz}(z') \tag{11.2-5}$$

where z' is the value of the z coordinate at the bottom of the slab. The amount leaving the slab per second through its top surface is

(11.2-6)

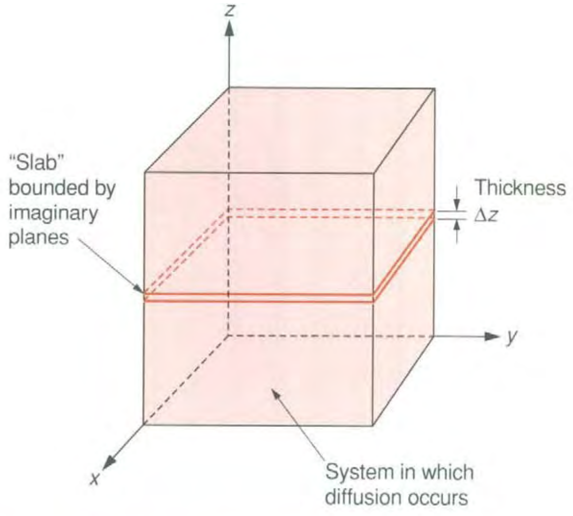

Figure 11.2. A Slab-shaped Portion of a Fluid System. This figure is used in the derivation of the one-dimensional version of the equation of continuity by considering the influx and efflux of one component into and out of the slab.

where we specify that J_{iz} can depend on z. The rate of change of the amount of substance i in the slab is the excess of the influx over the efflux:

$$\frac{dn_i}{dt} = \mathscr{A}[J_{iz}(z') - J_{iz}(z' + \Delta z)] \tag{11.2-7}$$

Since the concentration of substance i is the amount of i per unit volume, the rate of change of the concentration is

$$\frac{\partial c_i}{\partial t} = \frac{(dn_i/dt)}{\mathscr{A}\,\Delta z} = \frac{J_{iz}(z') - J_{iz}(z' + \Delta z)}{\Delta z} \tag{11.2-8}$$

The derivative $\partial c_i/\partial t$ is a partial derivative because this derivative is taken at fixed values of the coordinates. Now we take the limit that Δz approaches zero so that the right-hand side of Eq. (11.2-8) becomes a derivative. The result is the one-dimensional version of the equation of continuity:

$$\frac{\partial c_i}{\partial t} = -\frac{\partial J_{iz}}{\partial z} \tag{11.2-9}$$

Its physical content is the conservation of matter because it is equivalent to saying that rate of change in the concentration is just the difference between what arrives and what leaves. If a chemical reaction is using up or producing substance i, this equation must be modified.

The three-dimensional version of the equation of continuity is

$$\frac{\partial c_i}{\partial t} = -\left(\frac{\partial J_{ix}}{\partial x} + \frac{\partial J_{iy}}{\partial y} + \frac{\partial J_{iz}}{\partial z}\right) = -\nabla \cdot \mathbf{J}_i \tag{11.2-10}$$

where $\nabla \cdot \mathbf{J}_i$ is called the **divergence** of $\mathbf{J}_i$, defined in Eq. (B-38) 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 11.3

Derive Eq. (11.2-10) by considering a small cube instead of a slab in a fluid system.

We substitute Eq. (11.2-4) into Eq. (11.2-9) to obtain

$$\frac{\partial c_i}{\partial t} = \frac{\partial}{\partial z}\left(D_i \frac{\partial c_i}{\partial z}\right) \quad \text{(Fick's second law)} \tag{11.2-11}$$

This is **Fick's second law of diffusion** for the one-dimensional case. If D_i is independent of composition and is therefore independent of position,

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial^2 c_i}{\partial z^2} \quad \text{(the ``diffusion equation'')} \tag{11.2-12}$$

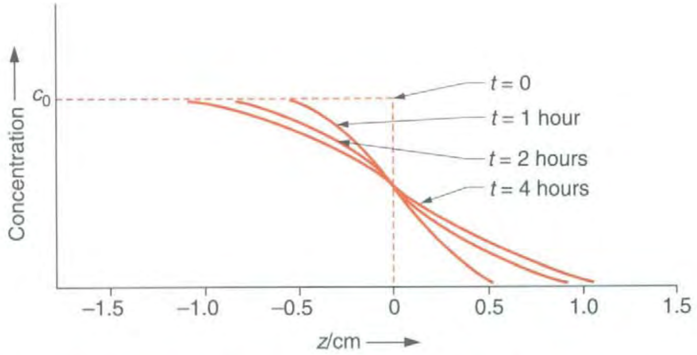

Figure 11.3. Concentration as a Function of Position in a Diffusing System, as in Eq. (11.2-14). This figure corresponds to the initial state with a uniform concentration of the diffusion component in the bottom half of the cell, and none in the top half. The concentration profile is given for the times indicated, showing that, for a typical liquid-state value of the diffusion coefficient, diffusion over a distance of a centimeter requires several hours.

This equation is called the **diffusion equation**. If the concentration depends on all three coordinates and if D_i is constant,

$$\frac{\partial c_i}{\partial t} = D_i\left[\frac{\partial^2 c_i}{\partial x^2} + \frac{\partial^2 c_i}{\partial y^2} + \frac{\partial^2 c_i}{\partial z^2}\right] = D_i \nabla^2 c_i \tag{11.2-13}$$

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**. It also occurs in the Hamiltonian operator of quantum mechanics.

Equation (11.2-12) is a partial differential equation that can be solved for some sets of initial conditions. For example, if a solution initially containing substance 2 at concentration c_0 is placed in the bottom half of a cell and pure solvent (substance 1) is carefully layered above it in the top half of the cell, the initial condition is

$$c_2(z, 0) = \begin{cases} c_0 & \text{if } z < 0 \\ 0 & \text{if } z > 0 \end{cases}$$

This initial condition fails to meet our criterion of small gradients at the location $z = 0$, but the state of the system rapidly becomes one in which the gradient of c_2 is fairly small and Fick's law seems to hold quite accurately for this case. The solution of Eq. (11.2-12) that satisfies this initial condition for a long cell is[2]

$$c_2(z, t) = \frac{c_0}{2}\left[1 - \mathrm{erf}(z/2\sqrt{D_2 t})\right] \tag{11.12-14}$$

where erf(...) is the error function, introduced in Chapter 10 and described in Appendix C. This solution is shown in Figure 11.3 for three values of t and for a value of D_2 equal to 1.0×10^{-9} m^2 s^{-1}, a typical value for ordinary liquids. This figure illustrates the fact that ordinary liquids require several hours to diffuse one centimeter.

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[2] See D. P. Shoemaker, C. W. Garland, and J. W. Nibler, *Experiments in Physical Chemistry*, 6th ed., McGraw-Hill, New York, 1996, pp. 134 ff for a solution pertaining to a cell of finite length.

Exercise 11.4

Show by substitution that the function of Eq. (11.2-14) satisfies Eq. (11.2-12). You will need the identity:

$$\frac{d}{dx}\int_0^x f(u)\,du = f(x) \tag{11.2-15}$$

Another case that can be mathematically analyzed is obtained 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. Let $z = 0$ at the center of the cell. An idealized representation of this initial condition is

$$c_2(z,0) = \begin{cases} \infty & \text{if } z = 0 \\ 0 & \text{if } z \neq 0 \end{cases}$$

This concentration function also fails to meet our criterion of small gradients, but Fick's law seems to hold fairly well for this case. For a long cell, a solution to Eq. (11.2-12) that matches this initial condition is

$$c_2(z,t) = \frac{n_0}{2\sqrt{\pi D_2 t}}e^{-z^2/4D_2t} \tag{11.2-16}$$

where the total amount of substance 2 initially present per unit cross-sectional area is denoted by n_0. This function is shown in Figure 11.4 for a value of D_2 equal to 1.0×10^{-9} m^2 s^{-1} and for three values of t. It is represented by a gaussian curve similar to the gaussian distribution introduced in Chapter 10.

Exercise 11.5

a. Show by substitution that the function in Eq. (11.2-16) satisfies Eq. (11.2-12).

b. Show that the same amount of substance 2 is present at a time $t = t_2$ as at time $t = t_1$ by showing that

$$\int_{-\infty}^{\infty} c_2(z,t)\,dz = n_0$$

which is independent of t. Since the cell is assumed to be long, we can use infinite limits for the integrals without serious numerical error.

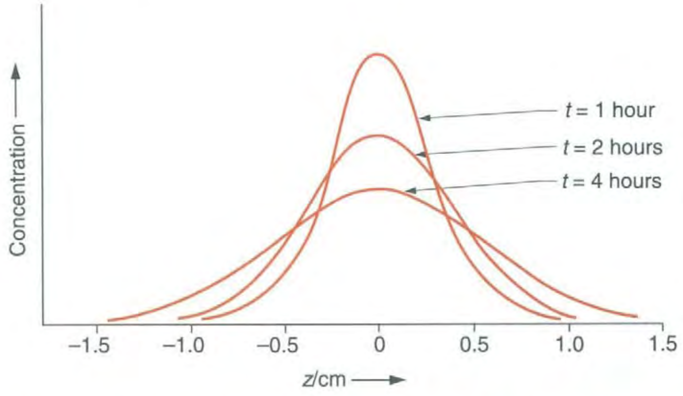

Figure 11.4. Concentration as a Function of Position in a Diffusing System with an Initial Thin Layer of Solute, as in Eq. (11.2-16). This figure corresponds to the initial state of a very thin layer of the diffusing substance at $z = 0$.

Since all of the molecules of substance 2 started out at $z = 0$, we can use Eq. (11.2-16) 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

$$\text{Fraction in slab} = \frac{c_2(z', t)\, dz}{\int_{-\infty}^{\infty} c_2(z, t)\, dz} = \frac{c_2(z', t)\, dz}{n_0} \tag{11.2-17}$$

where we have used the value of the integral from Exercise 11.5. This fraction is a probability much like those of Chapter 10, except that in Chapter 10 we were dealing with velocities instead of positions. The mean value of the coordinate z at time t is given by an expression analogous to that of Eq. (10.2-3):

$$\langle z(t) \rangle = \frac{1}{n_0} \int_{-\infty}^{\infty} z c_2(z, t)\, dz = 0 \tag{11.2-18}$$

The fact that the mean displacement in the z direction is zero means 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 change in the z coordinate is an inherently nonnegative quantity and gives 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:

$$z_{\text{rms}} = \langle z^2 \rangle^{1/2} = \left[\frac{1}{n_0} \int_{-\infty}^{\infty} z^2 c_2(z, t)\, dz \right]^{1/2} = [2D_2 t]^{1/2} \tag{11.2-19}$$

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 typical of a process which can be represented by a "random walk,"[3] which is a model process in which an object repeatedly takes a step of fixed length in a randomly chosen direction.

Exercise 11.6

Look up the integral and show that Eq. (11.2-19) is correct.

Although we obtained the root-mean-square distance traveled by a diffusion molecule by considering a special case in which all of the molecules started out at the same value of z, the individual molecules diffuse in the same way for other initial conditions, and we can use Eq. (11.2-19) for any kind of initial conditions, and for the x and y directions as well.

EXAMPLE 11.3

Find the root-mean-square distance in three dimensions diffused by sucrose molecules in 30.0 min in water at 25°C.

Solution

The root-mean-square distance traveled in three dimensions is

$$r_{\text{rms}} = [\langle x^2 \rangle + \langle y^2 \rangle + \langle z^2 \rangle]^{1/2} = [3\langle z^2 \rangle]^{1/2} = \sqrt{3} z_{\text{rms}}$$

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[3] L. E. Reichl, *A Modern Course in Statistical Physics*, University of Texas Press, Austin, 1980, pp. 151ff.

where we use the fact that all three directions are equivalent. From Table A.17 of Appendix A, the value of D at 25°C is $0.673 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$.

$$r_{\mathrm{rms}} = [6D_2t]^{1/2} = (6(0.673 \times 10^{-9}\ \mathrm{m^2\ s^{-1}})(30.0\ \mathrm{min})(60\ \mathrm{s\ min^{-1}}))^{1/2}$$
$$= 2.70 \times 10^{-3}\ \mathrm{m} = 0.270\ \mathrm{cm}$$

Newton's law of viscous flow is named for Sir Isaac Newton, 1642–1727, a great British mathematician and physicist who is famous for Newton's law of motion and for being one of the inventors of calculus.

Newton's law of viscous flow is the third linear law:

$$P_{zy} = \eta\left(\frac{\partial u_y}{\partial z}\right) \quad \text{(Newton's law)} \tag{11.2-20}$$

where P_{zy} is the force per unit area parallel to the upper plate in Figure 11.1 that is required to maintain the steady speed that corresponds to the rate of shear on the right-hand side of the equation. The first subscript on P_{zy} indicates that the upper plate is perpendicular to the z direction, and the second subscript indicates that the force is in the y direction (parallel to the plate). The derivative $(\partial u_y/\partial z)$ is a component of the velocity gradient and is the rate of shear. 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. There are some liquids, such as blood and polymer solutions, that do not obey Newton's law. These fluids are called **non-newtonian fluids** or **thixotropic fluids**, and are described by a viscosity coefficient that depends on the rate of shear.

EXAMPLE 11.4

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 11.1, 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 components of the velocity gradient has an average value of

$$\frac{\partial u_y}{\partial z} = \frac{\Delta u_y}{\Delta z} = \frac{0.250\ \mathrm{m\ s^{-1}}}{0.0500\ \mathrm{m}} = 5.00\ \mathrm{s^{-1}}$$

so that

$$P_{zy} = (0.001002\ \mathrm{kg\ m^{-1}\ s^{-1}})(5.00\ \mathrm{s^{-1}})$$
$$= 5.01 \times 10^{-3}\ \mathrm{kg\ m^{-1}\ s^{-2}} = 5.01 \times 10^{-3}\ \mathrm{N\ m^{-2}}$$

*Exercise 11.7

A certain sleeve bearing in a machine 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.

When laboratory measurements of viscosity coefficients are made, an apparatus like the idealized apparatus of Figure 11.1 is not ordinarily used. One simple apparatus used for liquids contains a tube of uniform diameter through which the liquid is forced by a

Poiseuille's equation is named for Jean Leonard Marie Poiseuille, 1797–1869, a French physician who studied the circulation of blood.

pressure difference. For laminar flow in an incompressible liquid, the **volume rate of flow** dV/dt, is given by **Poiseuille's equation**:

$$\frac{dV}{dt} = \frac{(P_2 - P_1)\pi R^4}{8L\eta} \quad \text{(Poiseuille's equation)} \tag{11.2-21}$$

where R is the radius of the tube, L is its length, and $P_2 - P_1$ is the difference in pressure between the ends of the tube.

The first part of the derivation of Poiseuille's equation is to find how the flow velocity of the fluid in the tube depends on position. If laminar flow occurs, the velocity will be parallel to the tube walls. Consider a portion of the fluid in the tube that is contained in an imaginary cylinder of radius r that is concentric with the tube walls, as shown in Figure 11.5. When a steady state has been reached, the frictional force due to viscosity at the surface of this cylinder will exactly balance the hydrostatic force on the liquid in the cylinder. From Newton's law of viscosity,

$$\frac{F}{\mathscr{A}} = \eta\left|\frac{du_z}{dr}\right| \tag{11.2-22}$$

where F is the magnitude of the force on the liquid, $\mathscr{A}$ is the area of the walls of the cylinder (not the area of its ends), and $|du_z/dr|$ is the magnitude of the velocity gradient, which is perpendicular to the axis. We take the axis of the cylinder as the z direction, and the perpendicular distance from the axis as the variable r.

The magnitude of the net force on the liquid in our imaginary cylinder is equal to the difference of the pressure at its ends times the cross-sectional area of the cylinder (assuming that the pressure does not depend on r) and the area of the cylinder is its circumference times its length:

$$F = (P_2 - P_1)\pi r^2 \qquad \mathscr{A} = 2\pi r L$$

Substitution of these equations into Eq. (11.2-22) gives

$$\frac{F}{\mathscr{A}} = \frac{(P_2 - P_1)r}{2L} = \eta\,\frac{du_z}{dr}$$

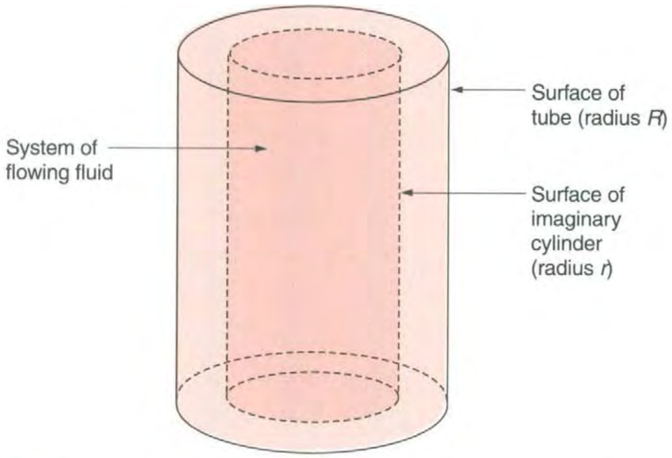

Figure 11.5. The Fluid in a Tube. When fluid undergoes laminar flow in a tube, the velocity at any part of the surface of the imaginary cylinder will equal that at any other part of the same cylinder.

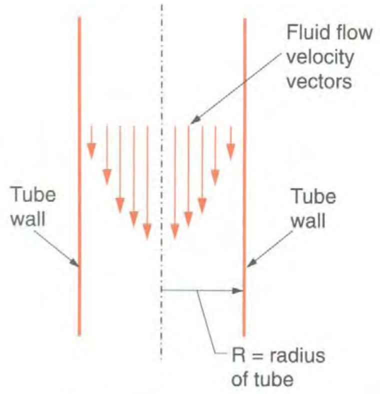

Figure 11.6. The Fluid Velocity in a Tube with Laminar Flow. This figure shows that the fluid velocity is a parabolic function, so that the rate of shear is a simple function of position.

This is a differential equation that can be solved by an integration. We divide both sides of the equation by η and multiply both sides by dr so that the right-hand side is then equal to the differential du_z. We integrate both sides from $r = R$ to $r = r'$, where r' is some value of r:

$$\int_R^{r'} \frac{du_z}{dr}\,dr = \int_{u_z(R)}^{u_z(r')} du_z = \frac{P_2 - P_1}{2L\eta}\int_R^{r'} r\,dr$$

If the liquid adheres to the tube walls, $u_z(R)$ will vanish, and carrying out the integrations gives

$$u_z(r') = \frac{P_2 - P_1}{4L\eta}(r'^2 - R^2) \tag{11.2-23}$$

This parabolic dependence of the flow velocity on position is represented in Figure 11.6 such that the length of each arrow is proportional to the flow velocity at its location.

The total rate of flow of the incompressible liquid through the tube can be computed from the flow velocity. Consider a cylindrical shell of thickness dr and radius r concentric with the walls of the tube. The volume of the fluid in this shell that flows out of the tube in one second (the contribution of this shell to dV/dt) is equal to the cross-sectional area of the shell times a length equal to the distance traveled in one second. Since the circumference of a shell of radius r is equal to $2\pi r$ and since its thickness is dr,

$$(\text{Contribution of shell to } dV/dt) = 2\pi r\,dr|u_z(r)|$$

The total volume rate of flow is the integral of the contributions of all such shells:

$$\frac{dV}{dt} = 2\pi\int_0^R r|u_z(r)|\,dr = 2\pi\frac{P_2 - P_1}{4L\eta}\int_0^R (R^2 r - r^3)\,dr$$

$$\frac{dV}{dt} = \frac{(P_2 - P_1)\pi R^4}{8L\eta} \quad \text{(Poiseuille's equation)} \tag{11.2-24}$$

This is Eq. (11.2-21), Poiseuille's equation for an incompressible liquid undergoing laminar flow in a tube of radius R. A different version holds for the flow of a gas.[4]

EXAMPLE 11.5

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 h.

Solution

From Table A.18 of Appendix A, the viscosity of water at this temperature is equal to 0.001002 kg $\text{m}^{-1}\ \text{s}^{-1}$.

$$\frac{dV}{dt} = \frac{(0.0500\ \text{atm})(101325\ \text{N m}^{-2}\ \text{atm}^{-1})(\pi)(0.00520\ \text{m})^4}{(8)(0.420\ \text{m})(0.001002\ \text{kg m}^{-1}\ \text{s}^{-1})} = 0.00346\ \text{m}^3\ \text{s}^{-1}$$

$$V = (0.00346\ \text{m}^3\ \text{s}^{-1})(3600\ \text{s}) = 12.4\ \text{m}^3$$

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[4] D. P. Shoemaker, C. W. Garland, and J. W. Nibler, *Experiments in Physical Chemistry*, 6th ed., McGraw-Hill, New York, 1996, pp. 126ff.

*Exercise 11.8

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 $0.004\ \mathrm{kg\ m^{-1}\ s^{-1}}$ can be used ("Blood is thicker than water"). Estimate the volume of blood flowing through the human circulatory system in $\mathrm{L\ min^{-1}}$, assuming Poiseuille's equation. The actual value is near $5\ \mathrm{L\ min^{-1}}$.

Poiseuille's equation is correct only if the fluid flow is laminar. If the flow 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 can be approximated by laminar flow. The **Reynolds number** is defined for flow in a cylindrical tube by

$$\mathscr{R} = \frac{R\langle u\rangle\rho}{\eta} \quad \text{(definition of Reynolds number)} \tag{11.2-25}$$

where R is the radius of the tube, ρ is the density 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 nearly always laminar if the Reynolds number is smaller than some value near 2000, no matter what the values of the individual quantities in Eq. (11.2-25) 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.

*Exercise 11.9

Estimate the Reynolds number for the flow of blood in a typical human capillary. Is the flow laminar?

Another method of measuring the viscosity is by using the frictional force that a fluid puts on a spherical object moving through the fluid. Viscosities can be measured by dropping a spherical ball into the fluid and measuring its rate of descent. For a spherical object moving at a velocity $\mathbf{v}$ through a fluid with viscosity η, **Stokes's law** is

$$\mathbf{F}_f = -6\pi\eta r\mathbf{v} \tag{11.2-26}$$

Stokes's 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.

where $\mathbf{F}_f$ is the frictional force, r is the radius of the spherical object, and $\mathbf{v}$ is its velocity. The negative sign indicates that the friction force is in the opposite direction to the velocity. Stokes's law holds only for velocities small enough that the flow around the sphere is laminar.

EXAMPLE 11.6

An iron sphere of density $7.874\ \mathrm{g\ mL^{-1}}$ is falling at a steady speed in glycerol at 20°C. The density of glycerol is $1.2613\ \mathrm{g\ mL^{-1}}$ and its viscosity at this temperature is 1.49 Pa s. If the radius of the sphere is 5.00 mm, find the speed.

Solution

If the speed is constant, the frictional force must be equal in magnitude to the gravitational force, which (corrected for buoyancy) is equal to

$$
\begin{aligned}
|\mathbf{F}_g| &= \frac{4\pi r^3}{3}(\rho_{\mathrm{Fe}} - \rho_{\mathrm{gly}})g \\
&= \frac{4\pi}{3}(5.00 \times 10^{-3}\ \mathrm{m})^3(7874\ \mathrm{kg\ m^{-3}} - 1261.3\ \mathrm{kg\ m^{-3}})(9.80\ \mathrm{m\ s^{-2}}) \\
&= 0.0339\ \mathrm{kg\ m\ s^{-2}} = 0.0339\ \mathrm{N} \\
v &= \frac{|\mathbf{F}_g|}{6\pi\eta r} = \frac{0.0339\ \mathrm{kg\ m\ s^{-2}}}{6\pi(1.49\ \mathrm{kg\ m^{-1}\ s^{-1}})(5.00 \times 10^{-3}\ \mathrm{m})} = 0.242\ \mathrm{m\ s^{-1}}
\end{aligned}
$$

*Exercise 11.10

Obtain an approximate Reynolds number for the flow in Example 11.6 by replacing the diameter of a tube by the diameter of the sphere and replacing the mean speed of the fluid by the speed of the sphere through the liquid (this is considered to be acceptable practice). Comment on your results.

Although Stokes's law was derived for macroscopic spherical objects, it is frequently applied as an approximation to molecules moving through a liquid. Since Stokes's law depends on a description of the fluid as a set of flowing layers without recognition of its molecular nature, application of Stokes's law to moving molecules is more meaningful for large molecules such as proteins than for small molecules that are nearly the same size as the solvent molecules. However, even for small molecules and ions we often say that Stokes's law defines an "effective radius" of a molecule or ion.

11.3 Transport Processes in the Hard-Sphere Gas

An elementary molecular theory for nonequilibrium processes in a hard-sphere gas is based on the theory of collisions in a hard-sphere gas presented in Chapter 10. We will apply this theory to self-diffusion and give the results of its application to heat conduction and viscous flow.

Self-Diffusion

For diffusion to take place there must be at least two substances present. In **self-diffusion** the molecules of the two substances have all of their properties in common but can somehow be distinguished from each other. This situation cannot actually occur but is approximated in the laboratory by using two substances that differ only by isotopic substitution. The molecular masses will be different but this difference can sometimes be made small by substituting isotopes of two elements. Diffusion of two substances that differ only by isotopic substitution is called **tracer diffusion**.

Consider a gaseous model system with two kinds of hard spherical molecules, both with the same molecular size and molecular mass. The model system is at a uniform temperature and a uniform pressure and is in a rectangular box with four vertical sides. The concentrations depend on z, the vertical coordinate, but the sum of the two concentrations is independent of position so as to avoid a pressure gradient. The process of diffusion will gradually eliminate the concentration gradient as the molecules mix. Figure 11.7 depicts our model system. In the interior of the system are three imaginary horizontal planes. The upper and lower planes are placed at a distance from the center plane equal to λ, the mean free path between two collisions with any kind of particle. Since all molecules are of the same size and mass, and since we are considering all kinds of collisions, the mean free path is given by Eq. (10.7-23):

$$\lambda = \frac{1}{\sqrt{2}\pi d^2 \mathscr{N}_t} \tag{11.3-1}$$

where $\mathscr{N}_t$ is the total number density, the sum of the number densities of the two substances:

$$\mathscr{N}_t = \mathscr{N}_1 + \mathscr{N}_2 \tag{11.3-2}$$

and where d is the effective hard-sphere diameter of the molecules.

We now assume that all molecules passing upward through the center plane last suffered collisions in the vicinity of the lower plane and were equilibrated at that location. Molecules passing through the center plane from above are assumed to have been equilibrated at the location of the upper plane. This assumption is the crucial assumption of the theory. It is not correct for every molecule, since the z component of every free path is not equal to the mean free path and since equilibrium might not be complete at each collision, but it should be roughly valid on the average. The number of

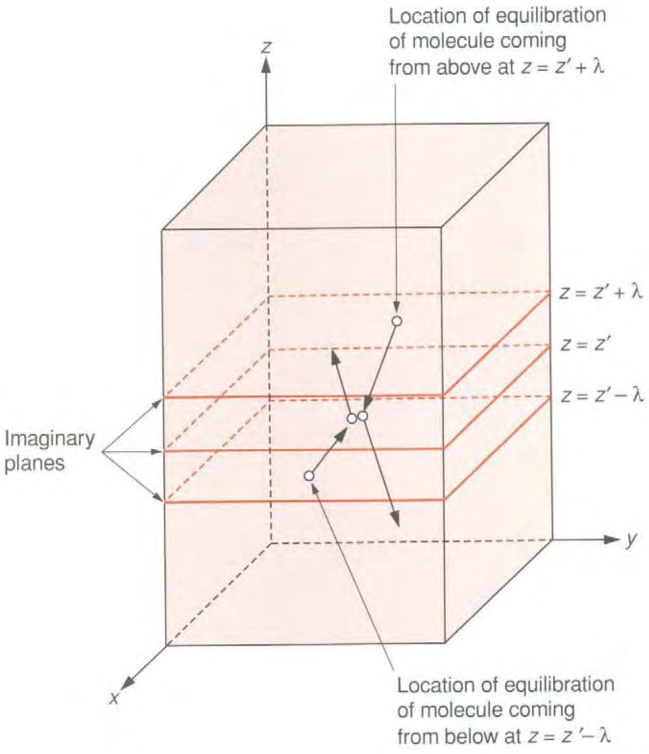

Figure 11.7. The Model System Showing Three Imaginary Planes for Analysis of Self-Diffusion in a Hard-Sphere Gas. The spacing between the planes is equal to the mean free path for the gas, and the planes are used in the derivation of the self-diffusion coefficient for the gas.

molecules of substance 1 passing upward through the center plane per unit area per unit time is given by Eq. (10.5-6):

$$\nu_1(\mathrm{up}) = \tfrac{1}{4}\mathcal{N}_1(z' - \lambda)\langle v\rangle \tag{11.3-3}$$

where $\langle v\rangle$ is the mean speed of the molecules and where the argument of $\mathcal{N}_1$ indicates that $\mathcal{N}_1$ is evaluated at $z' - \lambda$. The rate of molecules of substance 1 passing downward through unit area of the center plane is also given by Eq. (10.5-6) with the number density evaluated at $z' + \lambda$:

$$\nu_1(\mathrm{down}) = \tfrac{1}{4}\mathcal{N}_1(z' + \lambda)\langle v\rangle \tag{11.3-4}$$

The number densities are evaluated at the location at which the molecules had their last collision before approaching the center plane, because this is the location at which we assume they were equilibrated.

The magnitude of the diffusion flux equals the net amount (in moles) of the substance passing unit area of a plane perpendicular to the direction of diffusion per second. Since our sytem is uniform in the x and y directions, the diffusion flux is in the z direction, and is given by

$$J_{1z} = \frac{1}{N_{\mathrm{Av}}}[\nu_1(\mathrm{up}) - \nu_1(\mathrm{down})] \tag{11.3-5}$$

where the factor $1/N_{\mathrm{Av}}$ is needed to express the flux in moles instead of molecules. The expressions for the upward and downward rates are substituted into Eq. (11.3-5):

$$J_{1z} = \frac{\langle v\rangle}{4N_{\mathrm{Av}}}[\mathcal{N}_1(z' - \lambda) - \mathcal{N}_1(z' + \lambda)] = \frac{\langle v\rangle}{4}[c_1(z' - \lambda) - c_1(z' + \lambda)]$$

$$= -\frac{\langle v\rangle}{4}\left[\frac{c_1(z' + \lambda) - c_1(z' - \lambda)}{2\lambda}\right]2\lambda$$

where we have recognized that $c_1 = \mathcal{N}_1/N_{\mathrm{Av}}$ and where in the last equation we have multiplied and divided by 2λ.

If we were to take the limit of the quantity in square brackets as λ approached zero, it would become equal to the derivative $\partial c_1/\partial z$. We cannot take this limit since λ is determined by the properties of the system, but if c_1 is approximately a linear function of z, the quotient of finite differences is nearly equal to the derivative, and we can write

$$J_{1z} = -\frac{\langle v\rangle\lambda}{2}\frac{\partial c_1}{\partial z} \tag{11.3-6}$$

For the case of dependence only on the z coordinate, Fick's law is given by Eq. (11.2-4):

$$J_{1z} = -D_1\frac{\partial c_1}{\partial z} \tag{11.3-7}$$

Comparison of this with Eq. (11.3-6) shows that

$$D_1 = \frac{\langle v\rangle\lambda}{2} = \frac{1}{2}\left(\frac{8k_{\mathrm{B}}T}{\pi m}\right)^{1/2}\frac{1}{\sqrt{2}\pi d^2\mathcal{N}_{\mathrm{t}}} = \frac{1}{\pi d^2\mathcal{N}_{\mathrm{t}}}\left(\frac{k_{\mathrm{B}}T}{\pi m}\right)^{1/2} \tag{11.3-8}$$

where we have used Eq. (10.3-7) for the mean speed and Eq. (10.7-23) for the mean free path. Since substances 1 and 2 are of the same mass and size, D_1 and D_2 are equal.

Our theory was cruder than necessary. A more accurate theory for the hard-sphere gas takes into account the fact that the molecules do not all arrive at a given plane from a vertical distance equal to the mean free path. The diffusion coefficient obtained in this treatment has the same dependence on density, temperature, mass, and hard-sphere diameter as the expression of Eq. (11.3-8), and gives a value that is only about 18% different in size from that expression:

$$D_1 = \frac{3\pi}{16}\lambda\langle v\rangle = \frac{3}{8d^2\mathcal{N}_t}\left(\frac{k_B T}{\pi m}\right)^{1/2} \quad \text{(more accurate equation)} \tag{11.3-9}$$

One should use Eq. (11.3-9), not Eq. (11.3-8), for any numerical calculations. Except for the constant, the first version of Eq. (11.3-9) is easy to remember because it is so reasonable physically. The farther the molecules travel without collision, the faster they diffuse, and the faster they travel, the faster they diffuse.

EXAMPLE 11.7

Neglecting the mass difference, calculate the diffusion coefficient for isotopically substituted nitrogen molecules in ordinary nitrogen at 298 K and 1.00 atm.

Solution

We use the ideal gas law to calculate the number density:

$$\mathcal{N}_t = \frac{N}{V} = \frac{P}{k_B T} = \frac{101325\ \mathrm{N\ m^{-2}}}{(1.3807\times 10^{-23}\ \mathrm{J\ K^{-1}})(298\ \mathrm{K})} = 2.46\times 10^{25}\ \mathrm{m^{-3}}$$

From Table A.15, $d = 3.7\times 10^{-10}$ m.

$$D = \frac{3}{8d^2\mathcal{N}_t}\left(\frac{k_B T}{\pi m}\right)^{1/2} = \frac{3}{8\,d^2\mathcal{N}_t}\left(\frac{RT}{\pi M}\right)^{1/2}$$

$$= \frac{3}{8(3.7\times 10^{-10}\ \mathrm{m})^2(2.46\times 10^{25}\ \mathrm{m^{-3}})}\left(\frac{(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}})(298\ \mathrm{K})}{\pi(0.028\ \mathrm{kg\ mol^{-1}})}\right)^{1/2}$$

$$= 1.9\times 10^{-5}\ \mathrm{m^2\ s^{-1}}$$

Stop for a moment and consider what we have done. We have taken a mechanical model system and have analyzed its behavior from a molecular point of view. We have compared our result to an empirical macroscopic equation, Fick's law of diffusion. We have found they give the same dependence on the concentration gradient, with an explicit expression for the diffusion coefficient in the theoretical result. Experimental studies of the dependence of diffusion coefficients on temperature and density agree fairly well with Eq. (11.3-9). The calculated hard-sphere diameters computed from diffusion data depend somewhat on temperature. 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 expected to be smaller. Table A.19 gives some experimental values for self-diffusion coefficients.

***Exercise 11.11**

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.

Thermal Conduction

An analysis of heat conduction and viscous flow that is very similar to that for self-diffusion can be carried out.[5] For heat conduction in a hard-sphere gas, instead of counting molecules that pass the central plane, we compute the contributions that the molecules make to the kinetic energy that is transported. The molecular energy is expressed in terms of the heat capacity at constant volume. From Eq. (10.2-32), the heat capacity of a monatomic gas is

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,n} = \frac{3nR}{2} \qquad \text{or} \qquad c_V = \frac{3k_B}{2} \tag{11.3-10}$$

where c_V is the heat capacity per molecule. The mean molecular energy is

$$\langle \varepsilon \rangle = c_V T = \frac{3k_B T}{2} \tag{11.3-11}$$

An analysis similar to that leading to Eq. (11.3-9) is carried out, with the temperature depending on z and the net transport of $\langle \varepsilon \rangle$ being computed. The result is compared with Fourier's law of thermal conduction, Eq. (11.2-1) and an expression for the coefficient of thermal conductivity is deduced For a one-substance hard-sphere gas

$$\kappa = \frac{25\pi}{64} c_V \lambda \langle v \rangle \mathcal{N} = \frac{25\, c_V}{32\, d^2}\left(\frac{k_B T}{\pi m}\right)^{1/2} \tag{11.3-12}$$

This equation is at the level of accuracy of Eq. (11.3-9). For a polyatomic gas with rotational and vibrational energy the thermal conductivity is more complicated, since only part of the rotational and vibrational energy is transferred in a collision. We will not discuss this case.

Exercise 11.12

Carry out the derivation of Fourier's law of thermal conduction and obtain an expression for the thermal conductivity analogous to Eq. (11.3-8). Use a system of one component, assume that the temperature depends on the z coordinate, and that the molecules are equilibrated at the temperature of the plane from which they come to approach the central plane. Calculate the percent difference between your result and that of Eq. (11.3-12).

Viscous Flow

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. An analysis similar to that of self-diffusion can be carried out in which the net flow of the momentum is computed. The result is an expression for the viscosity coefficient:

$$\eta = \frac{5\pi}{32} m \lambda \langle v \rangle \mathcal{N} = \frac{5}{16\sqrt{\pi}} \frac{1}{d^2} \sqrt{m k_B T} \tag{11.3-13}$$

where this equation is at the level of accuracy of Eq. (11.3-9).

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[5] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York, 1954, pp. 9ff.

At a fixed value of $\mathcal{N}$, all three transport coefficients are proportional to the mean speed of the molecules, which means that they are proportional to the square root of the temperature. Therefore, a hard-sphere 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.

***Exercise 11.13**

Certain dimensionless ratios of physical constants are useful enough that they are called **dimensionless groups**. Show that for a hard-sphere gas each of the following ratios equals a dimensionless constant and find each constant:

$$\frac{\eta}{m\mathcal{N}D}, \quad \frac{c_V\eta}{\kappa m}, \quad \frac{Dc_V\mathcal{N}}{\kappa}$$

The Structure of Liquids and Transport Processes in Liquids

The structure and properties of a liquid are determined by the system's potential energy and its kinetic energy, whereas the properties of a gas are primarily determined by its kinetic energy. This makes the theoretical analysis of liquid behavior much more difficult than that of gases, although liquids obey the same linear laws as do gases. In Section 10.8, the molecular environment in a typical molecule in a liquid was described as a cage made up of neighboring molecules, in which the molecule is confined by the 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. However, 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 move past some of these neighbors 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^{-12} to 10^{-11} s (see Example 10.10). The molecule might move to a new cage every 10^{-9} to 10^{-8} 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 a frictional force representing the retarding effects of the interactions with the neighboring molecules. This force is approximately proportional to the negative of the average velocity of the molecules or ions:

$$\mathbf{F}_{\mathrm{f}} = -f\mathbf{v} \tag{11.4-1}$$

where $\mathbf{F}_{\mathrm{f}}$ is the frictional force and where f is called the **friction coefficient**. This equation is similar to Stokes's law, Eq. (11.2-26). Although Stokes's law was originally derived for a macroscopic sphere moving through a continuous fluid, we can write

$$f = 6\pi\eta r_{\mathrm{eff}} \tag{11.4-2}$$

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 in this way. For macromolecules (molecules of large molecular mass) and colloidal particles

(particles roughly 3 to 1000 nm in diameter) that are nearly spherical, Eq. (11.2-26) is found to be nearly as accurate as it is for macroscopic spheres.

Around 1905, Einstein devised a theory of **Brownian motion**, the irregular motion of colloidal particles suspended in a liquid. A colloidal particle is a particle that is considerably larger than solvent molecules but small enough to remain suspended without settling out under the force of gravity. 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

$$\langle z^2 \rangle = \frac{k_B T}{3\pi\eta r}\, t \tag{11.4-3}$$

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. (11.2-19) shows that the diffusion coefficient of the colloidal substance is given by

$$D_2 = \frac{k_B T}{f} = \frac{k_B T}{6\pi\eta r} \tag{11.4-4}$$

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. (11.4-3) 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. (11.4-3) depended on the assumption that the colloidal particle was bombarded randomly by solvent molecules. Perrin was able to obtain the value of Boltzmann's constant from Eq. (11.4-3), and thus calculated a value of Avogadro's constant using the known value of the ideal gas constant.

EXAMPLE 11.8

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 molecules to be spherical, calculate their radius. The viscosity coefficient of water at this temperature is equal to $1.002 \times 10^{-3}\ \mathrm{kg\ m^{-1}\ s^{-1}}$.

Solution

$$r = \frac{k_B T}{6\pi\eta D} = \frac{(1.3807 \times 10^{-23}\ \mathrm{J\ K^{-1}})(293\ \mathrm{K})}{6\pi(1.002 \times 10^{-3}\ \mathrm{kg\ m^{-1}\ s^{-1}})(6.9 \times 10^{-11}\ \mathrm{m^2\ s^{-1}})}$$
$$= 3.1 \times 10^{-9}\ \mathrm{m} = 3100\ \mathrm{pm} = 31\ \text{Å}$$

*Exercise 11.14

a. Estimate the molar volume of hemoglobin from the molecular size in Example 11.8.

b. Human hemoglobin has a density of $1.335\ \mathrm{g\ mL^{-1}}$ (a little larger than typical protein values, which run around $1.25\ \mathrm{g\ mL^{-1}}$). It has a molar mass of $68000\ \mathrm{g\ mol^{-1}}$. Calculate its molar volume and compare with your answer from part (a). State any assumptions.

The Temperature Dependence of Diffusion and Viscosity Coefficients in Liquids

From Eq. (11.3-9), we see that the self-diffusion coefficient of a hard-sphere gas is proportional to the square root of the temperature, and from Eqs. (11.3-12) and

(11.3-13) we see that the thermal conductivity and the viscosity depend on the temperature in the same way. This rather weak dependence on temperature is different from that of small molecules in liquids, in which coefficients of diffusion and viscosity depend quite strongly on temperature. Liquids are less viscous at higher temperatures, while diffusion coefficients in liquids increase as the temperature is raised. It is found experimentally that diffusion coefficients in liquids are usually quite well described by the formula

$$D = D_0 e^{-E_{ad}/RT} \tag{11.4-5}$$

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_{ad} is a positive parameter with the dimensions of energy, which is called an **activation energy**. It is similarly found that liquid viscosities are quite well described by the formula

$$\eta = \eta_0 e^{E_{a\eta}/RT} \tag{11.4-6}$$

where the symbols have similar meanings as in Eq. (11.4-5).

An elementary explanation of Eq. (11.4-5) is as follows: In order for a molecule in a liquid to push past some of its nearest neighbors and move into the next cage, it must possess a relatively high kinetic energy. If we identify ε_a as a minimum energy required to break out of a cage (an "activation energy"), then from Eq. (10.2-35) we see that the probability for a molecule to have a velocity corresponding to this energy is

$$(\text{Probability}) \propto e^{-\varepsilon_a/k_BT} = e^{-E_a/RT} \tag{11.4-7}$$

where k_B is Boltzmann's constant and where $E_a = N_{Av}\varepsilon_a$. It is therefore reasonable that a diffusion coefficient in a liquid would obey Eq. (11.4-5) with E_{ad} roughly equal to the molar energy required to move into the next cage.

In order for shearing flow to take place, layers of a liquid must flow past each other. This requires disruption of cages and much the same kind of activation energy as in diffusion. Note that the sign of the exponent in Eq. (11.4-6) is opposite from that in Eq. (11.4-5). This is because the rate of shear is proportional to the factor in Eq. (11.4-7), making the viscosity coefficient inversely proportional to it. It is found that the activation energy for viscosity is roughly equal to the activation energy for self-diffusion in the same liquid, giving further plausibility to this argument.

EXAMPLE 11.9

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 centipose (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 value of η_0 and $E_{a\eta}$.

Solution

We linearize Eq. (11.4-6) by taking logarithms:

$$\ln\left(\frac{\eta}{\eta_0}\right) = \frac{E_{a\eta}}{RT}$$

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).

$$\begin{aligned} E_{a\eta} &= (\mathrm{slope}) \times R = (1245\ \mathrm{K})(8.3145\ \mathrm{J\ K^{-1}\ mol^{-1}}) \\ &= 1.035 \times 10^{4}\ \mathrm{J\ mol^{-1}} = 10.4\ \mathrm{kJ\ mol^{-1}} \\ \eta_0 &= (1\ \mathrm{cP})e^{-4.279} = 1.39 \times 10^{-2}\ \mathrm{cP} = 1.39 \times 10^{-5}\ \mathrm{kg\ m^{-1}\ s^{-1}} \end{aligned}$$

The value of this energy of activation is typical of liquids with small nearly spherical molecules and is a reasonable size for the energy required (per mole) to push through a layer of neighboring molecules. As might be expected, it is somewhat smaller than the energy of vaporization of CCl_4, 33.9 kJ mol^{-1}.

***Exercise 11.15**

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 Example 11.9.

Sedimentation

Macromolecules and colloidal particles can sediment through a liquid under the force of gravity or under centrifugal force if they have a greater density than the liquid. Sedimentation experiments provide a means of determining the size of the particles or molecules through use of Eq. (11.4-2). To provide sufficiently rapid sedimentation of protein molecules, one must use 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 Eq. (D-16) of Appendix D:

$$F_c = mr\omega^2 \tag{11.4-8}$$

where ω is the **angular speed**, which is 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 vertical axis of rotation and has a sample cell with a transparent top and bottom so that a beam of light can shine through the cell each time it passes the location of the beam. When the rotor spins, the macromolecules will sediment toward the outside of the rotor if they are denser than the solvent, and the value of r, the distance from the axis of rotation, can be measured by passing a beam of light through the cell and 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 $v_{\mathrm{sed}} = dr/dt$ will attain a steady value. The centripetal force is then equal in magnitude to the frictional force given by Eq. (11.4-1). Since a macromolecule is immersed in a solvent, its centripetal force must be corrected for buoyancy, giving instead of Eq. (11.4-8)

$$F_c = (m - m_{\mathrm{solvent}})r\omega^2 \tag{11.4-9}$$

where m_{solvent} is the mass of solvent displaced by the macromolecule. If ρ_1 is the density of the solvent and ρ_2 is the density of the macromolecular substance, we have

$$m_{\text{solvent}} = \frac{\rho_1}{\rho_2} m = \frac{\rho_1}{\rho_2} \frac{M_2}{N_{\text{Av}}} \tag{11.4-10}$$

where M_2 is the molar mass of the macromolecular substance and N_{Av} is Avogadro's constant. Combination of Eqs. (11.4-1) and (11.4-9) gives

$$f v_{\text{sed}} = \frac{M_2}{N_{\text{Av}}}\left(1 - \frac{\rho_1}{\rho_2}\right) r\omega^2 \tag{11.4-11}$$

The **sedimentation coefficient** S is defined as the ratio of v_{sed} to the centrifugal acceleration, $r\omega^2$:

$$S = \frac{v_{\text{sed}}}{r\omega^2} \quad \text{(definition of } S\text{)} \tag{11.4-12}$$

so that

$$S = \frac{M_2}{N_{\text{Av}}} \frac{1 - \rho_1/\rho_2}{f} \tag{11.4-13}$$

The svedberg unit is named for Theodor (called The, pronounced "Tay") Svedberg, 1884–1971, Swedish biophysical chemist who received the 1926 Nobel Prize for his work in disperse systems (colloids, protein suspensions, etc.)

The sedimentation coefficient has the units of seconds and is ordinarily approximately equal to 10^{-13} s. The practical unit of sedimentation coefficients is the **svedberg**, defined so that 1 svedberg $= 10^{-13}$ s.

Equation (11.4-4) allows us to express f in terms of D_2, the diffusion coefficient of the macromolecular substance, giving

$$M_2 = \frac{RTS}{D_2(1 - \rho_1/\rho_2)} \tag{11.4-14}$$

where we have replaced $k_B N_{\text{Av}}$ by 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 11.4 can be observed in addition to the sedimentation rate.

EXAMPLE 11.10

The sedimentation coefficient of a sample of human hemoglobin in water is equal to 4.48 svedbergs at 20°C, and its density is 1.335 g mL^{-1}. The density of water at this temperature is equal to 0.998 g mL^{-1}. Use the value of the diffusion coefficient from Example 11.8 to determine the molar mass of hemoglobin.

Solution

$$\begin{aligned} M &= \frac{(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(293.15\ \text{K})(4.48 \times 10^{-13}\ \text{s})}{(6.9 \times 10^{-11}\ \text{m}^2\ \text{s}^{-1})(1 - 0.998/1.335)} \\ &= 63\ \text{J m}^{-2}\ \text{s}^2\ \text{mol}^{-1} = 63\ \text{kg mol}^{-1} \end{aligned}$$

The actual molar mass is near 68 kg mol^{-1}.

11.5 Transport in Electrolyte Solutions

Sections 10.8 and 11.4 contain some qualitative comments about the structure of liquids and transport processes in liquids. The motions of molecules in a liquid were crudely described as rattling about in a cage of adjacent molecules and occasionally moving into a neighboring cage. In an ionic solution, the motion of an ion is similar to the motion of a molecule in an ordinary liquid except that an ion will have an electrostatic force placed on it by an electric field. The electrostatic forces between ions are also important except at extremely low concentration, influencing the probability with which an ion will move into an adjacent cage.

Electric currents consist of drifting motions of charged particles. Electric currents in metallic conductors and in semiconductors are due to the motions of electrons, while electric currents in electrolyte solutions are due to the motions of ions. **Ohm's law** is an empirical law that describes both cases. It asserts that the current in a conducting system is proportional to the voltage imposed on the system:

$$I = \frac{V}{R} \tag{11.5-1}$$

where V is the voltage, I is the current (equal to the amount of charge passing a given point per second), and R is the resistance of the conductor. Ohm's law with a constant resistance is obeyed very nearly exactly by metallic conductors, to a good approximation by most electrolyte solutions, and less accurately by most semiconductors. Deviations from Ohm's law can be described by using Eq. (11.5-1) with a resistance R that is dependent on V.

Ohm found by painstaking experiments with homemade equipment (even including homemade wires) that the resistance of a conductor of uniform cross-sectional area 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 11.8 by

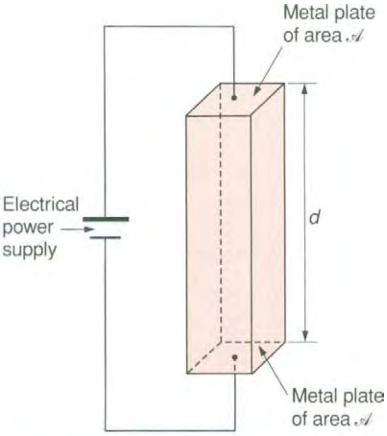

Figure 11.8. An Electrically Conducting System (Schematic). A cell of this shape allows us to relate the resistance of the cell to the resistivity and conductivity in a direct fashion, since the resistance is inversely proportional to the area $\mathscr{A}$ and directly proportional to the length d.

$$r = \frac{R\mathscr{A}}{d} \tag{11.5-2}$$

where $\mathscr{A}$ is the cross-sectional area and d is the length of the object. The resistivity is independent of d and $\mathscr{A}$; it depends only on the composition of the object, the temperature, and the pressure (the dependence on the pressure is usually very weak). The units of resistivity are ohm meters (ohm m). The reciprocal of the resistivity is called the **conductance** σ:

$$\sigma = \frac{1}{r} \tag{11.5-3}$$

The units of conductance are ohm^{-1} m^{-1} or S m^{-1}. The ohm^{-1} has been called the **mho**, but the SI name for ohm^{-1} is the **siemens**, denoted by S.

We define the **current density j** (do not confuse it with the unit vector **j**) as a vector with magnitude equal to the current per unit area and with the same direction as the current:

$$j = |\mathbf{j}| = \frac{I}{\mathscr{A}} \tag{11.5-4}$$

where $\mathscr{A}$ is the cross-sectional area of the conductor. The direction of an electric current is by convention the direction of apparent motion of positive charges. This convention was proposed by Benjamin Franklin, who was an excellent amateur physicist as well as a statesman and who also invented the designation of the two kinds of electric charge as positive and negative. Ohm's law can be written

$$j = \sigma\mathscr{E} \tag{11.5-5}$$

where $\mathscr{E}$ is the magnitude of the electric field, equal to V/d for an object like that of Figure 11.8.

Exercise 11.16

Show that Eq. (11.5-5) is correct

Let the mean velocity of cations be denoted by $\mathbf{v}_+$ and the mean velocity of anions be denoted by $\mathbf{v}_-$. The mean drift velocity is a vector average velocity. At equilibrium, even though the ions are moving about, the mean velocity vanishes because as many molecules will be moving in a given direction as in the opposite direction. If $\mathbf{v}_+$ or $\mathbf{v}_-$ is nonzero, it is often called a "drift velocity." The current density is the sum of a cation contribution and an anion contribution due to the drift velocities:

$$\mathbf{j} = \mathbf{j}_+ + \mathbf{j}_- \tag{11.5-6}$$

On the average, positive ions (cations) no farther from a fixed plane than a distance equal to v_+ times 1 s will pass in 1 s, and similarly for anions. The current density can be written

$$\mathbf{j} = z_+ N_{\mathrm{Av}} e c_+ \mathbf{v}_+ + |z_-| N_{\mathrm{Av}} e c_- v_- \tag{11.5-7}$$

where e is the charge on a proton, 1.6022×10^{-19} C and where N_{Av} is Avogadro's constant. The quantity z_+ is the valence of the cation (the number of proton charges on one ion) and z_- is the valence of the anion (a negative integer equal in magnitude to the number of electron charges on one ion). The concentrations of cations and anions in mol m^{-3} are denoted by c_+ and c_-, respectively.

Exercise 11.17

Show that Eq. (11.5-7) is correct.

If dissociation or ionization is complete and if the solution is made from c moles of electrolyte solute per cubic meter of solution,

$$c_+ = \nu_+ c \quad \text{and} \quad c_- = \nu_- c \tag{11.5-8}$$

where ν_+ is the number of cations per formula unit of the solute and ν_- is the number of anions per formula unit. For a single electrolyte solute these quantities must obey the electrical neutrality relation

$$\nu_+ z_+ + \nu_- z_- = 0 \tag{11.5-9}$$

The magnitude of the current density can also be written

$$j = F(z_+ c_+ v_+ + |z_-| c_- v_-) \tag{11.5-10}$$

where F is Faraday's constant, equal to the charge on 1 mol of protons, 96485 C mol^{-1}.

If the conductor represented in Figure 11.8 is an electrolyte solution, the ions that flow cannot pass out of the ends of the container. This means that if a direct current flowed, cations would accumulate at one end of the system and anions would accumulate at the other end, unless some electrochemical half-reactions consumed the ions at one end and produced them at the other. If this cannot be arranged, alternating current is used to measure the conductivities of an electrolyte solution. Since the current flows alternately in one direction and then the other, only small accumulations of ions occur at the ends of the system during one half of the cycle and these ions move back during the other half of the cycle.

EXAMPLE 11.11

For a system such as shown in Figure 11.8 with a solution containing c mol m^{-3} of NaCl, show that Ohm's law holds if the drift velocities are governed by Eq. (11.4-1). Use the relationship between the electric field and the force on a charged particle given in Eqs. (9.1-1) and (9.1-3). Express the conductance in terms of the friction coefficients f_+ and f_-.

Solution

The electrostatic force on an ion of charge ze in an electric field $\mathcal{E}$ is

$$\mathbf{F}_{\text{elec}} = ze\mathcal{E}$$

On the average, the ions are not accelerated if a steady current is flowing, so that

$$\mathbf{F}_{\text{elec}} = -\mathbf{F}_{\text{friction}} = f\mathbf{v}$$

Using this relationship and Eq. (11.5-10) for the case that $\nu_+ = \nu_- = 1$, we obtain

$$j = Fc\mathcal{E}e\left(\frac{1}{f_+} + \frac{1}{f_-}\right) \tag{11.5-11}$$

where f_+ is the friction coefficient for sodium ions and f_- is the friction coefficient of chloride ions. Comparison with Eq. (11.5-5) shows that the conductivity is

$$\sigma = Fce\left(\frac{1}{f_+} + \frac{1}{f_-}\right) \tag{11.5-12}$$

For a general binary electrolyte $\mathrm{M}_{\nu_+}\mathrm{X}_{\nu_-}$, the analogue of Eq. (11.5-12) is

$$\sigma = Fe\left(\frac{c_+z_+^2}{f_+} + \frac{c_-z_-^2}{f_-}\right) = Fce\left(\frac{\nu_+z_+^2}{f_+} + \frac{\nu_-z_-^2}{f_-}\right) \tag{11.5-13}$$

Exercise 11.18

Show that Eq. (11.5-13) 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 (one substance that comes close is KCl). The fraction of the current that is carried by a given type of ion is called its **transference number**, t:

$$t_i = \frac{j_i}{j_{\text{total}}} \tag{11.5-14}$$

From Eq. (11.5-13), it follows that if there is only one type of cation and one type of anion present,

$$t_+ = \frac{c_+z_+^2/f_+}{c_+z_+^2/f_+ + c_-z_-^2/f_-} = \frac{\nu_+z_+^2/f_+}{\nu_+z_+^2/f_+ + \nu_-z_-^2/f_-} \tag{11.5-15}$$

with a similar equation for t_-.

The **mobility** u_i of the ith type of ion is defined by

$$u_i = \frac{v_i}{\mathscr{E}} \tag{11.5-16}$$

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. The mobility is numerically equal to the mean drift velocity if the electric field is 1 V m^{-1}. The relation shown in Eq. (11.5-16) is equivalent to

$$u_i = \frac{|z_i|e}{f_i} = \frac{|z_i|e}{6\pi\eta r_i(\text{eff})} \tag{11.5-17}$$

where f_i is the friction coefficient for the ith type of ion, and where r_i(eff) is the effective radius of the ion. The second equality in this equation comes from Stokes's law, Eq. (11.2-26). Ions with equal valence magnitudes and with equal effective radii will have equal mobilities according to Stokes's law.

The conductivity can be written in terms of the mobilities:

$$\sigma = F(c_+z_+u_+ + c_-|z_-|u_-) \tag{11.5-18a}$$

$$\sigma = Fc(\nu_+z_+u_+ + \nu_-|z_-|u_-) \tag{11.5-18b}$$

*Exercise 11.19

Write the transference numbers in terms of the ion mobilities.

Ion mobilities are measured by several different techniques. The technique of **electrophoresis** is used in the study of the ion mobilities of protein molecules. In this technique a solution is placed between electrodes, across which a direct voltage is placed. Most protein molecules contain various weak acidic and basic functional groups, which ionize at different characteristic pH values. The protein molecules thus have a characteristic average charge that depends on pH. The mobility of the protein thus depends on pH, and electrophoresis experiments at different pH values can be used to separate mixtures of proteins.

It is found that the mobilities and friction coefficients of a given ion actually depend on the concentrations of the ions present so that Eq. (11.5-17) is correct only for very small concentrations. One reason for the dependence on concentration is that interionic forces are "long-range" forces. That is, while the forces between uncharged molecules decrease rapidly with distance, electrostatic forces decrease slowly with distance. Ions that are at a considerable distance exert significant forces, as stated in the discussion of the Debye–Hückel theory in Chapter 7. There are three important effects. The first is the **electrophoretic effect**, due to the fact that ions of the opposite charge are moving in the opposite direction from a given ion. At nonzero concentration, the attractive forces of these ions on the given ion tend to slow it down. The second effect is the **relaxation effect**. Every ion repels ions of its own charge and attracts ions of the opposite charge. Because of this there exists an "ion atmosphere" of excess charge of the opposite sign around every ion, as described in Chapter 7. 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 compared with its motion at infinite dilution. The third effect is that of solvation. At high concentrations, ions must compete with each other to attract solvent molecules. Since the effective size of ions can include some of the solvent molecules that are strongly attracted to the ions, any change in the solvation can affect the mobility. The electrophoretic effect and the relaxation effect vanish in the limit of infinite dilution and the solvation effect approaches concentration-independent behavior, so that ion mobilities and friction coefficients approach constant values in the limit of infinite dilution. 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 for the large mobilities 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 hydronium ion, H_3O^+, or the $H_5O_2^+$ ion. After such an ion is formed, a hydrogen ion on the other side of the ion can be released. This hydrogen ion can attach itself to a second water molecule, after which a different hydrogen ion is released on the other side of the second hydronium ion, and so on, providing a rapid apparent motion of hydrogen ions. The exchange of hydroxide ions is similar.

Some cations with a small radius, such as lithium, have somewhat lower mobilities and larger effective radii than might be expected. This is attributed to the fact that small cations are more strongly hydrated (more strongly bound to water molecules) than larger cations, because water molecules can approach closer to the center of charge of the smaller ion. These strongly bound water molecules are more likely to be carried along with the ions than are less strongly bound water molecules, increasing the apparent size of the ions.

*Exercise 11.20

a. Calulate the effective radii of the hydrogen ions from the ion mobilities.
b. Calculate the effective radius of the lithium ion from its ion mobility.

Another quantity that is commonly tabulated is the **molar conductivity**, denoted by Λ, and defined by

$$\Lambda = \frac{\sigma}{c} \tag{11.5-19}$$

where c is the stoichiometric concentration of the electrolyte in mol m^{-3} or in mol L^{-1}. From Eq. (11.5-18b),

$$\Lambda = \frac{\sigma}{c} = F(v_+ z_+ u_+ + v_- |z_-| u_-) \tag{11.5-20}$$

This quantity would be independent of concentration if the mobilities were indendent of concentration. At fairly small concentrations the molar conductivity actually depends linearly on the square root of the concentration, much like the logarithm of the activity coefficient according to the Debye–Hückel theory:

$$\Lambda = \Lambda_0 - Ac^{1/2} \tag{11.5-21}$$

This equation was discovered empirically by Kohlrausch in 1900. It also represents the results of the Debye–Hückel–Onsager theory, which provides an expression for the parameter A. In the limit of infinite dilution, Λ approaches a constant limit, just as do the mobility and friction coefficient:

$$\Lambda_0 = \lim_{c \to 0} \Lambda \tag{11.5-22}$$

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 such a sum. For a uni-univalent electrolyte,

$$\Lambda = \lambda_+ + \lambda_- \tag{11.5-23}$$

$$\Lambda_0 = (\lambda_+)_0 + (\lambda_-)_0 \tag{11.5-24}$$

where $(\lambda_+)_0$ and $(\lambda_-)_0$ are the limiting molar conductivities of the ions. Equation (11.5-24) is known as *Kohlrausch's law* and was discovered empirically around 1875. 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.

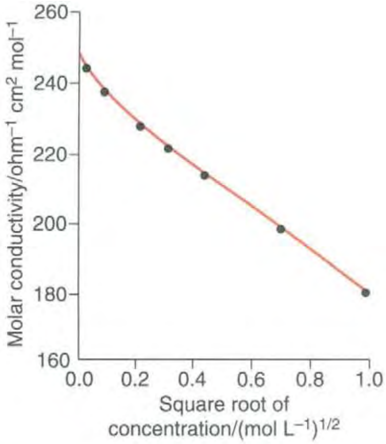

Figure 11.9. The Molar Conductivity of Sodium Hydroxide as a Function of the Square Root of the Concentration in mol L^{-1}. This figure shows the extrapolation to zero concentration, which delivers the limiting value of the molar conductivity.

EXAMPLE 11.12

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. (11.5-21), a plot of Λ versus $c^{1/2}$ should be nearly linear at small concentrations. Such a plot is shown in Figure 11.9. 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 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.

Since a weak electrolyte is only partially ionized at nonzero concentration, an extrapolation such as that in Example 11.12 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 11.21

***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 concentrations 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

Attempt an extrapolation as in Example 11.12 to determine the limiting molar conductivity.

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: heat conduction is described by Fourier's law, diffusion is described by Fick's law, and visous flow is described by Newton's law of viscous flow.

Transport processes in a hard-sphere gas can be analyzed theoretically. A formula for the self-diffusion coefficient was derived in this chapter, and similarly 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 conductance contribution for each type of ion that is inversely proportional to the friction coefficient.

Problems for Section 11.1

11.22. 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 gradients of the temperature and the concentration of component 2.

b. Write the expressions for the time derivatives of the temperature and the concentration of component 2.

Problems for Section 11.2

11.23. **a.** Show that the concentration expression in Problem 11.22 can satisfy Fick's second of diffusion, Eq. (11.2-13).

***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.

11.24. At 25.4°C, the diffusion coefficient of methane in glycerol equals $9.5 \times 10^{-10}\ \mathrm{m^2\ s^{-1}}$. Find the root-mean-square displacement in one direction of a methane molecule in (a) 60 min, and (b) 120 min.

***11.25.** 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 $D = 5 \times 10^{-10}\ \mathrm{m^2\ s^{-1}}$.

11.26. Find the root-mean-square distance in the z direction traveled by glucose molecules in 1.00 h in a dilute aqueous solution at 25°C.

***11.27.** 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 $r = 2.00$ mm.

b. Find dV/dt, the volume rate of flow through the tube.

c. Find $P_2 - P_1$ if the length of the tube is 0.500 m.

d. Find the value of the Reynolds number. Is the flow laminar?

11.28. 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?

11.29. 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?

11.30. The viscosity of dry air is given in poise as a function of temperature by the following formula[6]:

$$\eta = \frac{(1345.8 \times 10^{-7})T^{3/2}}{T + 110.4}$$

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.

***11.31.** An Ostwald viscometer[7] 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 $1.834\ \mathrm{g\ mL^{-1}}$ and that of water is $0.09982\ \mathrm{g\ mL^{-1}}$ at 20°C.

11.32. In a certain Ostwald viscometer (see previous problem), 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 $0.99823\ \mathrm{g\ mL^{-1}}$, and that of mercury is $13.5462\ \mathrm{g\ mL^{-1}}$.

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[6] *Tables of Thermal Properties of Gases*, table 1-B, U.S. Natl. Bur. Stand. Circ. 564, U.S. Government Printing Office, Washington, D.C., 1955.

[7] The Ostwald viscometer is named for Friedrich Wilhelm Ostwald, 1853–1932, who was one of the founders of physical chemistry. He received the 1909 Nobel Prize in chemistry for his work in catalysis.

***11.33.** **a.** A certain garden hose is supposed to be able to deliver 550 gallons of water per hour. If the hose is 50 ft long and has an inside diameter of 5/8 inch, estimate the water pressure necessary to deliver this much water. State any assumptions.

b. Calculate the Reynolds number for the flow in part (a), and determine whether the flow is laminar.

11.34. 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 min.

b. Calculate the Reynolds number and determine whether the flow is laminar.

11.35. **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.

Problems for Section 11.3

11.36. **a.** Calculate the self-diffusion coefficient of helium gas at STP 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 min by He and Ar atoms diffusing at STP in self-diffusion experiments.

***11.37.** **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.

11.38. 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.

11.39. 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.

11.40. 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

$$\mathbf{u}_1 - \mathbf{u}_2 = \frac{1}{x_1 x_2}\mathscr{D}_{12}\,\nabla x_1$$

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 $\mathscr{D}_{12}$ is called the mutual diffusion coefficient. For a mixture of hard spheres[8]

$$\mathscr{D}_{12} = \frac{3}{8\pi^{1/2}}\,\frac{1}{d_{12}^2\mathcal{N}_t}\left(\frac{k_B T}{2\mu}\right)^{1/2}$$

where μ is the reduced mass, $\mathcal{N}_t$ 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 11.36.

***11.41.** Calculate the mutual diffusion coefficient for helium and carbon dioxide at 298.15 K and 1.000 bar. See the previous problem.

11.42. At 20.0°C, the viscosity of ammonia gas is equal to $9.82 \times 10^{-6}\ \mathrm{kg\ m^{-1}\ s^{-1}}$. Find the effective hard-sphere diameter of ammonia molecules at this temperature.

***11.43.** 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.

11.44. For a temperature of 298 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.

Problems for Section 11.4

***11.45.** The following are data for the viscosity of benzene, with the viscosity in centipoise.

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[8] J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *op. cit.*, p. 14, 518 (note 5).

T/K	η/cP
273.15	0.912
283.15	0.758
293.15	0.652
303.15	0.564
313.15	0.503
323.15	0.442
333.15	0.392
343.15	0.358
253.15	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 11.9, and compare it with the enthalpy change of vaporization of benzene, 34.1 kJ mol^{-1}.

11.46. The diffusion coefficient of bovine serum albumin in water at 20.0°C equals 7×10^{-11} 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 g cm^{-3}, estimate the molecular mass and the molar mass.

c. Estimate the sedimentation coefficient of the protein.

***11.47.** The diffusion coefficient of horse heart myoglobin in water at 20°C is equal to 1.13×10^{-10} 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 g cm^{-3}, and find its molar mass.

11.48. Calculate the rms distance diffused in one direction in 30.0 min by hemoglobin molecules in water at 20°C. The value of the diffusion coefficient is 6.9×10^{-11} m^2 s^{-1}.

Problems for Section 11.5

11.49. a. Calculate the force on 1.000 mol of sodium ions (assumed localized in 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).

11.50. Calculate the transference numbers for H^+ and Cl^- ions in a dilute aqueous HCl solution at 25°C.

***11.51.** Calculate the effective radii of K^+ and Cl^- ions in dilute aqueous solution at 25°C.

11.52. Calculate the transference numbers for K^+ and Cl^- in a dilute aqueous KCl solution at 25°C.

***11.53. 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.

11.54. Calculate the transference numbers for each ion in an acetic solution, assuming that infinite-dilution values can be used. Does your answer depend on the extent of ionization? Explain your assertion.

General Problems

11.55. 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.

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 values 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. (11.3-9) 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 (e), calculate the effective hard-sphere diameter of argon atoms at 473 K and compare it with the value in Table A.15.

11.56. Calculate the root-mean-square distance diffused in three dimensions in 30.0 min 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

11.57. **a.** Derive an equation for the flow of heat that is analogous to Fick's second law of diffusion, Eq. (11.2-12). Assuming 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.

11.58. 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 $\mathcal{N}$.

***11.59.** 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 while that of a liquid decreases with increasing temperature.

12

The Rates of Chemical Reactions

OBJECTIVES

After studying this chapter, the student should:

1. understand and be able to use the vocabulary of chemical reaction rates;
2. be able to solve several simple rate laws and to solve a variety of problems related to these solutions;
3. be able to apply experimental techniques to the determination of rate laws and rate constants.

PRINCIPAL FACTS AND IDEAS

1. The rate of a chemical reaction is a function of the concentrations of the reactants and products, as well as of the temperature.
2. The rate law of a chemical reaction is the differential equation for the time rate of change of the concentration of a reactant or product.
3. Differential rate laws can often be solved to obtain integrated rate laws, which can be compared with experimental results.
4. Differential rate laws can be determined experimentally using the method of initial rates.
5. The differential rate law for a simple reaction with nonnegligible reverse reaction can be integrated to obtain an integrated rate law.
6. Two consecutive reactions constitute a simple mechanism for a chemical reaction, and the rate law can be integrated.
7. Specialized techniques exist for studying fast reactions.

12.1

The Macroscopic Description of Chemically Reacting Systems

In Chapter 11 we described nonequilibrium processes in fluid systems that do not undergo any chemical reactions. We now discuss uniform fluid systems in which chemical reactions can occur at constant temperature. These conditions can usually be met by carrying out the reaction in a constant-temperature bath and either stirring the system or using a sufficiently small system. It is possible to treat reactions in systems in which the temperature is not uniform,[1] but we will not discuss such reactions.

Consider a chemical reaction

$$aA + bB \rightarrow dD + fF \tag{12.1-1}$$

where the capital letters stand for chemical formulas, and the lower-case letters are stoichiometric coefficients. We define the rate of the reaction, denoted by r:

$$r = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{d}\frac{d[D]}{dt} = \frac{1}{f}\frac{d[F]}{dt} \tag{12.1-2a}$$

where [A] is the concentration ($\mathrm{mol\,L^{-1}}$ or $\mathrm{mol\,m^{-3}}$) of substance A, [B] is the concentration of substance B, etc., and where t is the time.

An equation similar to Eq. (12.1-2a) can be written for any other reaction, using the appropriate stoichiometric coefficients. In Eq. (8.1-1) a general reaction equation was written in the form

$$0 = \sum_{i=1}^{s} \nu_i \mathscr{F}_i$$

for which the rate can be written as

$$r = \frac{1}{\nu_i}\frac{d[\mathscr{F}_i]}{dt} \tag{12.1-2b}$$

This equation gives the same value for the rate for any choice of substance i taking part in the reaction.

We will assume that the rate of the reaction is a function of temperature, pressure, and the concentrations of the substances in the system. For reactions in nonideal solutions, it would be a better approximation to assume that reaction rates are functions of activities instead of concentrations, but we will assume that concentrations and activities are equal. In most reactions the rate will depend only on the concentrations of the substances occurring in the chemical equation. If a substance that does not occur in the chemical equation increases the rate, it is a **catalyst**.

The macroscopic rate of a chemical reaction is determined by measuring concentrations and is actually a net rate:

$$r = r_{\mathrm{net}} = r_{\mathrm{f}} - r_{\mathrm{r}} \tag{12.1-3}$$

where r_{f} is the forward rate, or the rate at which products form, and where r_{r} is the reverse rate, or the rate at which reactants form. Chemical reactions usually proceed smoothly toward a macroscopic equilibrium state in which the forward and reverse rates

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[1] See for example R. G. Mortimer, *J. Phys. Chem.*, **67**, 1938 (1963).

cancel each other. However, some oscillatory reactions do exist.[2] Figure 12.1 shows schematically how a nonoscillatory chemical reaction, A → B, approaches equilibrium.

In most reactions the forward rate depends only on the concentrations of the reactants, so that the forward reaction can be observed in the absence of the reverse reaction if the products are absent. If A and B are the reactants,

$$r_{\mathrm{f}} = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = r_{\mathrm{f}}([\mathrm{A}], [\mathrm{B}]) \quad \text{(no reverse reaction)} \tag{12.1-4}$$

If the function represented in Eq. (12.1-4) is known, it is called the **rate law** of the forward reaction. Similarly, the reverse reaction rate usually depends only on the concentrations of the products. If D and F are the reactants,

$$r_{\mathrm{r}} = \frac{1}{a}\frac{d[\mathrm{A}]}{dt} = r_{\mathrm{r}}([\mathrm{D}], [\mathrm{F}]) \quad \text{(no forward reaction)} \tag{12.1-5}$$

Equation (12.1-5) is the rate law of the reverse reaction.

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. For example,

$$r_{\mathrm{f}} = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = k_{\mathrm{f}}[\mathrm{A}]^{\alpha}[\mathrm{B}]^{\beta} \tag{12.1-6}$$

Equation (12.1-6) 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**. If there is more than one reactant in the rate law, these orders are sometimes called **partial orders**. The sum of the orders with respect to the different substances is called the **overall order**. If α and β are 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. Higher orders are similarly assigned. The orders are usually small positive integers, but other cases do occur. There are some reactions that are not described by Eq. (12.1-6). Such reactions are said not to have a definite order.

The proportionality constant k_{f} in Eq. (12.1-6) 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 negligible.[3] We will discuss the temperature dependence of reaction rates in Chapter 13, and will discuss only constant-temperature systems in this chapter.

One of the objectives of the kinetic study of a reaction is to determine the rate law. For a reaction with definite orders, this means to determine the orders with respect to each reactant and the value of the rate constant. There are at least two reasons why this is useful. The first is that it allows us to predict the rates of the reaction for new values of the concentrations without doing additional experiments. The second is that the form of the rate law usually provides information about the sequence of molecular steps making up 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, N.J., 1972, pp. 181ff.

12.2

Forward Reactions with One Reactant

In this section we discuss reactions with definite orders, a single reactant, and with negligible reverse reaction. Inspection of Figure 12.1 shows that when a reaction that converts A to B has approached equilibrium, the reverse rate cannot be neglected. We must avoid applying the results of this section to that case. 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 to determine the concentration of one of the reactants or products as a function of time as the reaction proceeds at constant temperature. A variety of analytical 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 of 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 or gain if a gas is lost or absorbed

Once we know from experiment how the concentration of a reactant or product depends on time, we must have a formula for the concentration as a function of time to compare this with. We now proceed to integrate differential rate laws for a number of cases to obtain such formulas.

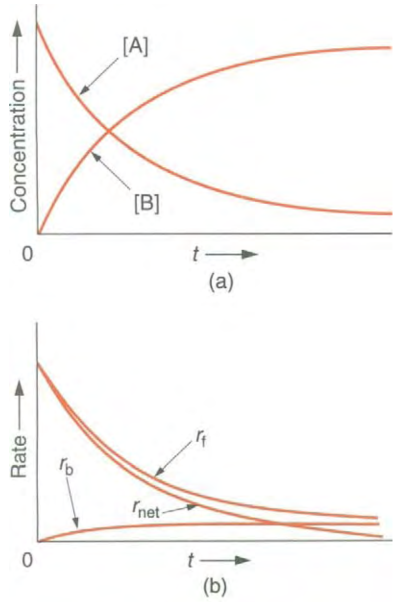

Figure 12.1. The Approach to Equilibrium of a Hypothetical Reaction. (a) The concentrations of the product B and the reactant A as functions of time. Both of the concentrations approach constant values at large values of the time. (b) The forward rate, the reverse rate, and the net rate as functions of time. The net rate approaches zero for large values of the time.

First-Order Reactions

Consider a first-order reaction without significant reverse reaction:

$$\mathrm{A} \rightarrow \text{products} \tag{12.2-1}$$

The differential rate law is

$$r = -\frac{d[\mathrm{A}]}{dt} = k_{\mathrm{f}}[\mathrm{A}] \tag{12.2-2}$$

To separate the variables we multiply Eq. (12.2-2) by dt and divide by [A]:

$$\frac{1}{[\mathrm{A}]}\frac{d[\mathrm{A}]}{dt}dt = \frac{1}{[\mathrm{A}]}d[\mathrm{A}] = -k_{\mathrm{f}}\,dt \tag{12.2-3}$$

We carry out a definite integration from time $t = 0$ to $t = t'$, where t' is a specific value of the time:

$$\int_0^{t'} \frac{1}{[\mathrm{A}]} d[\mathrm{A}] = -\int_0^{t'} k_\mathrm{f}\, dt \qquad (12.2\text{-}4)$$

$$\ln([\mathrm{A}]_{t'}) - \ln([\mathrm{A}]_0) = -k_\mathrm{f} t'$$

where the subscript on a concentration indicates the time at which it is measured. Taking antilogarithms of Eq. (12.2-4),

$$[\mathrm{A}]_t = [\mathrm{A}]_0 e^{-k_\mathrm{f} t} \quad \text{(first order, no reverse reaction)} \qquad (12.2\text{-}5)$$

where we have written t instead of t'. An indefinite integration can also be carried out, followed by evaluation of the constant of integration.

Exercise 12.1

Carry out an indefinite integration of Eq. (12.2-3). Evaluate the constant of integration to obtain Eq. (12.2-5).

For a reaction that involves a change in the number of moles of gaseous substances the progress of the reaction can be monitored by measuring the pressure. In this case, it is convenient to use partial pressures instead of concentrations.

EXAMPLE 12.1

The gas-phase reaction

$$N_2O_5 \rightarrow 2NO_2 + \tfrac{1}{2}O_2$$

is found to be first order. The rate constant at 337.6 K is equal to $5.12 \times 10^{-3}\ \mathrm{s}^{-1}$.[4] 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. Equation (12.2-5b) can be rewritten

$$P(N_2O_5)_t = P(N_2O_5)_0 e^{-k_\mathrm{f} t}$$

$$= (0.500\ \mathrm{atm}) \exp[-(5.12 \times 10^{-3}\ \mathrm{s}^{-1})(60.0\ \mathrm{s})] = 0.368\ \mathrm{atm}$$

The **half-life**, $t_{1/2}$, is defined as the time required for half of the starting compound to react. Since $[\mathrm{A}]_{t_{1/2}} = [\mathrm{A}]_0/2$, we can write from Eq. (12.2-4),

$$k_\mathrm{f} t_{1/2} = -\ln\left(\frac{[\mathrm{A}]_{t_{1/2}}}{[\mathrm{A}]_0}\right) = -\ln\left(\frac{1}{2}\right)$$

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[4] H. S. Johnston and Y. Tao, *J. Am. Chem. Soc.*, **73**, 2948 (1951).

or

$$t_{1/2} = \frac{\ln(2)}{k_{\mathrm{f}}} \approx \frac{0.69315}{k_{\mathrm{f}}} \quad \text{(first order, no reverse reaction)} \tag{12.2-6}$$

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. (12.2-4) gives

$$\tau = \frac{1}{k_{\mathrm{f}}} = \frac{t_{1/2}}{\ln(2)} \approx 1.4427 t_{1/2} \tag{12.2-7}$$

For a first-order reaction k_{f} has units of time^{-1} (s^{-1}, min^{-1}, etc.).

Exercise 12.2

***a.** Find the half-life and the relaxation time for the reaction of Example 12.1.
b. Verify Eq. (12.2-7).

Like some chemical reactions, 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.

***Exercise 12.3**

The half-life of ^{235}U is equal to 7.1×10^8 years.
a. Find the first-order rate constant.
b. Find the time required to 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

$$r = -\frac{d[\mathrm{A}]}{dt} = k_{\mathrm{f}}[\mathrm{A}]^2 \tag{12.2-8}$$

With the variables separated,

$$\frac{1}{[\mathrm{A}]^2}\frac{d[\mathrm{A}]}{dt}\,dt = \frac{d[\mathrm{A}]}{[\mathrm{A}]^2} = -k_{\mathrm{f}}\,dt \tag{12.2-9}$$

We carry out a definite integration from time $t = 0$ to time $t = t'$.

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_{t'}} \frac{d[\mathrm{A}]}{[\mathrm{A}]^2} = -k_{\mathrm{f}} \int_0^{t'} dt \tag{12.2-10}$$

The result of the integration is

$$\frac{1}{[\mathrm{A}]_{t'}} - \frac{1}{[\mathrm{A}]_0} = k_{\mathrm{f}} t' \quad \text{(second order, no reverse reaction)} \tag{12.2-11}$$

For a second-order reaction, k_f has units of concentration^{-1} time^{-1} (L mol^{-1} s^{-1}, m^3 mol^{-1} min^{-1}, etc.).

Exercise 12.4

Carry out an indefinite integration and evaluate the constant of integration to obtain Eq. (12.2-11) in an alternative way.

EXAMPLE 12.2

The gas-phase reaction

$$\mathrm{NO_3} \rightarrow \mathrm{NO_2} + \tfrac{1}{2}\mathrm{O_2}$$

is second order with respect to NO_3. At a temperature of 20°C and an initial concentration of NO_3 equal to 0.0500 mol L^{-1}, the concentration after 60.0 min is equal to 0.0358 mol L^{-1}. Find the value of the forward rate constant.

Solution

$$k_f = \frac{1}{t}\left(\frac{1}{[\mathrm{A}]_t} - \frac{1}{[\mathrm{A}]_0}\right) = \frac{1}{3600\ \mathrm{s}}\left[\frac{1}{0.0358\ \mathrm{mol\ L^{-1}}} - \frac{1}{0.0500\ \mathrm{mol\ L^{-1}}}\right]$$
$$= 2.2 \times 10^{-3}\ \mathrm{L\ mol^{-1}\ s^{-1}}$$

*Exercise 12.5

a. Find the concentration of NO_2 in the experiment of Example 12.2 after a total elapsed time of 145 min.

b. Find the concentration after 145 min if the initial concentration is 0.100 mol L^{-1}.

The half-life of the reaction is the time necessary for half of the initial amount of reactant to be consumed:

$$\frac{1}{[\mathrm{A}]_0/2} - \frac{1}{[\mathrm{A}]_0} = \frac{2}{[\mathrm{A}]_0} - \frac{1}{[\mathrm{A}]_0} = k_f t_{1/2} \tag{12.2-12}$$

where we have used the fact that $[\mathrm{A}]_{t_{1/2}} = [\mathrm{A}]_0/2$. Equation (12.2-12) leads to

$$t_{1/2} = \frac{1}{k_f[\mathrm{A}]_0} \quad \text{(second order, no reverse reaction)} \tag{12.2-13}$$

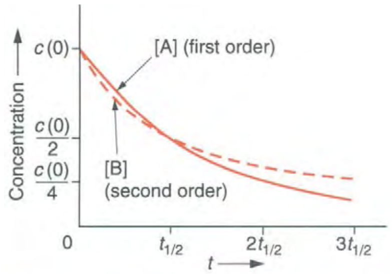

Figure 12.2. Comparison of the Concentrations of the Reactants of a First-Order Reaction and a Second-Order Reaction. This graph shows two hypothetical reactions which for the same initial concentration have equal initial half-lives. During the first half-life, the two curves do not differ very much from each other.

*Exercise 12.6

a. Find the half-life of the reaction of Example 12.2 with the given initial concentration.

b. Find the half-life of the reaction of Example 12.2 if the initial concentration is equal to 0.0200 mol L^{-1}.

c. Find the half-life of the reaction of Example 12.2 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 12.2 shows a hypothetical case: 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 $t_{1/2}$.

*Exercise 12.7

a. Find expressions for the time required for the concentration of the reactant in each of the reactions of Figure 12.2 to drop to one-sixteenth of its original value, assuming that the reverse reaction is absent. Express this time in terms of $t_{1/2}$.

b. Express this time in terms of the two forward rate constants and the initial concentrations.

*n*th-Order Reactions

The rate law for an *n*th-order reaction with a single reactant is

$$r = -\frac{d[\mathrm{A}]}{dt} = k_{\mathrm{f}}[\mathrm{A}]^n \tag{12.2-14}$$

where 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

$$-\frac{d[\mathrm{A}]}{[\mathrm{A}]^n} = k_{\mathrm{f}}\, dt \tag{12.2-15}$$

We perform a definite integration from $t = 0$ to $t = t'$

$$\int_{[\mathrm{A}]_0}^{[\mathrm{A}]_{t'}} \frac{d[\mathrm{A}]}{[\mathrm{A}]^n} = -k_{\mathrm{f}} \int_0^{t'} dt \tag{12.2-16}$$

The result is

$$\frac{1}{n-1}\left[\frac{1}{[\mathrm{A}]_{t'}^{n-1}} - \frac{1}{[\mathrm{A}]_0^{n-1}}\right] = k_{\mathrm{f}} t' \tag{12.2-17}$$

The half-life of an *n*th-order reaction without reverse reaction is found by substituting $[\mathrm{A}]_{t_{1/2}} = [\mathrm{A}]_0/2$ into Eq. (12.2-17). The result is

$$t_{1/2} = \frac{2^{n-1} - 1}{(n-1)k_{\mathrm{f}}[\mathrm{A}]_0^{n-1}} \tag{12.2-18}$$

This formula is not valid if $n = 1$ or $n = 0$. If $n = 1$, Eq. (12.2-6) applies.

Exercise 12.8

a. Verify Eq. (12.2-18).

b. 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.

c. In terms of $t_{1/2}$, how long will it take for $\frac{7}{8}$ of the reactant of part (b) 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

$$r = -\frac{d[\mathrm{A}]}{dt} = k_{\mathrm{f}}[\mathrm{A}]^0 = k_{\mathrm{f}} \tag{12.2-19}$$

The solution of this equation is

$$[\mathrm{A}]_t = \begin{cases} [\mathrm{A}]_0 - k_{\mathrm{f}}t & \text{if } 0 < t < [\mathrm{A}]_0/k_{\mathrm{f}} \\ 0 & \text{if } [\mathrm{A}]_0/k_{\mathrm{f}} < t \end{cases} \tag{12.2-20}$$

where the first line of the solution is obtained from Eq. (12.2-19). The second line of the solution is obtained from the fact that the reaction stops when the reactant has been consumed.

*Exercise 12.9

a. A hypothetical zero-order reaction has a rate constant equal to 0.0150 mol $\mathrm{L}^{-1}\,\mathrm{s}^{-1}$ at a certain temperature. If the initial concentration of the single reactant is 1.000 mol L^{-1}, find the concentration after a reaction time of 5.00 s at this temperature.

b. Find the time required for all of the reactant of part (a) to react at this temperature.

c. Find an expression for the half-life of a zero-order reaction and the value of the half-life of the reaction of part (a).

Determination of Reaction Order by Comparison of Experimental Data with Integrated Rate Laws

Since linear graphs are the easiest type to use and since concentrations are not linear functions of time except for zero order, one does not ordinarily use a graph of the concentration as a function of time to determine the reaction order. For each order, one plots the appropriate function of the concentration that will give a linear graph. 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([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, etc. To test for nonintegral orders, graphs of $1/((n-1)[\mathrm{A}]^{n-1})$ for various nonintegral values of n can also be made. The graph that is most nearly linear corresponds to the correct order. Figure 12.3 shows schematic graphs for zero, first, second, and third orders. Using commercially available software packages such as Excel, MathCad, Mathematica, CricketGraph and KaleidaGraph, one can construct the graphs and carry out least-squares (regression) fits to the data. The software automatically calculates the **correlation coefficient** (or its square), which is a measure of the accuracy of the fit of the function to the data. Some packages will print out a list of **residuals**, which are the differences between the data point and the least-squares line.

The Method of Half-Lives

Another way to determine the order of a reaction is to determine how the half-life of the reaction depends on the initial concentration. If the half-life of the reaction is

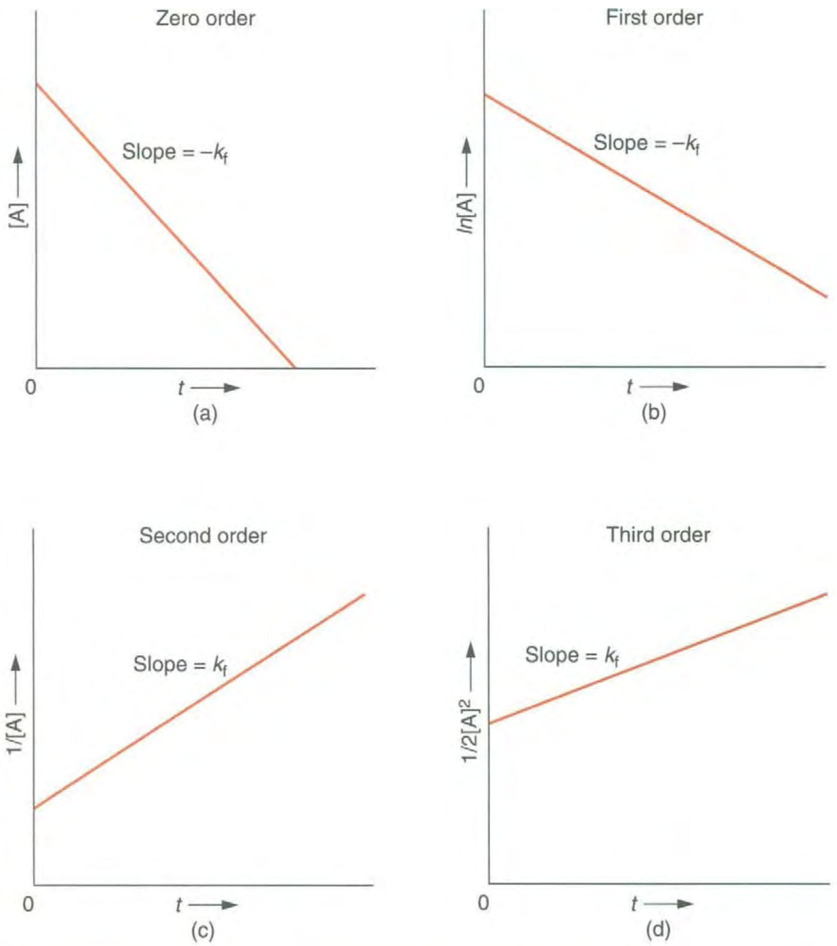

Figure 12.3. Linear Graphs for Zero, First, Second, and Third Order Reactions. (a) **Zero order.** (b) **First order.** (c) **Second order.** (d) **Third order.** In each case, the appropriate function of the concentration is plotted such that the graph is linear.

independent of concentration the reaction is first order. To test for other orders we take the logarithm of Eq. (12.2-18) to obtain:

$$\ln(t_{1/2}) = \ln\left(\frac{2^{n-1}-1}{(n-1)k_f}\right) - (n-1)\ln([\mathrm{A}]_0) \qquad (n \neq 1, n \neq 0) \qquad (12.2\text{-}21)$$

To use Eq. (12.2-21), one could perform a set of different experiments at the same temperature but with different initial concentrations, determine the half-life for each, and 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. (12.2-21). 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 12.3

For the gas-phase reaction at 300°C,

$$C_2F_4 \rightarrow \frac{1}{2}\text{cyclo-}C_4F_8$$

the following data on the concentration of C_2F_4 were taken. Using the half-life method, determine the order of the reaction and the rate constant at this temperature.

Time/min	Concentration/mol L^{-1}
0	0.0500
250	0.0250
750	0.0125
1750	0.00625
3750	0.00312

Solution

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 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 the logarithm of $t_{1/2}$ versus the logarithm of the initial concentration gives the order = 2.00 and $k_f = 0.080\ \text{L mol}^{-1}\ \text{min}^{-1} = 1.3 \times 10^{-3}\ \text{L mol}^{-1}\ \text{s}^{-1}$.

The Method of Initial Rates

In this method, one compares data directly with the differential rate laws instead of with the integrated rate laws. The method has two advantages: it is not necessary to integrate the rate law, and there is almost certainly no interference by the reverse reaction. The reaction is followed for a short time Δt for which there is a change $\Delta[\text{A}]$:

$$\Delta[\text{A}] = [\text{A}]_{\Delta t} - [\text{A}]_0 \tag{12.2-22}$$

The time Δt must be short enough that $\Delta[\text{A}] \ll [\text{A}]$. The initial rate is approximated by a quotient of finite differences:

$$r_{\text{initial}} = -\frac{d[\text{A}]}{dt} \approx -\frac{\Delta[\text{A}]}{\Delta t} \tag{12.2-23}$$

One could alternatively measure the concentration at several times and use a graphical or numerical procedure to obtain a better approximation to the derivative $d[\text{A}]/dt$ at $t = 0$.

If there is only one reactant, the logarithm of Eq. (12.1-6) is

$$\ln(r_{\text{initial}}) = \ln(k_f) + \alpha \ln([A]_0) \tag{12.2-24}$$

To determine the order and the rate constant, one carries out several experiments at the same temperature but with different initial values of [A]. Plots of the logarithm of the initial rate as a function of the logarithm of the initial concentration are constructed or a linear least-squares fit is performed. The slope of the line best fitting the data points is the order of the reaction, and the intercept is the logarithm of the rate constant.

The method of initial rates has the disadvantage that several experiments must be carried out. A modification to the above method would be to determine the value of $\Delta[A]/\Delta t$ and the value of [A] at different times in a single experiment and to use these values in Eq. (12.2-24).

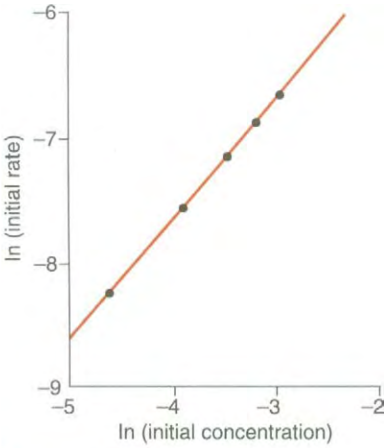

Figure 12.4. This figure shows the data points and the least-squares line fitting the natural logarithm of the initial rate to the natural logarithm of the initial concentration.

EXAMPLE 12.4

Assume that the following data were obtained 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} h^{-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 $\ln(r_{\text{initial}})$ against $\ln([C_2H_5Cl]_0)$ gives

$$\alpha = 1.00, \quad \ln(k_f) = -3.64, \quad k_f = 0.026\ h^{-1}$$

Figure 12.4 shows the graph of the data points and the least-squares line. The correlation coefficient squared was equal to 1.000.

12.3 Forward Reactions with More Than One Reactant

Reactions with more than one reactant are harder to deal with than reactions of a single reactant. In a few cases the differential rate law can be integrated to obtain an integrated rate law, and in other cases we can use the method of initial rates or the method of isolation.

Integration of the Differential Rate Law That Is First Order in Each of Two Reactants

Consider a reaction

$$aA + bB \rightarrow \text{products} \tag{12.3-1}$$

where a and b represent stoichiometric coefficients. The rate law is

$$r = -\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = k_{\mathrm{f}}[\mathrm{A}][\mathrm{B}] \tag{12.3-2}$$

We first assume that the reactants are in the stoichiometric ratio:

$$\frac{[\mathrm{A}]_0}{[\mathrm{B}]_0} = \frac{a}{b} \tag{12.3-3}$$

The concentrations will remain in this ratio during the reaction.

Exercise 12.10

Show that if Eq. (12.3-3) holds then

$$\frac{[\mathrm{A}]_t}{[\mathrm{B}]_t} = \frac{a}{b} \tag{12.3-4}$$

for all values of t greater than 0.

Equation (12.3-2) appears to have two dependent variables, [A] and [B]. However, we can express the equation in terms of a single dependent variable $x(t)$:

$$x(t) = \frac{[\mathrm{A}]_0 - [\mathrm{A}]_t}{a} = \frac{[\mathrm{B}]_0 - [\mathrm{B}]_t}{b} \tag{12.3-5}$$

We can now write Eq. (12.3-2) in the form

$$\frac{dx}{dt} = k_{\mathrm{f}}([\mathrm{A}]_0 - ax)([\mathrm{B}]_0 - bx) \tag{12.3-6a}$$

$$= k_{\mathrm{f}}ab\left(\frac{[\mathrm{A}]_0}{b} - x\right)\left(\frac{[\mathrm{B}]_0}{b} - x\right) = k_{\mathrm{f}}ab\left(\frac{[\mathrm{A}]_0}{a} - x\right)^2 \tag{12.3-6b}$$

where we have used the fact that $[\mathrm{B}]_0/b = [\mathrm{A}]_0/a$ for a stoichiometric mixture.

The variables can be separated in Eq. (12.3-6b) by dividing by $([\mathrm{A}]_0/a - x)^2$ and multiplying by dt:

$$\frac{dx}{\left(\frac{[\mathrm{A}]_0}{a} - x\right)^2} = k_{\mathrm{f}}ab\,dt \tag{12.3-7}$$

We integrate both sides of Eq. (12.3-7) from $t = 0$ to $t = t'$:

$$\frac{1}{\frac{[\mathrm{A}]_0}{a} - x(t')} - \frac{1}{\frac{[\mathrm{A}]_0}{a}} = k_{\mathrm{f}}abt'$$

which, if we replace t' by t, is the same as

$$\frac{1}{[\mathrm{A}]_t} - \frac{1}{[\mathrm{A}]_0} = k_{\mathrm{f}}bt \tag{12.3-8}$$

Equation (12.3-8) is the same as Eq. (12.2-11) except for the appearance of the factor b in the right-hand side.

EXAMPLE 12.5

The destruction of the ozone layer of the atmosphere might involve the reaction:

$$\mathrm{NO} + \mathrm{O_3} \rightarrow \mathrm{NO_2} + \mathrm{O_2}$$

The reaction is first order in each reactant and the rate constant is equal to $1.3 \times 10^6\ \mathrm{L\,mol^{-1}\,s^{-1}}$ at 298 K. For initial concentrations of NO and O_3 both equal to $1.00 \times 10^{-6}\ \mathrm{mol\,L^{-1}}$, find the concentrations of NO and O_3 at time $t = 2.00\ \mathrm{s}$.

Solution

$$\frac{1}{[\mathrm{NO}]} = \frac{1}{[\mathrm{NO}]_0} + k_f t = \frac{1}{1.00 \times 10^{-6}\ \mathrm{mol\,L^{-1}}} + (1.3 \times 10^6\ \mathrm{L\,mol^{-1}\,s^{-1}})(2.00\ \mathrm{s})$$
$$= 3.6 \times 10^6\ \mathrm{L\,mol^{-1}}$$

$$[\mathrm{NO}] = [\mathrm{O_3}] = \frac{1}{3.6 \times 10^6\ \mathrm{L\,mol^{-1}}} = 2.8 \times 10^{-7}\ \mathrm{mol\,L^{-1}}$$

***Exercise 12.11**

a. Find the expression for the half-life of the reaction of Eq. (12.3-1) for the case of a stoichiometric mixture.

b. Find the half-life of the reaction in Example 12.5 with the given initial concentrations.

c. Find the half-life of the reaction in Example 12.5 with initial concentrations both equal to $5.00 \times 10^{-5}\ \mathrm{mol\,L^{-1}}$.

If the reactants are not mixed in the stoichiometric ratio, we separate the variables in Eq. (12.3-6a) to obtain

$$\frac{1}{([\mathrm{A}]_0 - ax)([\mathrm{B}]_0 - bx)}\,dx = k_f\,dt \tag{12.3-9}$$

This equation can be integrated by the method of partial fractions. We write

$$\frac{1}{([\mathrm{A}]_0 - ax)([\mathrm{B}]_0 - bx)} = \frac{G}{[\mathrm{A}]_0 - ax} + \frac{H}{[\mathrm{B}]_0 - bx} \tag{12.3-10}$$

where G and H are guaranteed by a theorem of algebra to be constants. These constants are

$$G = \frac{1}{[\mathrm{B}]_0 - b[\mathrm{A}]_0/a} \quad \text{and} \quad H = \frac{1}{[\mathrm{A}]_0 - a[\mathrm{B}]_0/b}$$

Exercise 12.12

Verify the expressions for G and H.

When the expressions for G and H are substituted into Eq. (12.3-10) and the resulting expression is substituted into Eq. (12.3-9), a definite integration gives

$$\frac{1}{a[\mathrm{B}]_0 - b[\mathrm{A}]_0}\ln\left(\frac{[\mathrm{B}]_t[\mathrm{A}]_0}{[\mathrm{A}]_t[\mathrm{B}]_0}\right) = k_f t \tag{12.3-11}$$

Exercise 12.13

Verify Eq. (12.3-11).

EXAMPLE 12.6

For the reaction of Example 12.5, $[\mathrm{NO}]_0 = 1.00 \times 10^{-6}\ \mathrm{mol\ L^{-1}}$ and $[\mathrm{O_3}]_0 = 5.00 \times 10^{-7}\ \mathrm{mol\ L^{-1}}$. Find the concentration of ozone after 3.50 s.

Solution

Let O_3 be denoted by A and NO be denoted by B. Use of Eq. (12.3-11) 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, $x = 4.27 \times 10^{-7}$, so that $[\mathrm{O_3}] = 0.73 \times 10^{-7}\ \mathrm{mol\ L^{-1}}$.

The Method of Initial Rates for Two or More Reactants

For a reaction with several reactants, the method of initial rates provides the most convenient way to determine the rate law and the rate constant. The method is very similar to that with a single reactant, which led to Eq. (12.2-14). Consider the reaction:

$$a\mathrm{A} + b\mathrm{B} + f\mathrm{F} \rightarrow \text{products} \tag{12.3-12}$$

for which the initial rate can be written as

$$-\frac{1}{a}\frac{\Delta[\mathrm{A}]}{\Delta t} \approx r_{\mathrm{initial}} = k_{\mathrm{f}}[\mathrm{A}]_0^{\alpha}[\mathrm{B}]_0^{\beta}[\mathrm{F}]_0^{\phi} \tag{12.3-13}$$

Several experiments are carried out at the same fixed temperature and 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

$$\ln(r_{\mathrm{initial}}) = \ln(k_{\mathrm{f}}[\mathrm{B}]_0^{\beta}[\mathrm{F}]_0^{\phi}) + \alpha\ln([\mathrm{A}]_0) \tag{12.3-14}$$

The first term on the right-hand side of this equation has the same value in all of these experiments. A plot of $\ln(r_{\mathrm{initial}})$ as a function of $\ln([\mathrm{A}]_0)$ should give a straight line with slope equal to α.

Additional experiments are carried out in which the initial concentration of each of the other substances is varied in turn, keeping all other initial concentrations fixed. Equations analogous to Eq. (12.3-14) allow the order with respect to each substance to be determined. After all of the orders are determined, everything in the right-hand side of Eq. (12.3-13) is known but 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 from each experiment and then to average the values.

EXAMPLE 12.7

Assume that the following data were taken at 298 K for the gas-phase reaction:

$$2NO + Cl_2 \rightarrow 2NOCl$$

$[NO]/\mathrm{mol\,L^{-1}}$	$[Cl_2]/\mathrm{mol\,L^{-1}}$	Initial rate$/\mathrm{mol\,L^{-1}\,s^{-1}}$
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 it is best to proceed algebraically instead of with least-squares fits 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

$$\frac{r_2}{r_1} = \frac{2.8 \times 10^{-4}\ \mathrm{mol\,L^{-1}\,s^{-1}}}{7.1 \times 10^{-5}\ \mathrm{mol\,L^{-1}\,s^{-1}}} = 4.0$$

$$= \frac{k[NO]_2^{\alpha}[Cl_2]_2^{\beta}}{k[NO]_1^{\alpha}[Cl_2]_1^{\beta}} = \frac{[NO]_2^{\alpha}}{[NO]_1^{\alpha}} = \left(\frac{0.0400\ \mathrm{mol\,L^{-1}}}{0.0200\ \mathrm{mol\,L^{-1}}}\right)^{\alpha} = 2.00^{\alpha}$$

$$\alpha = \frac{\ln(4.0)}{\ln(2.00)} = 2.0$$

The order with respect to Cl_2 is obtained from the first and the third experiments:

$$\frac{r_3}{r_1} = \frac{1.4 \times 10^{-4}\ \mathrm{mol\,L^{-1}\,s^{-1}}}{7.1 \times 10^{-5}\ \mathrm{mol\,L^{-1}\,s^{-1}}} = 2.0$$

$$= \frac{k[NO]_3^{\alpha}[Cl_2]_3^{\beta}}{k[NO]_1^{\alpha}[Cl_2]_1^{\beta}} = \frac{[Cl_2]_3^{\beta}}{[Cl_2]_1^{\beta}} = \left(\frac{0.0400\ \mathrm{mol\,L^{-1}}}{0.0200\ \mathrm{mol\,L^{-1}}}\right)^{\beta} = 2.00^{\beta}$$

$$\beta = \frac{\ln(2.0)}{\ln(2.00)} = 1.0$$

The reaction is second order with respect to NO and first order with respect to Cl_2. We compute the rate constant from the data of the first experiment

$$k_f = \frac{r_{\mathrm{initial}}}{[NO]^2[Cl_2]} = \frac{(7.1 \times 10^{-5}\ \mathrm{mol\,L^{-1}\,s^{-1}})}{(0.0200\ \mathrm{mol\,L^{-1}})^2(0.0200\ \mathrm{mol\,L^{-1}})} = 8.9\ \mathrm{L^2\,mol^{-2}\,s^{-1}}$$

The average value calculated from all three experiments is $8.8\ \mathrm{L^2\,mol^{-2}\,s^{-1}}$. This problem is so simple that it could have been solved by inspection, noticing that the rate quadrupled when [NO] was doubled and doubled when $[Cl_2]$ was doubled.

The Method of Isolation

In this method, an experiment is carried out in which the initial concentration of one reactant is made much smaller than the concentrations of the other reactants. During the reaction the fractional changes in the large concentrations are negligible, 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.

(12.3-12), if [A] is much smaller than [B] and [F], the relative changes in [B] and [F] will be small. We write

$$-\frac{1}{a}\frac{d[\mathrm{A}]}{dt} = (k_{\mathrm{f}}[\mathrm{B}]^{\beta}[\mathrm{F}]^{\phi})[\mathrm{A}]^{\alpha} \tag{12.3-15}$$

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. (12.2-11) can be transcribed to obtain

$$\frac{1}{[\mathrm{A}]_t} = \frac{1}{[\mathrm{A}]_0} + (k_{\mathrm{f}}[\mathrm{B}]^{\beta}[\mathrm{F}]^{\phi})t \tag{12.3-16}$$

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

$$\mathrm{A} + \mathrm{S} \rightarrow \text{products} \tag{12.3-17}$$

and that the rate law is

$$r = -\frac{d[\mathrm{A}]}{dt} = k[\mathrm{S}]^{\sigma}[\mathrm{A}]^{\alpha} = k_{\mathrm{app}}[\mathrm{A}]^{\alpha} \tag{12.3-18}$$

where σ is the order with respect to the solvent. [S] is almost constant in a dilute solution. The quantity k_{app} is equal to $k[\mathrm{S}]^{\sigma}$ and is almost constant. It 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. However, the actual rate constant k and the order with respect to the solvent cannot be determined unless the concentration of the solvent can be varied. 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 **pseudo second-order**, and so on.

12.4 Inclusion of a Reverse Reaction. Chemical Equilibrium

So far, we have treated only reactions for which the reverse reaction could be neglected. We now include a reverse reaction for the simplest case, that the reaction is first order in both directions and that there is one product and one reactant:

$$\mathrm{A} \underset{k_{\mathrm{r}}}{\overset{k_{\mathrm{f}}}{\rightleftharpoons}} \mathrm{B} \tag{12.4-1}$$

where k_{f} is the rate constant for the forward reaction and k_{r} is the rate constant for the reverse reaction. Other cases, such as second order in one direction and first order in the other direction and reactions with more than two substances, are much more difficult to treat and we will not discuss them explicitly.

The net (observable) rate of the reaction is given by the difference between the forward rate and the reverse rate:

$$r_{\mathrm{net}} = -\frac{d[\mathrm{A}]}{dt} = k_{\mathrm{f}}[\mathrm{A}] - k_{\mathrm{r}}[\mathrm{B}] \tag{12.4-2}$$

At equilibrium,

$$r_{\mathrm{net(eq)}} = 0 = k_{\mathrm{f}}[\mathrm{A}]_{\mathrm{eq}} - k_{\mathrm{r}}[\mathrm{B}]_{\mathrm{eq}} \tag{12.4-3}$$

Equation (12.4-3) is the same as

$$K_{\mathrm{eq}} = \frac{k_{\mathrm{f}}}{k_{\mathrm{r}}} = \frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} \tag{12.4-4}$$

where K_{eq} is the equilibrium constant for the reaction. 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 (12.4-4) can apply to a more general case as shown in the following exercise.

Exercise 12.14

Assume that for the reaction

$$a\mathrm{A} + b\mathrm{B} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} d\mathrm{D} + f\mathrm{F} \tag{12.4-5}$$

the forward and reverse rates of the reaction are given by

$$r_{\mathrm{f}} = k_{\mathrm{f}}[\mathrm{A}]^a[\mathrm{B}]^b \quad \text{and} \quad r_{\mathrm{r}} = k_{\mathrm{r}}[\mathrm{D}]^d[\mathrm{F}]^f \tag{12.4-6}$$

That is, assume that the order with respect to each substance is equal to its stoichiometric coefficient (which might or might not be the case in a real reaction). Show that

$$K_{\mathrm{eq}} = \frac{k_{\mathrm{f}}}{k_{\mathrm{r}}} \tag{12.4-7}$$

We subtract Eq. (12.4-3) from Eq. (12.4-2) to obtain

$$-\frac{d[\mathrm{A}]}{dt} = k_{\mathrm{f}}([\mathrm{A}] - [\mathrm{A}]_{\mathrm{eq}}) - k_{\mathrm{r}}([\mathrm{B}] - [\mathrm{B}]_{\mathrm{eq}}) \tag{12.4-8}$$

Equation (12.4-8) appears to contain two dependent variables. However, we can express [B] in terms of [A]. Assume that initially only substance A is present so that $[\mathrm{B}]_0 = 0$:

$$[\mathrm{B}] = [\mathrm{A}]_0 - [\mathrm{A}] \quad \text{and} \quad [\mathrm{B}]_{\mathrm{eq}} = [\mathrm{A}]_0 - [\mathrm{A}]_{\mathrm{eq}}$$

so that

$$[\mathrm{B}] - [\mathrm{B}]_{\mathrm{eq}} = [\mathrm{A}]_0 - [\mathrm{A}] - ([\mathrm{A}]_0 - [\mathrm{A}]_{\mathrm{eq}}) = -[\mathrm{A}] + [\mathrm{A}]_{\mathrm{eq}} \tag{12.4-9}$$

When the relation of Eq. (12.4-9) is substituted into Eq. (12.4-8), we get

$$-\frac{d[\mathrm{A}]}{dt} = (k_{\mathrm{f}} + k_{\mathrm{r}})([\mathrm{A}] - [\mathrm{A}]_{\mathrm{eq}}) \tag{12.4-10}$$

Since $[\mathrm{A}]_{\mathrm{eq}}$ is a constant for any particular initial condition, we can replace $d[\mathrm{A}]/dt$ by $d([\mathrm{A}] - [\mathrm{A}]_{\mathrm{eq}})/dt$. Equation (12.4-10) is identical to Eq. (12.2-2) except for the symbols used, and the solution is obtained by transcribing Eq. (12.2-5) with appropriate changes in symbols:

$$[\mathrm{A}]_{t'} - [\mathrm{A}]_{\mathrm{eq}} = ([\mathrm{A}]_0 - [\mathrm{A}]_{\mathrm{eq}})e^{-(k_\mathrm{f}+k_\mathrm{r})t'} \tag{12.4-11}$$

Exercise 12.15

Carry out the separation of variables to obtain Eq. (12.4-11).

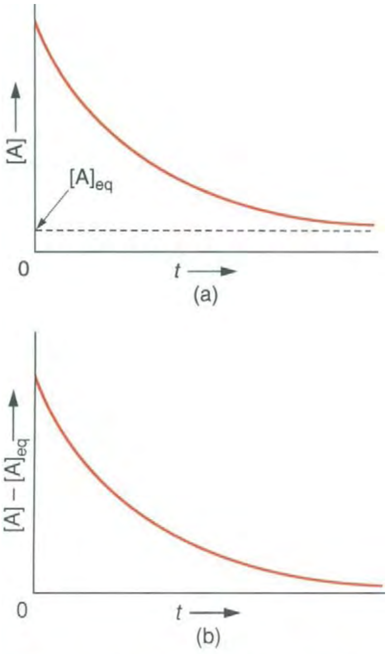

Figure 12.5. Concentration of the Reactant in a Hypothetical Reaction with Forward and Reverse Reactions. **(a)** [A] as a function of time. **(b)** [A] − [A]$_{\mathrm{eq}}$ as a function of time.

Figure 12.5 shows the concentration of a hypothetical reactant as a function of time. $[\mathrm{A}] - [\mathrm{A}]_{\mathrm{eq}}$ decays exponentially, as did [A] in the case of Figure 12.2.

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

$$t_{1/2} = \frac{\ln(2)}{k_\mathrm{f} + k_\mathrm{r}} \tag{12.4-12}$$

Exercise 12.16

Verify Eq. (12.4-12).

The **relaxation time** τ is the time required for $[\mathrm{A}] - [\mathrm{A}]_{\mathrm{eq}}$ to drop to $1/e$ of its original value:

$$\tau = \frac{1}{k_\mathrm{f} + k_\mathrm{r}} \tag{12.4-13}$$

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.

*Exercise 12.17

For a hypothetical isomerization with $k_\mathrm{f} = 17.7\ \mathrm{min}^{-1}$ and $k_\mathrm{r} = 32.2\ \mathrm{min}^{-1}$, find the final composition if the initial concentration of A is equal to $0.175\ \mathrm{mol\ L}^{-1}$ and the initial concentration of B is equal to zero. Find the half-life and the relaxation time. Find the composition at time $t = 0.100\ \mathrm{min}$.

Exercise 12.18

The treatment of the reaction

$$\mathrm{A} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \mathrm{B}$$

can be carried out for $[\mathrm{B}]_0 \neq 0$. Carry out this analysis and compare your results with those corresponding to the assumption that $[\mathrm{B}]_0 = 0$.

12.5 Consecutive Reactions and Competing Reactions

We now consider two cases in which two reactions are linked together. The first case is that of consecutive reactions in which the product of the first reaction is the reactant of a succeeding reaction. The second case is that of competition between two reactions with the same reactant. We consider only the cases in which both reactions are first order with a single reactant.

Consecutive Reactions

Consider the case that a single reactant forms a second substance in a first-order reaction with a negligible reverse reaction, and that this substance forms a product in another first-order reaction with a negligible reverse reaction:

$$\mathrm{A} \xrightarrow{k_1} \mathrm{B} \xrightarrow{k_2} \mathrm{F} \tag{12.5-1a}$$

where k_1 is the rate constant for the first step and k_2 is the rate constant for the second step. We number the reactions as follows:

$$(1) \qquad \mathrm{A} \rightarrow \mathrm{B} \tag{12.5-1b}$$

$$(2) \qquad \mathrm{B} \rightarrow \mathrm{F} \tag{12.5-1c}$$

Equation (12.5-1) constitutes a **reaction mechanism**. Many chemical reactions consist of two or more sequential steps analogous to Eqs. (12.5-1b) and (12.5-1c). When the steps in a sequence of reactions are numbered, the rate constants for the steps are labeled with the number of the step. If both forward and reverse reactions are included in step number i, the rate constant for the forward reaction will be called k_i and the rate constant for the reverse reaction will be called k_i'.

The reaction shown in Eq (12.5-1b) has the same rate law as Eq. (12.2-2),

$$\frac{d[\mathrm{A}]}{dt} = -k_1\, dt \tag{12.5-2}$$

The rate law for the reaction of Eq. (12.5-1c) is

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_2[\mathrm{B}] \tag{12.5-3}$$

Equations (12.5-2) and (12.5-3) are a set of simultaneous differential equations. However, the first equation does not contain [B] and can be solved separately. Its solution has already been obtained:

$$[\mathrm{A}]_t = [\mathrm{A}]_0 e^{-k_1 t} \tag{12.5-4}$$

This solution can be substituted into Eq. (12.5-3) to obtain a single differential equation relating [B] and t:

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}]_0 e^{-k_1 t} - k_2[\mathrm{B}] \tag{12.5-5}$$

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

$$[\mathrm{B}]_t = \frac{k_1[\mathrm{A}]_0}{k_2 - k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \tag{12.5-6}$$

Exercise 12.19

Substitute the function of Eq. (12.5-6) into the original differential equation of Eq. (12.5-5) and show that it satisfies this equation.

The concentration of the final product F is obtained from

$$[\mathrm{F}] = [\mathrm{A}]_0 - [\mathrm{A}] - [\mathrm{B}] \tag{12.5-7}$$

Figure 12.6a 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 12.6b shows the concentrations for the case that $k_1 = 0.500\ \mathrm{s}^{-1}$ and $k_2 = 0.100\ \mathrm{s}^{-1}$. Since the reverse reactions are assumed to be negligible, the final state is complete conversion to the product F in both cases. 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. If $k_1 = k_2$, the solution of (12.5-6) cannot be used since it is not permissible to divide by zero. See Problem 12.44 for the solution in this case.

If steps 1 and 2 have reverse reactions,

$$(1) \qquad \mathrm{A} \rightleftharpoons \mathrm{B} \tag{12.5-8a}$$

$$(2) \qquad \mathrm{B} \rightleftharpoons \mathrm{F} \tag{12.5-8b}$$

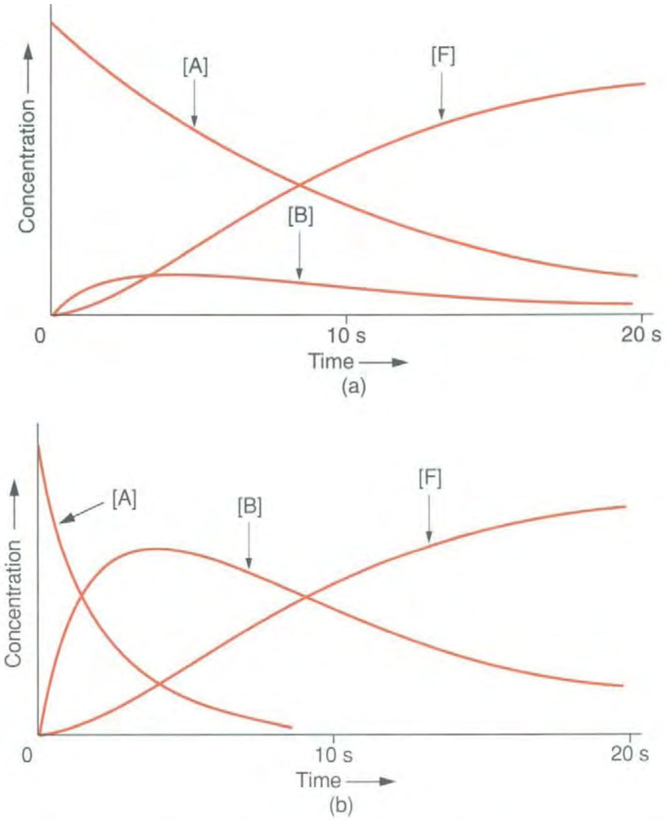

Figure 12.6. The Concentrations of Substances A, B, and F for Consecutive Reactions. (a) **The case that $k_1 = 0.10\ \mathrm{s}^{-1}$ and that $k_2 = 0.50\ \mathrm{s}^{-1}$.** The intermediate B is used up rapidly and [B] remains small. (b) **The case that $k_1 = 0.50\ \mathrm{s}^{-1}$ and that $k_2 = 0.10\ \mathrm{s}^{-1}$.** [B] rises to a larger value in the intermediate stages of the reaction.

the differential equations giving the rates are

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] + k_1'[\mathrm{B}] \tag{12.5-9a}$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] + k_1'[\mathrm{B}] - k_2[\mathrm{B}] + k_2'[\mathrm{F}] \tag{12.5-9b}$$

$$\frac{d[\mathrm{F}]}{dt} = k_2[\mathrm{B}] - k_2'[\mathrm{F}] \tag{12.5-9c}$$

This set of simultaneous differential equations presents a more difficult mathematical problem than if the reverse reactions are negligible. It can be solved but we will not present the solution.[5] In this case, both steps are at equilibrium when the entire reaction is at equilibrium:

$$\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{k_1}{k_1'} = K_1 \tag{12.5-10}$$

and

$$\frac{[\mathrm{F}]_{\mathrm{eq}}}{[\mathrm{B}]_{\mathrm{eq}}} = \frac{k_2}{k_2'} = K_2 \tag{12.5-11}$$

The equilibrium constant K for the overall reaction is equal to

$$K = \frac{[\mathrm{F}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{[\mathrm{F}]_{\mathrm{eq}}}{[\mathrm{B}]_{\mathrm{eq}}}\frac{[\mathrm{B}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = K_1K_2 = \frac{k_1}{k_1'}\frac{k_2}{k_2'} \tag{12.5-12}$$

The relationships shown in Eq. (12.5-12) are valid for any stepwise reaction: *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.*

Competing (Parallel) Reactions

In many syntheses a side reaction occurs that consumes part of the reactants but gives a product other than the one desired. We consider the case of two such competing reactions, both of which are assumed to be first order with negligible reverse reaction.

$$(1) \qquad \mathrm{A} \rightarrow \mathrm{F} \tag{12.5-13a}$$

$$(2) \qquad \mathrm{A} \rightarrow \mathrm{G} \tag{12.5-13b}$$

The rates of the two reactions combine to give

$$-\frac{d[\mathrm{A}]}{dt} = (k_1 + k_2)[\mathrm{A}] \tag{12.5-14}$$

This equation is the same as Eq. (12.2-2) except that k_f is replaced by $k_1 + k_2$, and the solution is

$$[\mathrm{A}]_t = [\mathrm{A}]_0 e^{-(k_1+k_2)t'} \tag{12.5-15}$$

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[5] T. M. Lowry and W. T. John, *J. Chem. Soc.*, **97**, 2634 (1910).

The half-life for the disappearance of A is

$$t_{1/2} = \frac{\ln(2)}{k_1 + k_2} \tag{12.5-16}$$

In other words, [A] decreases as in a single first-order reaction except that the sum of the rate constants appears instead of a single rate constant.

Consider the concentrations of the two products. We have

$$\frac{d[\mathrm{F}]}{dt} = k_1[\mathrm{A}] = k_1[\mathrm{A}]_0 e^{-(k_1+k_2)t} \tag{12.5-17}$$

The right-hand side of this equation does not contain [F], so we can multiply by dt and integrate to obtain

$$[\mathrm{F}]_{t'} - [\mathrm{F}]_0 = [\mathrm{F}]_{t'} = \frac{-k_1[\mathrm{A}]_0}{k_1 + k_2}(e^{-(k_1+k_2)t'} - 1) \tag{12.5-18}$$

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:

$$[\mathrm{G}]_{t'} - [\mathrm{G}]_0 = [\mathrm{G}]_{t'} = \frac{-k_2[\mathrm{A}]_0}{k_1 + k_2}(e^{-(k_1+k_2)t'} - 1) \tag{12.5-19}$$

The ratio [F]/[G] is thus the same at any time:

$$\frac{[\mathrm{F}]}{[\mathrm{G}]} = \frac{k_1}{k_2} \tag{12.5-20}$$

Exercise 12.20

For the reactions shown in Eq. (12.5-13) 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,

$$\frac{[\mathrm{F}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{k_1}{k_1'} = K_1 \tag{12.5-21a}$$

$$\frac{[\mathrm{G}]_{\mathrm{eq}}}{[\mathrm{A}]_{\mathrm{eq}}} = \frac{k_2}{k_2'} = K_2 \tag{12.5-21b}$$

so that

$$\frac{[\mathrm{F}]_{\mathrm{eq}}}{[\mathrm{G}]_{\mathrm{eq}}} = \frac{k_1}{k_1'}\frac{k_2'}{k_2} = \frac{k_1}{k_2}\frac{k_2'}{k_1'} = \frac{K_1}{K_2} \tag{12.5-22}$$

Depending on the values of the four rate constants, this ratio might differ significantly from the ratio in Eq. (12.5-20). If F is a desired product and G is an undesired product of a side reaction, 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").

12.6 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 forced into a mixing chamber. 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. The position dependence of the concentration is translated into time dependence from knowledge of the flow rate.

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, using the mixing chamber as a spectrophotometer cell. Figure 12.7 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 of from 1 ms to 1 s can be studied by either of the two flow methods.

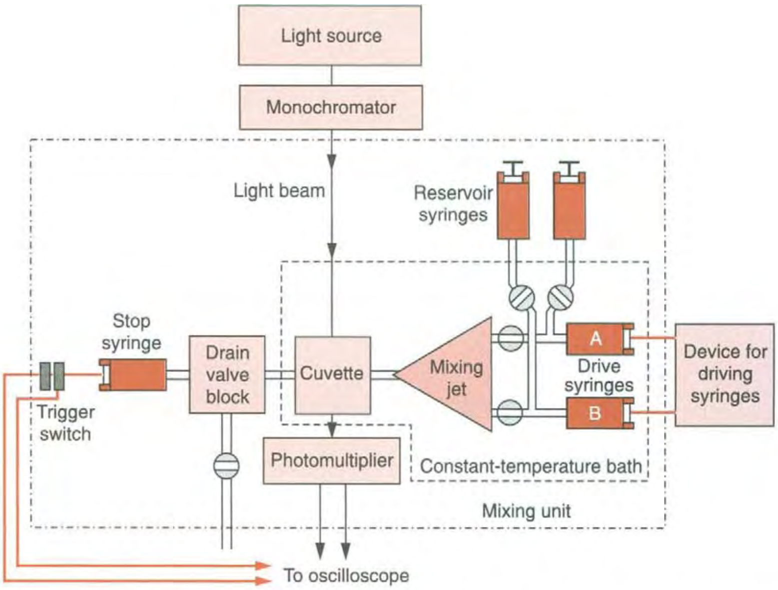

Figure 12.7. A Stopped-Flow Apparatus (Schematic). The reaction takes place in the cuvette. A flow of reactants is established and the reaction reaches a steady state. The flow is suddenly stopped, and the reaction relaxes to equilibrium. The concentration of a reactant or a product is monitored spectrophotometrically.

Relaxation Techniques

These techniques do not rely on mixing but use the fact that equilibrium compositions depend on temperature and sometimes on pressure. The experiment begins with a system at equilibrium and the temperature or pressure is suddenly changed so that the system is no longer at equilibrium. The relaxation of the system to its new equilibrium state is then monitored. Figure 12.8 shows the range of reaction half-lives for which each of several techniques can be used.

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 reactants and products at equilibrium at a fairly low pressure. On the other side is a "driver" gas at a much 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 and the concentration of a reactant or product is monitored spectrophotometrically. This method is applied to reactions that have half-lives in the range from 1 ms to 1 μs, but it is limited to gas-phase reactions.

In the **flash photolysis method**[6] a brief burst of light irradiates the system. If this light is absorbed it can quickly change the composition of the system and its temperature. The concentration of a reactant or product is then measured spectroscopically as a function of time as the system relaxes to its new equilibrium. Figure 12.9 shows schematically an apparatus for flash photolysis. Flash photolysis differs from the shock-wave technique in that the irradiation ordinarily does more than change the temperature of the system. Photochemical processes can produce new species so that the system is far from equilibrium immediately after the irradiation.

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 in pressure can be achieved by rupturing a diaphragm. The T-jump technique usually

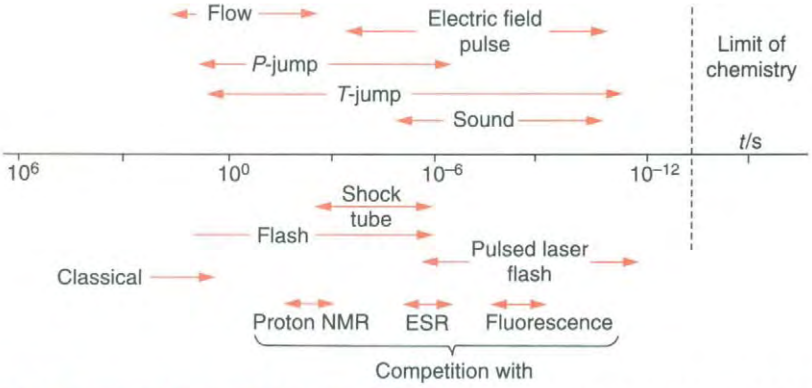

Figure 12.8. Reaction Times for Various Techniques. Classical techniques are those where the reactants are simply poured together. The fastest technique is the pulsed laser flash technique, followed by the temperature-jump technique.

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[6] See G. Porter, *J. Chem. Soc., Faraday Trans. 2*, **82**, 2445 (1986) for a historical survey.

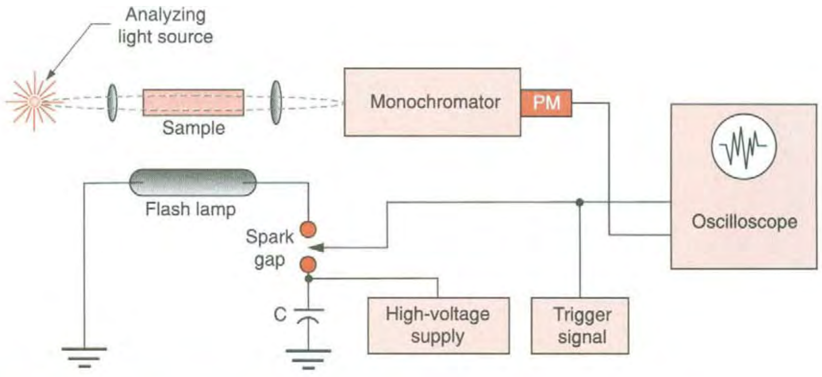

Figure 12.9. A Flash Photolysis Apparatus (Schematic). The reaction mixture is subjected to a flash from the flash lamp, and the concentration of a reactant or product (or possibly an intermediate) is monitored spectrophotometrically. PM denotes a photomultiplier.

produces a larger effect and is more commonly used than the *P*-jump technique, which will produce a significant change in equilibrium composition only for a gas-phase reaction. After the temperature or pressure change, the system relaxes to its new equilibrium state. The concentration of a reactant or product is usually monitored spectroscopically, although the reaction of hydrogen ions and hydroxide ions was monitored by measurement of the electrical conductivity.

Consider a system in which the reaction can occur:

$$(1) \qquad \mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{C} \tag{12.6-1}$$

Assume that this reaction is second order overall in the forward direction and first order in the reverse direction.

Suppose that a temperature or pressure jump is suddenly imposed on the system at time $t = 0$. The system then relaxes to its new equilibrium state under conditions of constant temperature and pressure. The time to accomplish the *T*-jump or *P*-jump should not be greater than 10% of the half-life of the reaction. Figure 12.10 shows schematically the concentrations of A, B, and C before and after a *T*-jump.

The initial concentration $[\mathrm{A}]_0$ was the equilibrium concentration at the temperature prior to the temperature jump, but since the equilibrium constant of the reaction depends on temperature, $[\mathrm{A}]_0$ is not equal to the new equilibrium concentration, denoted by $[\mathrm{A}]_{\mathrm{eq}}$. The same is true of [B] and [C]. We now let

$$\Delta[\mathrm{A}] = [\mathrm{A}]_t - [\mathrm{A}]_{\mathrm{eq}} \tag{12.6-2a}$$

$$\Delta[\mathrm{B}] = [\mathrm{B}]_t - [\mathrm{B}]_{\mathrm{eq}} \tag{12.6-2b}$$

$$\Delta[\mathrm{C}] = [\mathrm{C}]_t - [\mathrm{C}]_{\mathrm{eq}} \tag{12.6-2c}$$

We assume that $|\Delta[\mathrm{A}]| \ll [\mathrm{A}]$, $|\Delta[\mathrm{B}]| \ll [\mathrm{B}]$, and $|\Delta[\mathrm{C}]| \ll [\mathrm{C}]$, since it is not possible to change the equilibrium composition very much with a temperature jump or a pressure jump. A temperature jump is usually limited to about 20°C and a pressure jump is limited to 2 or 3 atm.

From the stoichiometry of the reaction shown in Eq. (12.6-1),

$$\Delta[\mathrm{A}] = \Delta[\mathrm{B}] = -\Delta[\mathrm{C}] \tag{12.6-3}$$

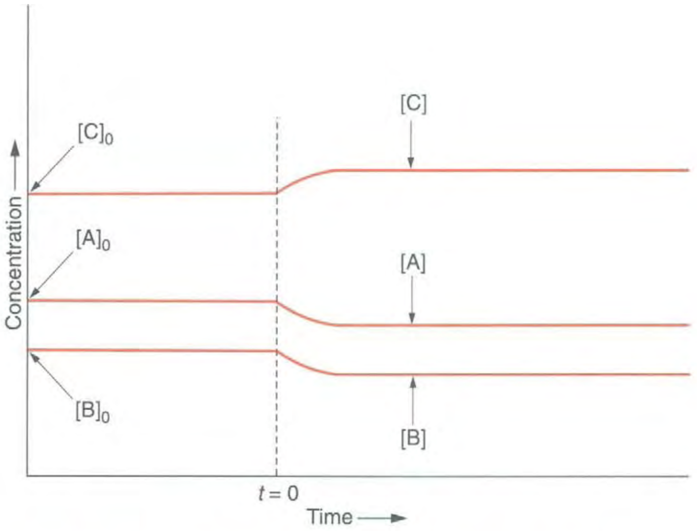

Figure 12.10. The Behavior of A System in a T-Jump Experiment. Prior to the temperature jump, the system is at equilibrium at one temperature. After the temperature jump, the system relaxes to its new equilibrium state.

so that we can express the concentrations in terms of Δ[C]:

$$[\mathrm{C}] = [\mathrm{C}]_{\mathrm{eq}} + \Delta[\mathrm{C}] \tag{12.6-4a}$$

$$[\mathrm{A}] = [\mathrm{A}]_{\mathrm{eq}} - \Delta[\mathrm{C}] \tag{12.6-4b}$$

$$[\mathrm{B}] = [\mathrm{B}]_{\mathrm{eq}} - \Delta[\mathrm{C}] \tag{12.6-4c}$$

The differential equation for the net rate is

$$\mathrm{Rate} = \frac{d\Delta[\mathrm{C}]}{dt} = k_1[\mathrm{A}][\mathrm{B}] - k_1'[\mathrm{C}] \tag{12.6-5}$$

To solve this differential equation, we must write it in terms of one dependent variable, which we do using Eq. (12.6-4):

$$\begin{aligned}\frac{d\Delta[\mathrm{C}]}{dt} &= k_1([\mathrm{A}]_{\mathrm{eq}} - \Delta[\mathrm{C}])([\mathrm{B}]_{\mathrm{eq}} - \Delta[\mathrm{C}]) - k_1'([\mathrm{C}]_{\mathrm{eq}} + \Delta[\mathrm{C}]) \\ &= k_1[\mathrm{A}]_{\mathrm{eq}}[\mathrm{B}]_{\mathrm{eq}} - k_1'[\mathrm{C}]_{\mathrm{eq}} - k_1([\mathrm{A}]_{\mathrm{eq}} + [\mathrm{B}]_{\mathrm{eq}})\Delta[\mathrm{C}] \\ &\quad - k_1'\Delta[\mathrm{C}] + k_1(\Delta[\mathrm{C}])^2\end{aligned} \tag{12.6-6}$$

The first two terms on the right-hand side of the final version of Eq. (12.6-6) cancel because the first is the forward rate at equilibrium and the second is the reverse rate at equilibrium. The final term on the right-hand side is much smaller than the others because the deviation from equilibrium is small so that $(\Delta[\mathrm{C}])^2 \ll |\Delta[\mathrm{C}]|$. We neglect this term, which linearizes the equation:

$$\frac{d\Delta[\mathrm{C}]}{dt} = -(k_1([\mathrm{A}]_{\mathrm{eq}} + [\mathrm{B}]_{\mathrm{eq}}) + k_1')\,\Delta[\mathrm{C}] \tag{12.6-7}$$

Equation (12.6-7) is exactly like Eq. (12.2-2) except for the symbols used, so we can write the solution:

$$\Delta[\mathrm{C}] = \Delta[\mathrm{C}]_0 e^{-t/\tau} \tag{12.6-8}$$

where

$$\frac{1}{\tau} = k_1([\mathrm{A}]_{\mathrm{eq}} + [\mathrm{B}]_{\mathrm{eq}}) + k_1' \qquad (12.6\text{-}9)$$

The quantity τ is the relaxation time for $\Delta[\mathrm{C}]$. The relaxation is exponential because we linearized the equation.

Exercise 12.21

a. Verify the steps of algebra leading to Eq. (12.6-7).
b. Verify that Eq. (12.6-8), with Eq. (12.6-9), is a solution to Eq. (12.6-7).
c. Write the expressions for $\Delta[\mathrm{A}]$ and $\Delta[\mathrm{B}]$.

The reaction of hydrogen ions and hydroxide ions in water can be written as

$$\mathrm{H_3O^+ + OH^- \rightleftharpoons 2H_2O} \qquad (12.6\text{-}10)$$

which has the general form

$$\mathrm{A + B \rightleftharpoons 2C} \qquad (12.6\text{-}11)$$

Assume that the reaction is second order in both directions. We write

$$[\mathrm{C}] = [\mathrm{C}]_{\mathrm{eq}} + \Delta[\mathrm{C}] \qquad (12.6\text{-}12a)$$

$$[\mathrm{A}] = [\mathrm{A}]_{\mathrm{eq}} - \tfrac{1}{2}\Delta[\mathrm{C}] \qquad (12.6\text{-}12b)$$

$$[\mathrm{B}] = [\mathrm{B}]_{\mathrm{eq}} - \tfrac{1}{2}\Delta[\mathrm{C}] \qquad (12.6\text{-}12c)$$

When Eqs. (12.6-12) 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

$$\Delta[\mathrm{C}] = \Delta[\mathrm{C}]_0 e^{-t/\tau} \qquad (12.6\text{-}13)$$

where

$$\frac{1}{\tau} = k_1\frac{[\mathrm{A}]_{\mathrm{eq}} + [\mathrm{B}]_{\mathrm{eq}}}{2} + 2k_1'[\mathrm{C}]_{\mathrm{eq}} \qquad (12.6\text{-}14)$$

EXAMPLE 12.8

At 25°C, the forward rate constant of Eq. (12.6-10) 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. (12.5-3), 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 nearly equal to unity, to the equilibrium constant for the reaction of Eq. (12.6-10) with all concentrations in terms of molarities:

$$K_1 = \frac{k_1}{k_1'} = \frac{[\mathrm{H_2O}]^2}{[\mathrm{H^+}][\mathrm{OH^-}]} = \frac{(55.35\ \mathrm{mol\ L^{-1}})^2}{1.008 \times 10^{-14}\ \mathrm{mol^2\ L^{-2}}} = 3.039 \times 10^{17}$$

$$k_1' = \frac{k_1}{K_1} = \frac{1.4 \times 10^{11}\ \mathrm{L\ mol^{-1}\ s^{-1}}}{3.039 \times 10^{17}} = 4.6 \times 10^{-7}\ \mathrm{L\ mol^{-1}\ s^{-1}}$$

b. From Eq. (12.6-14)

$$\begin{aligned}\frac{1}{\tau} &= \frac{(1.4\times 10^{11}\ \mathrm{L\ mol^{-1}\ s^{-1}})(2\times 1.004\times 10^{-7}\ \mathrm{mol\ L^{-1}})}{2} \\ &\quad + 2(4.6\times 10^{-7}\ \mathrm{L\ mol^{-1}\ s^{-1}})(55.35\ \mathrm{mol\ L^{-1}}) \\ &= 1.4\times 10^{4}\ \mathrm{s^{-1}} \\ \tau &= 7.1\times 10^{-5}\ \mathrm{s}\end{aligned}$$

Similar expressions for the relaxation time can be derived for other rate laws.[7]

Exercise 12.22

a. Verify Eq. (12.6-14).

b. For the reaction equation

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{X} + \mathrm{Y}$$

assumed second order in both directions, show that the relaxation is exponential, with relaxation time given by

$$\frac{1}{\tau} = k_1([\mathrm{A}]_{\mathrm{eq}} + [\mathrm{B}]_{\mathrm{eq}}) + k_1'([\mathrm{X}]_{\mathrm{eq}} + [\mathrm{Y}]_{\mathrm{eq}}) \qquad (12.6\text{-}15)$$

Summary of the Chapter

A rate law of the form

$$\mathrm{Rate} = k[\mathrm{A}]^{\alpha}[\mathrm{B}]^{\beta}$$

is said to have definite order, 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 experimental determination of the rate law involve comparison of the integrated rate equation with concentration data. 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, 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.

The case of two consecutive first-order reactions without reverse reactions was considered. This is a simple example of a reaction mechanism. It was found that the concentration of the reactive intermediate rose and then fell as the reaction proceeded.

Some techniques were presented for studying fast reactions that cannot be studied by classical experimental techniques. These techniques included continuous-flow and

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[7] K. J. Laidler, *Chemical Kinetics*, 3d ed., Harper and Row, New York, 1987, p. 38.

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.

PROBLEMS

Problem for Section 12.1

***12.23.** Consider the chemical reaction balanced two different ways:

$$2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$$

and

$$\text{NO} + \tfrac{1}{2}\text{Cl}_2 \rightarrow \text{NOCl}$$

a. If the rate of the reaction according to the first version is 7.1×10^{-5} mol L^{-1} s^{-1}, what is the rate of the reaction according to the second version?

b. What is the rate of change of the concentration of each substance? Does this quantity differ for the two versions?

Problems for Section 12.2

12.24. Write the reaction equation of Example 12.1 in the form

$$2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$$

with the rate equation

$$-\frac{1}{2}\frac{d[\text{N}_2\text{O}_5]}{dt} = k_\text{f}''[\text{N}_2\text{O}_5]$$

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 12.1.

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 N_2O_5 after a reaction time of 100.0 s.

***12.25.** The following data were taken for the decomposition of dinitrogen trioxide at some fixed temperature:

t/s	0	184	526	867	1877
$[\text{N}_2\text{O}_3]$/mol 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.

12.26. A certain reaction was studied at a fixed temperature. It was found that if the initial concentration of the single reactant was equal to 4.86×10^{-3} mol L^{-1}, the half-life of the reaction was equal to 399 s. When the initial concentration was 2.28×10^{-3} mol L^{-1}, the half-life was equal to 696 s. Find the order of the reaction and the value of the rate constant.

***12.27.** 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.

12.28. 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.

*12.29. Methyl acetate is hydrolyzed in approximately $1\ \mathrm{mol\,L^{-1}}$ hydrochloric acid at 25°C. Aliquots of equal volume are removed and titrated with NaOH solution. These results are:

Time/s	339	1242	2745	4546	∞
Volume of base/mL	26.34	27.80	29.70	31.81	39.81

Neglect the reverse reaction. Show that the reaction is pseudo-first order and find the value of the rate constant at this temperature.

Problems for Section 12.3

12.30. The rate constant for the forward reaction

$$H^+ + OH^- \rightarrow 2H_2O$$

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 $1.00 \times 10^{-3}\ \mathrm{mol\,L^{-1}}$.

*12.31. The following reaction is first order in each reactant:

$$C_6H_5N(CH_3)_2 + CH_3I \rightarrow C_6H_5N(CH_3)_3^+ + I^-$$

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.

12.32. 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 dimethylphenylamine is equal to $0.0500\ \mathrm{mol\,L^{-1}}$. Assume that the reverse reaction can be neglected.

12.33. Assume that the reaction

$$A + B \rightarrow \text{products}$$

is second order with respect to A and first order with respect to B. Integrate the rate differential equation

$$-\frac{d[A]}{dt} = k[A]^2[B]$$

to obtain the result

$$kt = \left(\frac{1}{[B]_0 - [A]_0}\right)\left(\frac{1}{[A]} - \frac{1}{[A]_0}\right) + \frac{1}{([B]_0 - [A]_0)^2}\ln\left(\frac{[B]_0[A]}{[A]_0[B]}\right)$$

12.34. For the reaction

$$aA + bB + cC \rightarrow \text{products}$$

assume that the rate law is third order overall:

$$\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} = k_f[A][B][C]$$

Integrate the rate law for the case of a stoichiometric mixture, such that

$$[A] : [B] : [C] = a : b : c$$

12.35. For the reaction of the previous problem, integrate the rate law for the case of a nonstoichiometric mixture, using the method of partial fractions.

12.36. The reaction

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

is catalyzed by iodide ions. Since the iodide ions are not consumed, we can determine the pseudo-order with respect to 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 $0.02\ \mathrm{mol\,L^{-1}}$ KI at 25°C:

Time/min	Volume of 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 pseudo-order with respect to 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 O_2 evolved at a time of 35.00 s.

***12.37.** The decomposition of benzenediazonium chloride in water is given by the reaction equation

$$C_6H_5N_2^+ + 2H_2O \rightarrow C_6H_5OH + N_2 + H_3O^+$$

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	$P_\infty - P$
0	22.62
60	22.08
120	21.55
240	20.47
360	19.45
480	18.48
600	17.60
900	15.49
1200	13.62
1800	10.54
2400	8.15
3000	6.34
3600	4.88
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.

Problems for Section 12.4

12.38. For the reaction $A \rightleftharpoons B$, which is first order in both directions, the initial concentration of A is 1.000 mol L^{-1} and that of B is 0.

a. Draw a graph of the concentrations of A and B as a function of time for the case that $k_f = 10.0\ s^{-1}$ and $k_r = 1.00\ s^{-1}$.

b. Repeat part (a) for $k_f = k_r = 10.0\ s^{-1}$.

c. Calculate the half-life of the reaction for both part (a) and part (b).

***12.39.** Calculate the concentration of each substance after a reaction time of 0.35 s for the reaction of part (a) of the previous problem.

12.40. Consider the same reaction as in Section 12.4, which is first order in each direction: $A \rightleftharpoons B$.

a. Integrate the rate differential equation for the case that the initial concentrations of both A and B are nonzero.

b. Draw a graph of the concentrations of A and B as a function of time for the case that $[A] = [B] = 1.00$ mol L^{-1}, $k_f = 10.0\ s^{-1}$ and $k_r = 1.00\ s^{-1}$.

c. For the reaction of part (b), find the concentration of each substance after a reaction time of 0.35 s.

12.41. Consider the reaction $2A \rightleftharpoons B + C$. 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.[8]

Problems for Section 12.5

12.42. For the consecutive first-order reaction without reverse reactions considered in Section 12.5, assume that $k_1 = 0.01000\ s^{-1}$ and $k_2 = 0.1000\ s^{-1}$. If $[A]_0 = 0.100$ mol L^{-1}, find the value of each concentration at $t = 10.00$ s and at $t = 100.0$ s.

12.43. **a.** For the consecutive first-order reactions without reverse reactions, make a graph of [A], [B], and [F] in the case that $k_1 = 0.0100\ s^{-1}$ and $k_2 = 0.100\ s^{-1}$. Assume that $[A]_0 = 1.00$ mol L^{-1} and that B and F are initially absent.

b. For the values of part (a), make a graph of $d[A]/dt$, $d[B]/dt$, and $d[F]/dt$.

12.44. **a.** For the consecutive first-order reactions without reverse reactions $A \rightarrow B \rightarrow F$, 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. (12.5-6) as $k_1 \rightarrow k_2$, using l'Hopital's rule.[9]

b. Draw a graph showing [A], [B], and [F] as functions of time for the case that $k_1 = k_2 = 0.100\ s^{-1}$ and $[A]_0 = 1.00$ mol L^{-1}.

c. Draw a graph showing [A], [B], and [F] as functions of time for the case that $k_1 = 0.099\ s^{-1}$ and $k_2 = 0.101\ s^{-1}$ and $[A]_0 = 1.00$ mol L^{-1}. Compare it with your graph from part (b).

12.45. Consider the competing reactions with significant reverse reactions:

1. $A \rightleftharpoons F$
2. $A \rightleftharpoons G$

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[8] See Robert G. Mortimer, *Mathematics for Physical Chemistry*, 2nd ed., Academic Press, New York, 1999, pp. 228ff, or any calculus textbook.

[9] See any calculus textbook.

Assume that all of the reactions are first order. 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.

Problems for Section 12.6

12.46. **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.

12.47. 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.

12.48. For the reaction at 298 K,

$$CH_3CO_2^- + H^+ \rightleftharpoons CH_3CO_2H$$

$k_f = 4.5 \times 10^{10}\ \text{L mol}^{-1}\ \text{s}^{-1}$ and $k_r = 8.0 \times 10^5\ \text{s}^{-1}$. 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.

General Problems

***12.49.** The reaction

$$NO + H_2 \rightarrow H_2O + \tfrac{1}{2}N_2$$

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_{H_2}(initial)/kPa	P_{NO}(initial)/kPa	$-\dfrac{dP}{dt}$/kPa 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_{H_2}(initial) = 100 kPa and P_{NO}(initial) = 100 kPa, find the initial rate.

c. For the initial pressures of part (b), find the pressure of each substance 100 s after the start of the reaction.

d. For P_{NO}(initial) = 200 kPa and P_{H_2}(initial) = 5.00 kPa, find the time for half of the hydrogen to react.

e. For P_{NO}(initial) = 5.00 kPa and P_{H_2}(initial) = 200 kPa, find the time for half of the nitric oxide to react.

12.50. 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 with 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.

13

Chemical Reaction Mechanisms

OBJECTIVES

After studying this chapter, the student should:

1. understand the relationship between molecularity and order in an elementary reaction;
2. be able to solve problems involving the collision theory of gas-phase reactions;
3. be able to deduce a rate law from a proposed mechanism by either of two approximation schemes;
4. understand the molecular basis of catalysis;
5. be able to solve problems involving the Michaelis–Menten equation for enzyme-catalyzed reactions;
6. understand kinetics experiments that give molecular information.

PRINCIPAL FACTS AND IDEAS

1. An elementary reaction is a chemical process that cannot be broken down into simpler steps. For elementary processes, the overall order equals the molecularity.
2. The sequence of elementary molecular steps that accomplishes a chemical reaction is the mechanism of that reaction.
3. The temperature dependence of gas-phase reaction rates can be understood by the collision theory of reactions.
4. The rate law for a given mechanism can often be deduced approximately from the mechanism.
5. Catalysts provide alternate mechanisms for chemical reactions.
6. In some cases, mechanisms can be verified by detection of reaction intermediates.

13.1 Reaction Mechanisms and Elementary Processes in Gases

One of the gas-phase reactions that endanger the ozone layer in the earth's upper atmosphere is

$$2NO_2 + O_3 \rightarrow N_2O_5 + O_2 \tag{13.1-1}$$

As is the case with almost all chemical reactions, this reaction does not take place in a single step. The forward **reaction mechanism** is thought to consist of the following steps:[1]

$$(1) \qquad NO_2 + O_3 \rightarrow NO_3 + O_2 \tag{13.1-2a}$$

$$(2) \qquad NO_3 + NO_2 \rightarrow N_2O_5 \tag{13.1-2b}$$

NO_3 is called a **reactive intermediate**. It is produced and then consumed and does not occur in the stoichiometric equation. The steps of a mechanism must add to give the stoichiometric equation, although one or more of the steps might have to be multiplied by small integers before summing the steps in order to recover the stoichiometric equation. The reactive intermediate must cancel in this summation.

The steps of Eq. (13.1-2) 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 molecules that are involved in it. Both steps in the mechanism of Eq. (13.1-2) are **bimolecular**. That is, they involve two reactant particles. **Unimolecular** steps involve a single particle. **Termolecular** processes involve three particles. Termolecular processes are relatively slow due to the smallness of the probability that three molecules will collide or diffuse together at once. Elementary processes involving four or more reactant particles probably do not occur in chemical reaction mechanisms.

Bimolecular Gas-Phase Reactions

Bimolecular elementary processes in gases involve the two-molecule collisions that we discussed in Chapter 10. At ordinary pressures the collision rate in a gas is very large, typically several billion collisions per second for a single molecule. If every collision in a reactive mixture led to chemical reaction, gas-phase reactions would be very rapid, coming to completion in a few nanoseconds. Since gas-phase reactions are almost never this rapid, apparently only a small fraction of all collisions lead to chemical reaction.

We first consider a bimolecular elementary process involving two molecules of substance number 1, whose formula is abbreviated by $\mathcal{F}_1$.

$$\mathcal{F}_1 + \mathcal{F}_1 \rightarrow \text{products} \tag{13.1-3}$$

We make an important assumption: *The fraction of binary collisions that lead to chemical reaction in a gas-phase bimolecular elementary process depends only on the temperature.* We discuss the validity of this assumption in Section 13.3.

Equation (10.7-24) gives the rate of two-body collisions, which is proportional to the square of the concentration of the substance. If we assume that at a fixed temperature a fraction f of the collisions leads to reaction, the rate of the forward reaction is also

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[1] H. S. Johnston and D. M. Yost, *J. Chem. Phys.*, **17**, 386 (1949).

proportional to the square of the concentration of the substance, and the reaction is second order:

$$\text{Rate} = -\frac{1}{2}\frac{d[\mathcal{F}_1]}{dt} = \frac{fZ_{11}}{N_{\text{Av}}} = \frac{1}{N_{\text{Av}}} f\pi d_1^2 \left(\frac{4k_{\text{B}}T}{\pi m_1}\right)^{1/2} \mathcal{N}_1^2 \tag{13.1-4}$$

where m_1 is the mass of a molecule of the reacting substance, d_1 is its effective hard-sphere diameter, and $\mathcal{N}_1$ is its number density. We divide by Avogadro's constant to express the rate in moles per second rather than molecules per second.

By comparison with Eq. (12.1-6) we can write an expression for the forward rate constant:

$$k = f\pi d_1^2 \left(\frac{4k_{\text{B}}T}{\pi m_1}\right)^{1/2} N_{\text{Av}} \quad \text{(bimolecular, one reactant)} \tag{13.1-5}$$

The SI units of k in Eq. (13.1-5) are $\text{m}^3\,\text{mol}^{-1}\,\text{s}^{-1}$. If concentrations and rates are to be measured in $\text{mol}\,\text{L}^{-1}$, an additional conversion factor is needed, equal to $1000\,\text{L}\,\text{m}^{-3}$, to give k the units $\text{L}\,\text{mol}^{-1}\,\text{s}^{-1}$.

Exercise 13.1

Show that Eq. (13.1-5) is correct. Remember that a factor of $\frac{1}{2}$ occurs in the definition of the rate as in Eq. (12.1-6), that each reactive collision uses up two molecules of substance 1, and that a factor of $\frac{1}{2}$ was introduced into Eq. (10.7-24) to avoid overcounting of collisions.

The quantity πd_1^2 is the cross-sectional area of the collision cylinder depicted in Figure 10.19 and is the area of the "target" with which the center of a molecule can collide. The quantity $f\pi d_1^2$ is an effective cross-sectional area, or the area of the "target" that actually leads to reaction. It is called the **reaction cross section**.

In the case of a bimolecular elementary process involving one molecule each of substance 1 and substance 2, the elementary bimolecular process is first order in each substance and second order overall. The rate constant is given by

$$k = f\pi d_{12}^2 \left(\frac{8k_{\text{B}}T}{\pi \mu_{12}}\right)^{1/2} N_{\text{Av}} \quad \text{(bimolecular, two reactants)} \tag{13.1-6}$$

where d_{12} is the collision diameter for a collision of a molecule of substance 1 with a molecule of substance 2, and where μ_{12} is the reduced mass of molecules of mass m_1 and m_2, defined in Eq. (10.7-29) and in Appendix B:

$$\mu_{12} = \frac{m_1 m_2}{m_1 + m_2} \tag{13.1-7}$$

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 13.2

a. Show that Eq. (13.1-6) is correct.

***b.** For a hypothetical bimolecular elementary reaction of a gaseous substance with an effective hard-sphere diameter of 3.00×10^{-10} m and a molar mass of $0.060\,\text{kg}\,\text{mol}^{-1}$, the rate constant is equal to 6.0×10^{-4} m^3 mol^{-1} s^{-1} at 298 K. Find the fraction of collisions that lead to reaction.

Termolecular Gas-Phase Reactions

A termolecular elementary process must involve a three-body collision, which can be pictured as a collision of a third particle with a pair of molecules that is undergoing a binary collision. The number of three-body collisions is proportional to the number of pairs of particles that are in the process of colliding with each other and is also proportional to the number of "third" particles. The number of colliding pairs is proportional to the square of the number density (or the product of two number densities). If we again assume that the fraction of three-body collisions that lead to reaction is fixed at constant 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 Gas-Phase Reactions

Unimolecular elementary processes are qualitatively different from bimolecular and termolecular processes since they involve a single molecule. We assert another important result: *Gaseous unimolecular elementary processes are first order.* That is, they have a rate that is proportional to the number of molecules available to react. We will discuss unimolecular processes in Section 13.4, when we will find that the above assertion is an oversimplification that applies only at sufficiently high pressure.

The Molecularity Equals the Order for Any Elementary Gas-Phase Process

To summarize our results, we define the molecularity of an elementary process with respect to any substance as the number of molecules of that substance involved in the process. Our results for gas-phase elementary reactions are summarized: *For a gaseous elementary process, the order with respect to any substance is equal to the molecularity of that substance and the overall molecularity is equal to the sum of the molecularities of all substances.* This equality of order and molecularity holds only for elementary processes. A reaction that is first order could have a multistep mechanism that has no unimolecular steps in it. The order of a process does not imply anything about its molecularity unless it is an elementary process.

13.2 Elementary Reactions in Liquid Solutions

A chemical reaction in a liquid solution is qualitatively different from a gas-phase reaction. The reacting molecules must diffuse together before reacting, and the product molecules will diffuse apart after the reaction. We will speak of a process that has a one-step chemical part as an elementary process in spite of the occurrence of the two diffusion processes. Some reactions in solutions 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 1.4×10^{11} L mol^{-1} s^{-1}. If solutions could be mixed instantaneously to give a solution containing hydrogen ions at 0.10 mol L^{-1} and hydroxide ions at 0.10 mol L^{-1}, this rate constant would correspond to a half-life of 7×10^{-11} s, or 0.07 ns.

Exercise 13.3

Verify the half-life value given above.

The rapidity of some liquid-state reactions at first seems surprising since ordinary diffusion processes in liquids take hours or days to occur. The reason for the large difference between the time required for ordinary diffusion processes and for the diffusion processes in liquid-state chemical reactions is the difference between the average distances traveled by the molecules. In an ordinary diffusion process, the root-mean-square distance traveled by molecules might be a few centimeters, while the mean distance between reacting molecules in a solution might be a few nanometers.

EXAMPLE 13.1

a. Estimate the mean distance between a molecule of substance 2 and the nearest-neighbor molecule of substance 3 in a 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 1.0×10^{-9} 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

$$V_{\text{cube}} = \frac{1\ \text{L}}{0.10\ \text{mol}}\ \frac{1\ \text{mol}}{6.0 \times 10^{23}\ \text{mol}^{-1}}\ \frac{1\ \text{m}^3}{1000\ \text{L}} = 1.7 \times 10^{-26}\ \text{m}^3$$

$$\text{Side of cube} = d = (1.7 \times 10^{-26}\ \text{m}^3)^{1/3} = 2.6 \times 10^{-9}\ \text{m} = 2.6\ \text{nm}.$$

b. From Eq. (17.2-19),

$$\langle x^2 \rangle^{1/2} = \sqrt{2Dt}$$

$$t = \frac{d^2}{2D} = \frac{(2.6 \times 10^{-9}\ \text{m})^2}{2(1.0 \times 10^{-9}\ \text{m}^2\ \text{s}^{-1})} = 3.4 \times 10^{-9}\ \text{s} = 3.4\ \text{ns}$$

A solute molecule in a liquid solution can be pictured as being temporarily confined in a cage of other molecules, colliding repeatedly with the molecules making up the cage. In Chapter 10, we concluded that collisions of a molecule in a typical liquid are roughly one hundred times more frequent than collisions of a molecule in a typical gas. This means that a molecule might undergo several collisions per picosecond. Since the molecules making up the cage are also moving, an avenue can occasionally open up for a molecule to move out of a cage into an adjacent cage. However, a molecule or ion will typically undergo hundreds of collisions in one cage before it moves into an adjacent cage.

If substance 2 can react with substance 3, a molecule of substance 2 can react only if it is in a cage in which a molecule of substance 3 is one of the "cage" molecules. Motion of a type-2 molecule into a cage containing a type-3 molecule (or vice versa) is called an **encounter**. It is an interesting fact that the average rate of 2–3 collisions in a liquid is approximately the same as the rate of 2–3 collisions in a gas having concentrations equal to the concentrations in the liquid. The collision rate when molecules of substance 2 and molecules of substance 3 are in the same cage is much higher, but each molecule of type 2 spends much of its time in cages containing no molecule of type 3, and vice versa.

Bimolecular Liquid-Phase Reactions

In a **diffusion-limited** or **diffusion-controlled** bimolecular elementary reaction between substances 2 and 3, the chemical part of the reaction is so rapid that every encounter of a type 2 molecule with a type 3 molecule leads to reaction. The rate is therefore controlled (limited) by the rate at which the reactant molecules diffuse together. The reaction of hydrogen ions and hydroxide ions in water is an example of a diffusion-limited bimolecular elementary reaction.

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 fixed molecules of type 3. On the average, the motion of the substance 2 molecules toward the fixed molecules of type 3 constitutes a diffusion flux that obeys Fick's law of diffusion, given in Equation (11.2-3):

$$\mathbf{J}_2 = -D_2 \nabla c_2$$

where the vector $\mathbf{J}_2$ is called the diffusion flux. Its magnitude is the net amount of substance 2 diffusing per unit area per unit time and its direction is the average direction in which the molecules are diffusing. The diffusion coefficient is denoted by D_2. The gradient operator, represented by ∇, is defined in Eq. (B-37) of Appendix B. The magnitude of ∇c_2 is equal to the derivative of c_2 in the direction of most rapid change of c_i. The important physical fact is that the rate of diffusion is greater if the derivative of the concentration is greater.

In this case of a diffusion-limited reaction, 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 concentration of type 2 molecules closer to the center of the substance 3 molecule than this distance vanishes. The distance d_{23} is called the **reaction diameter**. It is not necessarily equal to the hard-sphere collision diameter of the reacting molecules. Since the reactants react as soon as they encounter each other, a concentration gradient is set up. A solution to Fick's law of diffusion is sought such that the concentration is time-independent and vanishes at distances less than or equal to d_{23} from the fixed type 3 molecule. The diffusion flux gives the rate of reaction, since all molecules that diffuse up to the sphere of radius d_{23} are assumed to react.

The diffusion flux is proportional to the bulk concentration of substance 2 (the concentration at distances far from any type 3 molecule), and the rate of reaction is also proportional to the concentration of (fixed) type 3 molecules, so 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 given by

$$k = 4\pi N_{\mathrm{Av}} D_2 d_{23} \tag{13.2-1}$$

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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, pp. 212ff.

where N_{Av} is Avogadro's constant. When the fact that the type 3 molecules are also moving is included, the result is[3]

$$k = 4\pi N_{\mathrm{Av}}(D_2 + D_3)d_{23} \quad \begin{pmatrix}\text{diffusion-limited}\\ \text{second-order reaction}\\ \text{with two reactants}\end{pmatrix} \tag{13.2-2}$$

where D_3 is the diffusion coefficient of substance 3. Equation (13.2-2) is used in preference to Eq. (13.2-1) for calculations.

If two molecules of substance 2 react in a diffusion-controlled reaction, the reaction is second order in that substance. By an analysis that is analogous to that leading to Eq. (13.2-2),

$$k = \frac{1}{2}4\pi N_{\mathrm{Av}}(2D_2)d_{22} = 4\pi N_{\mathrm{Av}}D_2 d_{22} \quad \begin{pmatrix}\text{diffusion-limited}\\ \text{second-order reaction}\\ \text{with one reactant}\end{pmatrix} \tag{13.2-3}$$

where d_{22} is the reaction diameter for two type 2 molecules. The factor $\frac{1}{2}$ in Eq. (13.2-3) is included because of the factor of $\frac{1}{2}$ in the definition of the rate in Eq. (12.1-5) for a substance with stoichiometric coefficient equal to 2.

EXAMPLE 13.2

Calculate the rate constant for the diffusion-limited reaction, assumed to be elementary:

$$2\mathrm{I} \rightarrow \mathrm{I}_2$$

in carbon tetrachloride solution at 298 K. Take the reaction diameter equal to 4.0×10^{-10} m and the diffusion coefficient of iodine atoms in CCl_4 as $4.2 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$.

Solution

$$\begin{aligned} k &= 4\pi(6.02 \times 10^{23}\ \mathrm{mol^{-1}})(4.2 \times 10^{-9}\ \mathrm{m^2\ s^{-1}})(4.0 \times 10^{-10}\ \mathrm{m}) \\ &= 1.3 \times 10^{7}\ \mathrm{m^3\ mol^{-1}\ s^{-1}} = 1.3 \times 10^{10}\ \mathrm{L\ mol^{-1}\ s^{-1}} \end{aligned}$$

According to a theory of Debye[4] the formula for the rate constant shown in Eq. (13.2-2) must be modified if the reactants are ions. The formula given must be multiplied by the **electrostatic factor** f:

$$f = \frac{y}{e^y - 1} \tag{13.2-4}$$

where

$$y = \frac{z_2 z_3 e^2}{4\pi\varepsilon d_{23} k_B T} \tag{13.2-5}$$

The respective valences 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. (7.4-1).

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[3] K. J. Laidler, *Chemical Kinetics*, Harper and Row, New York, 1987, pp. 212ff.

[4] P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).

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 13.3

The diffusion coefficient of H^+ in water at 25°C is equal to $9.31 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$, and that of OH^- is equal to $5.26 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$. Estimate the reaction diameter d. The value of the dielectric constant for water is equal to 78.4 at 25°C. (The dielectric constant is the ratio of the permittivity of the medium to that of a vacuum.) The value of k at this temperature is $1.4 \times 10^{11}\ \mathrm{L\ mol^{-1}\ s^{-1}}$.

Solution

From Eq. (13.2-5), we first obtain the relation between y and d:

$$y = \frac{(-1)(1.6022 \times 10^{-19}\ \mathrm{C})^2}{4\pi(78.4)(8.85 \times 10^{-12}\ \mathrm{C^2\ N^{-1}\ m^{-2}})(1.38 \times 10^{-23}\ \mathrm{J\ K^{-1}})(298\ \mathrm{K})d} = -\frac{7.15 \times 10^{-10}\ \mathrm{m}}{d}$$

Since the reaction diameter d occurs both in the expression for k in Eq. (13.2-2) and in the expression for f in Eq. (13.2-5), 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 on, 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 $8.64 \times 10^{-10}\ \mathrm{m} = 0.864\ \mathrm{nm}$.

The reaction diameter for the reaction between hydrogen ions and hydroxide ions is somewhat larger than the sum of the radii of these ions. The explanation for this is that water is the solvent for the reaction, and water ionizes to form hydrogen and hydroxide ions. Water molecules can exchange hydrogen and hydroxide ions. One or two water molecules combine with a hydrogen ion to form an H_3O^+ ion or an $H_2O_5^+$ ion. Either of these ions can then lose a different hydrogen ion to a second water molecule, which then passes a still different hydrogen ion to a third water molecule, and so on. Similarly, a water molecule can lose a hydrogen ion to a hydroxide ion, forming a hydroxide ion in a new location. These exchange processes also explain the large magnitudes of the diffusion coefficients of hydrogen and hydroxide ions in water and the large mobilities of these ions in water.

*Exercise 13.4

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 (11.4-4) relates a diffusion coefficient to the radius of the diffusing molecules and the viscosity of the solvent:

$$D_2 = \frac{k_B T}{f} = \frac{k_B T}{6\pi\eta r}$$

where r is the effective radius of the molecule and η is the viscosity of the solvent. If we use this relation in Eq. (13.2-2) and assume that $d_{23} = r_2 + r_3$, we obtain

$$k = \frac{4N_{\text{Av}}k_BT}{6\eta}\left(\frac{1}{r_2}+\frac{1}{r_3}\right)(r_2+r_3) = \frac{2RT}{3\eta}\left(2+\frac{r_2}{r_3}+\frac{r_3}{r_2}\right) \tag{13.2-6}$$

If r_2 and r_3 are nearly equal, Eq. (13.2-6) becomes

$$k \approx \frac{8RT}{3\eta} \quad \text{(two different reacting substances)} \tag{13.2-7a}$$

so that k is independent of the identity of the reactants. If the two reacting molecules are of the same substance, we must divide by 2 in order to avoid counting the same encounter twice:

$$k \approx \frac{4RT}{3\eta} \quad \text{(single reacting substance)} \tag{13.2-7b}$$

EXAMPLE 13.4

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. (13.2-7) as an approximation and assume that the reactants are uncharged:

$$k = \frac{8(8.3145\ \text{J K}^{-1}\ \text{mol}^{-1})(298\ \text{K})}{3(8.904\times 10^{-4}\ \text{kg m}^{-1}\ \text{s}^{-1})}$$
$$= 7.4\times 10^{6}\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1} = 7.4\times 10^{9}\ \text{L mol}^{-1}\ \text{s}^{-1}$$

If a reaction is slightly slower than the rate of encounters it is known as a **partially diffusion-limited reaction**. Solution reactions that are much slower than diffusion-limited reactions are called **activation-limited reactions**. In an activation-limited process, the reaction will not occur immediately for every encounter. After the encounter occurs, the motions of the molecules must produce a high-energy collision as in a gas-phase reaction. The molecules might have to undergo many encounters before a collision occurs with relative kinetic energy larger than the critical value. For activation-limited reactions we will assume, as with gaseous reactions, that only a fraction of collisions will lead to reaction, and that this fraction depends only on the temperature. For an activation-limited reaction between type 2 molecules and type 3 molecules, 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, such 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.

Unimolecular and Termolecular Liquid-Phase Reactions

Unimolecular elementary processes in liquids exhibit first-order kinetics, as in the gas phase. 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 are also third order if the fraction of collisions that lead to reaction is independent of the concentration.

General Statement That Molecularity Equals Order in Elementary Processes

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.*

13.3

The Temperature Dependence of Rate Constants. The Collision Theory of Bimolecular Gaseous Reactions

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.

Reaction rates depend strongly on temperature, nearly always increasing when the temperature is raised. A common rule of thumb is that the rate of a reaction doubles if the temperature is raised by 10°C. The first quantitative generalizations about the temperature dependence of rate constants were published in the last half of the nineteenth century, and various empirical formulas were proposed.[5] The most widely used empirical relation is that of Arrhenius, which was proposed in 1889. This formula has gained wide acceptance because it is based on a physical picture of elementary processes.

Arrhenius pointed out that typical rate constants for gaseous reactions are much smaller than they would be if every collision led to reaction and that the typical temperature dependence of reaction rate constants is much too strong to be explained by the temperature dependence of collision rates. He postulated that "activated" molecules (with high energy) must exist in order to react and that the numbers of such activated molecules would be governed by the Boltzmann probability distribution of Eq. (1.5-17) or Eq. (10.2-35). This assumption leads to the **Arrhenius relation**:

$$k = Ae^{-\varepsilon_a/k_B T} \tag{13.3-1}$$

The quantity ε_a is the energy relative to the ground-state 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**. It is common to express Eq. (13.3-1) in terms of a molar activation energy E_a, which is equal to ε_a times Avogadro's constant.

$$k = Ae^{-E_a/RT} \tag{13.3-2}$$

where $E_a = N_{Av}\varepsilon_a$ is the molar activation energy. Experimental molar activation energy values are usually in the range 50 to 200 kJ mol^{-1}, somewhat smaller than energies

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[5] K. J. Laidler, *op. cit.*, pp. 40ff (Note 3).

required to break chemical bonds. Equation (13.3-2) is quite accurate for liquid-phase reactions as well as for gas-phase reactions.

EXAMPLE 13.5

For the gas-phase reaction

$$H_2 + I_2 \rightarrow 2HI$$

at 373.15 K, the rate constant is equal to 8.74×10^{-15} L mol^{-1} s^{-1}. At 473.15 K it is equal to 9.53×10^{-10} 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. (13.3-1) gives

$$E_a = \frac{R \ln\left(\dfrac{k(T_2)}{k(T_1)}\right)}{\dfrac{1}{T_1} - \dfrac{1}{T_2}} \tag{13.3-3}$$

Substitution of the values gives

$$\begin{aligned} E_a &= \frac{(8.3145 \text{ J K mol}^{-1}) \ln\left(\dfrac{9.53 \times 10^{-10}}{8.74 \times 10^{-15}}\right)}{\dfrac{1}{373.15 \text{ K}} - \dfrac{1}{473.15 \text{ K}}} \\ &= 1.70 \times 10^5 \text{ J mol}^{-1} = 170 \text{ kJ mol}^{-1} \\ A &= ke^{E_a/RT} \\ &= (8.74 \times 10^{-15} \text{ L mol}^{-1} \text{ s}^{-1}) \exp\left(\frac{1.70 \times 10^5 \text{ J mol}^{-1}}{(8.3145 \text{ J K mol}^{-1})(373.15 \text{ K})}\right) \\ &= 5.47 \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1} \end{aligned}$$

If more than two data points were given, a plot or a linear least-squares fit of ln(k) versus $1/T$ could be used.

Exercise 13.5

***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

$$E_a = RT^2\left(\frac{d \ln(k)}{dT}\right) \quad \text{(definition of } E_a\text{)} \tag{13.3-4}$$

Show that if k is given by Eq. (13.3-2), Eq. (13.3-4) gives the same E_a as in Eq. (13.3-2) if A is temperature-independent.

The Collision Theory of Bimolecular Elementary Gas-Phase Reactions

The basic assumption of this theory is that the initiation of the reaction involves an inelastic collision in which energy is transferred from translational kinetic energy to energy of internal motions. The energy that can be transferred to internal motion is not the total kinetic energy of the two particles. If two rapidly moving molecules happen to be moving in nearly the same direction with nearly the same speed, they can have rather large kinetic energies, but not transfer much of their kinetic energies if they collide. It is the energy of motion of one particle relative to the other that determines the amount of energy transferred. We assume that the probability of reaction equals zero if the relative speed is smaller than a certain critical value that is characteristic for a given reaction, and that the probability equals unity for relative speeds larger than this value, as shown in Figure 13.1a. This corresponds to a reaction cross section equal to zero for relative speeds smaller than the critical value, and equal to the collision cross section for values larger than the critical value. We will improve on this assumption later.

Consider a bimolecular elementary reaction between molecules of substance 1 and substance 2. Equation (10.7-33) gives the total rate of collisions per unit volume that involve molecules of type 1 and type 2:

$$Z_{12} = z_{1(2)}\mathcal{N}_2 = z_{2(1)}\mathcal{N}_1 = \sqrt{\frac{8k_BT}{\pi\mu_{12}}}\pi d_{12}^2\mathcal{N}_1\mathcal{N}_2 \tag{13.3-5}$$

We want to consider 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 $d^3\mathbf{v}_2$. To make Eq. (13.3-5) apply to our case, we replace the mean relative speed by our particular relative speed, $|\mathbf{v}|$, and multiply by the probability that the first molecule has its velocity in the infinitesimal range $d^3\mathbf{v}_1$ and that the second molecule has its velocity in the infinitesimal range $d^3\mathbf{v}_2$. We write this collision rate as dZ_{12}:

$$dZ_{12} = \pi d_{12}^2\mathcal{N}_1\mathcal{N}_2|\mathbf{v}|g(\mathbf{v}_1)d^3\mathbf{v}_1 g(\mathbf{v}_2)d^3\mathbf{v}_2 \tag{13.3-6}$$

where $\mathcal{N}_1$ is the number density of molecules of type 1, where $\mathcal{N}_2$ is the number density of molecules of type 2, where d_{12} is the collision diameter of the molecule pair, and where g is the probability distribution of Eq. (10.2-34). The relative velocity $\mathbf{v}$ is given by

$$\mathbf{v} = \mathbf{v}_2 - \mathbf{v}_1 \tag{13.3-7}$$

The magnitude of the relative velocity is the relative speed.

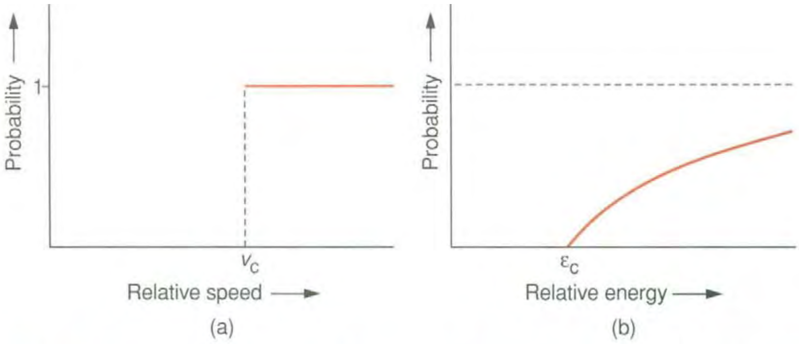

Figure 13.1. Probability of Reaction as a Function of Relative Speed. (a) **First assumption.** The probability of reaction is assumed to rise suddenly from zero to unity at a critical relative speed. (b) **Assumed probability of reaction as a function of relative kinetic energy according to equation (13.3-18).** This curve gives a more reasonable assumed behavior than does the curve of (a). The reaction probability is assumed to rise gradually from zero above a critical relative energy and to approach unity asymptotically.

In order to obtain the total rate of collisions that lead to reaction, we integrate over all velocities that satisfy the condition

$$v = |\mathbf{v}_2 - \mathbf{v}_1| > v_c \tag{13.3-8}$$

where v_c is the minimum relative speed that can lead to reaction. 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 given by the three-dimensional version of Eq. (D-29) of Appendix D

$$\mathcal{K} = \tfrac{1}{2}MV_c^2 + \tfrac{1}{2}\mu v^2 \tag{13.3-9}$$

where $M = m_1 + m_2$, and where $\mu = m_1 m_2/M$ is the reduced mass of the particles. The first term on the right-hand side of Eq. (13.3-9) is the kinetic energy of the center of mass and the second term is the relative kinetic energy. Using Eq. (10.2-34) for the probability distributions, we can write after changing variables,

$$dZ_{12} = \pi d_{12}^2 \mathcal{N}_1 \mathcal{N}_2 \left(\frac{m_1}{2\pi k_B T}\right)^{3/2} \left(\frac{m_2}{2\pi k_B T}\right)^{3/2} v e^{-MV^2/2k_B T} e^{-\mu v^2/2k_B T}\, d^3\mathbf{V}\, d^3\mathbf{v} \tag{13.3-10}$$

Exercise 13.6

Verify Eq. (13.3-10).

We integrate Eq. (13.3-10) over all values of $\mathbf{V}$ and over the values of $\mathbf{v}$ that satisfy Eq. (13.3-8). Integration over $\mathbf{V}$ is just like the integration in Eq. (10.2-20), and gives a factor of $(2\pi k_B T/M)^{3/2}$:

$$Z_{12}(\text{reactive}) = \pi d_{12}^2 \mathcal{N}_1 \mathcal{N}_2 \left(\frac{2\pi k_B T}{M}\right)^{3/2} \left(\frac{m_1}{2\pi k_B T}\right)^{3/2} \left(\frac{m_2}{2\pi k_B T}\right)^{3/2} \int v e^{-\mu v^2/2k_B T}\, d^3\mathbf{v} \tag{13.3-11}$$

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 Eq. (13.3-8). We use a tabulated indefinite integral to obtain

$$\int_{v_c}^{\infty} e^{-\mu v^2/2k_B T} v^3\, dv = \frac{1}{2} e^{-\mu v_c^2/2k_B T} \left(\frac{2k_B T}{\mu}\right)\left(v_c^2 + \frac{2k_B T}{\mu}\right)$$

The final result is

$$Z_{12}(\text{reactive}) = \pi d_{12}^2 N_1 N_2 (8k_B T/\pi\mu)^{1/2} (1 + \mu v_c^2/2k_B T) e^{-\mu v_c^2/2k_B T} \tag{13.3-12}$$

Comparison of this equation with Eq. (13.1-4) shows that we have an expression for the fraction of collisions that lead to reaction in a bimolecular elementary process:

$$f = \left(1 + \frac{\mu v_c^2}{2k_B T}\right) e^{-\mu v_c^2/2k_B T} \tag{13.3-13}$$

Exercise 13.7

Verify Eq. (13.3-12).

The critical value of the relative kinetic energy is given by

$$\varepsilon_c = \tfrac{1}{2}\mu v_c^2 \qquad (13.3\text{-}14)$$

so that Eq. (13.3-12) can be written

$$Z_{12}(\text{reactive}) = \pi d_{12}^2 \mathcal{N}_1 \mathcal{N}_2 \left(\frac{8k_BT}{\pi\mu}\right)^{1/2} \left(1 + \frac{\varepsilon_c}{k_BT}\right) e^{-\varepsilon_c/k_BT} \qquad (13.3\text{-}15)$$

which corresponds to

$$k = N_{Av}\pi d_{12}^2 \left(\frac{8k_BT}{\pi\mu}\right)^{1/2} \left(1 + \frac{E_c}{RT}\right) e^{-E_c/RT} \qquad (13.3\text{-}16)$$

where N_{Av} is Avogadro's constant, where we let

$$E_c = N_{Av}\varepsilon_c \qquad (13.3\text{-}17)$$

and where we use the fact that the ideal gas constant R is equal to $N_{Av}k_B$.

Equation (13.3-16) is not quite the same as the Arrhenius formula, Eq. (13.3-1), since the preexponential factor in Eq. (13.3-16) depends on T. However, the exponential factor depends so much more strongly on temperature than does the preexponential factor in Eq. (13.3-16) that 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.

EXAMPLE 13.6

For the reaction of Example 13.5, calculate the fractional change in the exponential factor and in the preexponential factor in Eq. (13.3-16) 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

$$\frac{\exp(-2.045 \times 10^4\ \text{K}/303.15\ \text{K})}{\exp(-2.045 \times 10^4\ \text{K}/293.15\ \text{K})} = 10.0$$

The ratio of the preexponential factors is

$$\frac{(303.15\ \text{K})^{1/2}(1 + 2.045 \times 10^4\ \text{K}/303.15\ \text{K})}{(293.15\ \text{K})^{1/2}(1 + 2.045 \times 10^4\ \text{K}/293.15\ \text{K})} = 0.984$$

The change in the pre-exponential factor is negligible.

Equation (13.3-16) corresponds to the probability of reaction shown in Figure 13.1a. A more realistic assumption is that the probability of reaction is given by

$$\text{Probability} = \begin{cases} 0 & \text{if } E_r < E_c \\ 1 - E_c/E_r & \text{if } E_r > E_c \end{cases} \qquad (13.3\text{-}18)$$

as represented in Figure 13.1b. This probability can be defended as follows: A collision with a relative kinetic energy barely great enough to initiate a reaction should have a lower probability of producing a reaction than unity, since some of the translational energy could get transferred into "inactive" internal motions of the molecules that do not lead to reaction. Collisions with a larger relative kinetic energy should provide plenty of energy even if some is lost in inactive internal motions and should have a larger probability of reaction.

When the probability of Eq. (13.3-18) is introduced into the integration of Eq. (13.3-11), the result is[6]

$$k = N_{\mathrm{Av}} \pi d_{12}^2 \left(\frac{8k_{\mathrm{B}}T}{\pi\mu} \right)^{1/2} e^{-E_{\mathrm{c}}/RT} \tag{13.3-9}$$

This formula also does not exactly agree with the Arrhenius formula, since the preexponential factor still depends on temperature. However, the difference is numerically fairly small. We will use Eq. (13.3-19) in preference to Eq. (13.3-16) as the result of the collision theory of bimolecular reactions.

EXAMPLE 13.7

Assuming the activation energy and the value of the rate constant at 373 K from Example 13.5, find the effective collision diameter of a hydrogen molecule and an iodine molecule.

Solution

Assuming that E_{c} and E_{a} can be identified with each other, and using Eq. (13.3-19),

$$\pi d^2 = \left(\frac{\pi\mu}{8k_{\mathrm{B}}T} \right)^{1/2} \frac{k}{N_{\mathrm{Av}}} e^{E_{\mathrm{a}}/RT} = \frac{k}{\langle v_{\mathrm{rel}} \rangle N_{\mathrm{Av}}} e^{E_{\mathrm{a}}/RT}$$

The value of $\langle v_{\mathrm{rel}} \rangle$ is 1988 m s^{-1}, so that

$$d^2 = \frac{8.74 \times 10^{-18}\ \mathrm{mol^{-1}\ s^{-1}}}{\pi(1988\ \mathrm{m\ s^{-1}})(6.022 \times 10^{23}\ \mathrm{mol^{-1}})} e^{54.794} = 1.45 \times 10^{-21}\ \mathrm{m^2}$$

$$d = 3.8 \times 10^{-11}\ \mathrm{m} = 38\ \mathrm{pm} = 0.38\ \mathrm{\mathring{A}}$$

The value of the collision diameter in Example 13.7 is too small by a factor of about 10, which is typical of the collision theory. There is a simple explanation for the smallness of the collision diameter: the molecules not only have to collide with at least a minimum relative energy, but in many reactions must also be oriented properly with respect to each other in order to react. For example, an organic molecule with a functional group would be much more likely to react if struck on the functional group than if struck on the hydrocarbon portion of the molecule.

To account for the orientation dependence an additional 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. (13.3-19) becomes

$$k = N_{\mathrm{Av}} \varphi \pi d_{12}^2 \left(\frac{8k_{\mathrm{B}}T}{\pi\mu} \right)^{1/2} e^{-E_{\mathrm{c}}/RT} \tag{13.3-20}$$

*Exercise 13.8

Find the value of the steric factor for the reaction of Example 13.7 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.

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[6] K. J. Laidler, *op. cit.*, pp. 85ff (Note 3).

Liquid-State Reactions

The temperature dependence of rate constants for both gaseous and liquid-state reactions is reasonably well described by the Arrhenius formula, Eq. (13.3-2). For activation-limited reactions in liquid phases, 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. Diffusion coefficients commonly have a temperature dependence given by Eq. (11.4-5),

$$D = D_0 e^{-E_{ad}/RT}$$

which depends on temperature in much the same way as in the Arrhenius formula. Diffusion-limited reaction rates therefore have much the same dependence on temperature as other reactions. The activation energies are somewhat smaller, often near the values for the energies of activation for diffusion processes, which again is what we would expect.

*Exercise 13.9

For the reaction

$$2I \rightarrow I_2$$

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 11.9.

We will continue our discussion of the theories of chemical reaction rates in Chapter 21, when we consider the activated complex theory of chemical reaction rates in dilute gases. This theory postulates that in order for an elementary process to occur, an activated complex must be formed, and that an activation energy is required to form this complex from the reactants.

13.4 Reaction Mechanisms and Rate Laws

Unfortunately, there is no way to take an experimentally determined rate law for a given reaction and deduce the correct mechanism from it. For example, the reaction

$$H_2 + I_2 \rightarrow 2HI$$

is second order overall. The rate law could indicate that this reaction is a bimolecular elementary reaction, and such was once thought to be the case. However, there are alternative mechanisms that also conform to the same rate law, and the reaction is now thought to proceed by several competing mechanisms, including the elementary mechanism.[7]

Although we cannot directly deduce a mechanism from a rate law, we can often deduce the rate law that corresponds to a given assumed mechanism and compare this equation with the experimental rate law. If the two do not match, the mechanism must be incorrect. If they do match, the mechanism might be correct. There are sometimes

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[7] K. J. Laidler, *op. cit.*, pp. 297ff (Note 3); Sullivan, *J. Chem. Phys.*, **46**, 73 (1967).

other types of experiments that can be done, including direct detection of reaction intermediates, molecular beam experiments, and radioactive tracer experiments. The results can sometimes verify a possible mechanism. However, we must regard even a well-accepted mechanism as tentative.

Since a proposed mechanism consists of elementary steps, we can deduce a rate differential equation 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 consecutive reactions of Eq. (12.5-1). However, they are generally not so easily solved as was that set of two equations. For example, consider the reaction of Eq. (13.1-1):

$$2NO_2 + O_3 \rightarrow N_2O_5 + O_2$$

If the reaction were elementary it would be termolecular and the reaction would be third order overall with the rate law:

$$\text{Rate} = \frac{d[N_2O_5]}{dt} = -\frac{d[O_3]}{dt} = k[NO_2]^2[O_3] \quad \left(\begin{array}{c}\text{rate law}\\ \text{for one-step}\\ \text{mechanism}\end{array}\right) \tag{13.4-1}$$

However, the reaction is found experimentally to be second order overall.

The accepted mechanism of the forward reaction is

$$\begin{array}{ll}(1) & NO_2 + O_3 \rightarrow NO_3 + O_2\\ (2) & NO_3 + NO_2 \rightarrow N_2O_5\end{array}$$

No reverse reactions for the individual steps are included, so the reverse of the entire reaction cannot be described by this mechanism. For this mechanism, we can write the set of simultaneous differential equations

$$\frac{d[O_3]}{dt} = -k_1[NO_2][O_3] \tag{13.4-2a}$$

$$\frac{d[N_2O_5]}{dt} = k_2[NO_3][NO_2] \tag{13.4-2b}$$

There are as many independent differential rate equations as there are steps in the mechanism, and this is generally true. However, we have some choice as to which concentration time derivatives are used for the left sides of the equations.

Exercise 13.10

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. (13.4-2a) and (13.4-2b), and that this equation is therefore not independent of the other two equations.

The differential equations of Eq. (13.4-2) are nonlinear. That is, they have terms that are not proportional to the individual dependent variables. This makes them more difficult to solve than the equations of Eqs. (12.5-2) and (12.5-3). We do not attempt a solution of this set of equations, but apply a common approximation scheme that reduces the set of differential equations to a single rate law.

The Rate-Limiting Step Approximation

Let us assume that the elementary reaction of Eq. (13.4-2b) is much more rapid than that of Eq. (13.4-2a). We mean by this assumption that $k_2 \gg k_1$, not that the actual rate of the second step is greater during the reaction (which cannot be since one of its reactants is furnished by the first step). The inherently rapid second step uses up a molecule of NO_3 very quickly after it is produced by the slow first step. Since the products of the first step are immediately used up, the rate of the reaction is controlled by the first step. We call the slow first step the **rate-limiting step** or **rate-determining step**. The rate law of the forward reaction is Eq. (13.4-2a), the rate differential equation of the slow first step:

$$-\frac{d[O_3]}{dt} = k_1[NO_2][O_3]$$

and the forward reaction is second order overall. The rapid second step plays no role in determining the rate law, since the rate of the reaction is controlled by the first step. This rate law agrees with experiment, so the mechanism of Eq. (13.1-2) is possibly correct, although other mechanisms can be found that predict the same rate law.

If a step other than the first step is much slower than all other steps, the slow step will still be the rate-limiting step. However, 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 rate law. Consider the gaseous reaction

$$2O_3 \rightarrow 3O_2 \tag{13.4-3}$$

This reaction is thought to proceed by the mechanism

$$(1) \quad O_3 + M \rightleftharpoons O_2 + O + M \quad \text{(fast)} \tag{13.4-4a}$$
$$(2) \quad O + O_3 \rightarrow 2O_2 \quad \text{(slow)} \tag{13.4-4b}$$

where M stands for any molecule, such as an O_2 molecule or a molecule of another substance (if other substances are present). An inelastic collision with the molecule M is needed to provide the energy for breaking the bond in the O_3 molecule.

The second step is assumed to be the rate-determining step. Because of the slowness of the second step a reverse reaction for the first step must be included to allow for the possibility that this reverse reaction is rapid compared with the second step. We do not include the reverse reaction for the second step and will obtain only the forward rate law. The rate differential equation for the second step is

$$\left.\frac{d[O_2]}{dt}\right|_{\text{step 2}} = 2k_2[O_3][O] \tag{13.4-5}$$

where 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 equation for the step. If this factor were omitted, the definition of k_2 would be changed and it would be twice as large as with this assignment. Step 1 also produces O_2. However, the rate of this step is controlled by the rate of step 2. When step 2 produces two molecules of O_2, step 1 produces one molecule of O_2 along with the one atom of O that is needed for step 2 to produce two molecules of O_2. When we obtain the rate of O_2 formation from the second step, we will multiply it by 3/2 to obtain the rate of the reaction.

Equation (13.4-5) cannot be solved by itself because of the presence of [O], a concentration that is not known. We invoke the **equilibrium approximation**, which is the assumption that all steps prior to the rate-limiting step are at equilibrium. These equilibria are sometimes called **preequilibria**. This assumption is not strictly correct while the reaction is proceeding, but if the rate-limiting step really is much slower than all previous steps, it gives relations among the concentrations that are accurate enough for some purposes.

The equilibrium expression for the first step of the mechanism is

$$K_1 = \frac{k_1}{k_1'} = \frac{[O_2][O][M]}{[O_3][M]} \tag{13.4-6}$$

where we display the relation between the equilibrium constant K_1 and the rate constants shown in Eq. (12.4-7). This equation could also have been derived by equating the forward and reverse rates of step 1. The effect of writing Eq. (13.4-6) is the replacement of a differential equation with an algebraic equation. Equation (13.4-6) is solved for [O], giving

$$[O] = K_1 \frac{[O_3][M]}{[O_2][M]} = K_1 \frac{[O_3]}{[O_2]}$$

This is substituted into Eq. (13.4-5) to obtain

$$\left.\frac{d[O_2]}{dt}\right|_{\text{step 2}} = 2k_2[O_3][O] = 2k_2K_1\frac{[O_3]^2}{[O_2]}$$

We write the rate of the reaction:

$$\begin{aligned} \text{Rate} &= \frac{1}{3}\frac{d[O_2]}{dt} = \frac{1}{3}\left(\left.\frac{d[O_2]}{dt}\right|_{\text{step 2}} + \left.\frac{d[O_2]}{dt}\right|_{\text{step 1}}\right) \\ &= \left(\frac{1}{3}\right)\left(\frac{3}{2}\right)\left.\frac{d[O_2]}{dt}\right|_{\text{step 2}} = \left(\frac{1}{3}\right)\left(\frac{3}{2}\right)2k_2K_1\frac{[O_3]^2}{[O_2]} = k_2K_1\frac{[O_3]^2}{[O_2]} \end{aligned} \tag{13.4-7}$$

The factor 3/2 comes from the fact that step 1 produces one molecule of O_2 for every two molecules produced by step 2. The order with respect to O_2 is -1. Equation (13.4-7) holds for the forward rate only if some O_2 is present, since O_2 (a product) occurs in the rate law.

*Exercise 13.11

For the gaseous reaction

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

the mechanism

$$\begin{aligned} &(1) \quad 2NO + H_2 \rightleftharpoons N_2 + H_2O_2 \\ &(2) \quad H_2O_2 + H_2 \rightarrow 2H_2O \end{aligned}$$

has been proposed.

a. Find the rate law if step 1 is rate-limiting and the reverse reaction of step 1 is omitted.

b. Find the rate law if the second step is rate-limiting and the reverse reaction of step 1 is included.

The Steady-State Approximation

This approximation (which is also called the "quasi-steady-state approximation") is the second approximation scheme that is used to produce a single rate law from a set of differential equations. It is used when there is not a step that is sufficiently slow compared with the others that the rate-limiting step approximation can be applied accurately. It consists of the assumption that the rate of change of the concentration of one or more reactive intermediates is negligibly small, so that the reactive intermediate is approximately in a "steady state." The steady-state approximation is generally a good approximation only if the concentration of the intermediate is small. Improvements on the simple steady-state approximation have been developed.[8]

Consider the successive reactions of Section 12.5, which constitute a simple mechanism. If the first step is fast compared with the second step, as in Figure 12.6b, the concentration of the intermediate B becomes large during the reaction. Since the concentration is large, its time derivative is fairly large for most values of the time. If the second step is fast compared with the first step, the concentration of the intermediate B remains small, as in Figure 12.6a. Unless it oscillates, a small quantity has a small time derivative so that $d[\mathrm{B}]/dt$ will have a small magnitude compared with the $d[\mathrm{A}]/dt$ and $d[\mathrm{F}]/dt$. Numerical solutions to sets of simultaneous rate differential equations have shown that the approximation quite often gives accurate results.[9]

EXAMPLE 13.8

Apply the steady-state approximation to the mechanism of Eq. (13.4-4).

Solution

We write two differential equations by inspection of Eq. (13.4-4), using the relation between molecularity and order of elementary reactions:

$$\frac{d[\mathrm{O_2}]}{dt} = k_1[\mathrm{O_3}][\mathrm{M}] - k_1'[\mathrm{O_2}][\mathrm{O}][\mathrm{M}] + 2k_2[\mathrm{O}][\mathrm{O_3}] \tag{13.4-8a}$$

$$\frac{d[\mathrm{O}]}{dt} = k_1[\mathrm{O_3}][\mathrm{M}] - k_1'[\mathrm{O_2}][\mathrm{O}][\mathrm{M}] - k_2[\mathrm{O}][\mathrm{O_3}] \tag{13.4-8b}$$

We choose [O] as the quantity whose derivative is written in Eq. (13.4-8b) since O is a reactive intermediate whose concentration is presumably small with a small time derivative. We approximate $d[\mathrm{O}]/dt$ by zero according to the steady-state approximation

$$0 = k_1[\mathrm{O_3}][\mathrm{M}] - k_1'[\mathrm{O_2}][\mathrm{O}][\mathrm{M}] - k_2[\mathrm{O}][\mathrm{O_3}] \tag{13.4-8c}$$

We subtract Eq. (13.4-8c) from Eq. (13.4-8a) to obtain

$$\frac{d[\mathrm{O_2}]}{dt} = 3k_2[\mathrm{O}][\mathrm{O_3}] \tag{13.4-8d}$$

We solve Eq. (13.4-8c) for [O]:

$$[\mathrm{O}] = \frac{k_1[\mathrm{O_3}][\mathrm{M}]}{k_1'[\mathrm{O_2}][\mathrm{M}] + k_2[\mathrm{O_3}]} \tag{13.4-9}$$

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[8] See for example L. O. Jay, A. Sandu, F. A. Potra, and G. R. Carmichael, *SIAM Journal of Scientific Computing*, **18**, 182 (1997).

[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).

and substitute this into Eq. (13.4-8d) to obtain the rate law

$$\frac{1}{3}\frac{d[O_2]}{dt} = k_2[O_3]\frac{k_1[O_3][M]}{k_1'[O_2][M] + k_2[O_3]} = \frac{k_1k_2[O_3]^2[M]}{k_1'[O_2][M] + k_2[O_3]} \qquad (13.4\text{-}10)$$

Comparison of Eq. (13.4-10) with Eq. (13.4-7) shows that if

$$k_1'[O_2][M] \gg k_2[O_3]$$

then Eq. (13.4-10) becomes the same as Eq. (13.4-7). This corresponds to the assumption on which the rate-limiting step approximation was based—that both the forward and reverse rates of the first step are much larger than the rate of the second step.

Exercise 13.12

Apply the steady-state approximation to the reaction of Exercise 13.11.

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 13.11 be obtained?

The Lindemann Mechanism

There is a problem with unimolecular gas-phase reactions that was recognized in the late nineteenth century. It is hard to imagine how a molecule could undergo either an endothermic or an exothermic unimolecular process without colliding with another molecule to transfer energy. For a time there was a theory called the radiation theory, which asserted that the necessary energy transfer took place by the absorption or emission of radiation. However, around 1920 Lindemann[10] proposed that a unimolecular elementary process is neither strictly unimolecular nor strictly elementary. Consider a gas-phase reaction

$$A \rightarrow B + C \qquad (13.4\text{-}11)$$

This could represent the thermal decomposition of cyclopentene, C_5H_8, in which case B stands for cyclopentadiene, C_5H_6, and C stands for H_2. This reaction occurs spontaneously when cyclopentene is heated to 500°C.

The forward reaction for this class of reactions is found experimentally to be described by the rate law (without definite orders):

$$\text{Rate} = \frac{d[B]}{dt} = \frac{k[A]^2}{k' + k''[A]} \qquad (13.4\text{-}12)$$

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[10] A. Lindemann, *Trans. Faraday Soc.*, **17**, 598 (1922).

where k, k', and k'' are temperature-dependent coefficients. Lindemann proposed the following mechanism, which was also advanced by Christiansen:[11]

$$\text{(1)} \qquad \mathrm{A} + \mathrm{A} \rightleftharpoons \mathrm{A}^* + \mathrm{A} \qquad (13.4\text{-}13\text{a})$$

$$\text{(2)} \qquad \mathrm{A}^* \rightarrow \mathrm{B} + \mathrm{C} \qquad (13.4\text{-}13\text{b})$$

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, and is able to decompose according to step 2. Step 1 is not a chemical reaction in the usual sense, since no new substance is created. One possibility is that the inelastic collision in step 1 excites vibrations in the A molecule in such a way that the vibrational energy can eventually rupture a chemical bond. If another substance M is present, the second molecule of A in step 1 could be replaced by an M molecule.

We apply the steady-state approximation and write two differential equations,

$$\frac{d[\mathrm{A}^*]}{dt} = k_1[\mathrm{A}]^2 - k_1'[\mathrm{A}][\mathrm{A}^*] - k_2[\mathrm{A}^*] \approx 0 \qquad (13.4\text{-}14)$$

$$\frac{d[\mathrm{B}]}{dt} = k_2[\mathrm{A}^*] \qquad (13.4\text{-}15)$$

It is important to choose the concentration of the reactive intermediate A* as one of the concentrations whose time derivatives are written. Imposing the steady-state approximation and setting this time derivative equal to zero gives an algebraic equation as in Eq. (13.4-14). This equation is solved for [A*] to obtain

$$[\mathrm{A}^*] = \frac{k_1[\mathrm{A}]^2}{k_2 + k_1'[\mathrm{A}]} \qquad (13.4\text{-}16)$$

and this equation is substituted into Eq. (13.4-15) to give

$$\text{Rate} = \frac{d[\mathrm{B}]}{dt} = \frac{k_1 k_2[\mathrm{A}]^2}{k_2 + k_1'[\mathrm{A}]} \qquad (13.4\text{-}17)$$

This equation agrees with Eq. (13.4-12), with the parameters k, k', and k'' identified in terms of the rate constants for the steps of the mechanism. As with the rate-limiting step approximation, we have reduced a set of two differential equations to a single rate law by replacing a differential equation by an algebraic equation.

We write Eq. (13.4-17) in the form

$$\text{Rate} = \frac{d[\mathrm{B}]}{dt} = \frac{k_1 k_2[\mathrm{A}]}{k_2 + k_1'[\mathrm{A}]}[\mathrm{A}] = k_{\mathrm{uni}}[\mathrm{A}] \qquad (13.4\text{-}18)$$

where k_{uni} depends on [A] as indicated. If the pressure or concentration of substance A is large enough that $k_2 \ll k_1'[\mathrm{A}]$, 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

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[11] J. S. Christiansen, Ph.D. Dissertation, University of Copenhagen, 1921.

$k_2 \gg k_1'[\mathrm{A}]$, then k_{uni} decreases in value and the rate law approaches second order. This region of low pressure or concentration is called the "fall-off region."

EXAMPLE 13.9

a. Find the rate law predicted by the mechanism of Eq. (13.4-13) if the second step is rate-determining. What condition turns the expression of Eq. (13.4-14) into this result?

b. Find the rate law predicted by the mechanism of Eq. (13.4-13) if the forward reaction of the first step is rate-determining.

Solution

a. The equilibrium approximation gives

$$K_1 = \frac{k_1}{k_1'} = \frac{[\mathrm{A}][\mathrm{A}^*]}{[\mathrm{A}]^2} = \frac{[\mathrm{A}^*]}{[\mathrm{A}]} \qquad (13.4\text{-}19)$$

When Eq. (13.4-19) is substituted into Eq. (13.4-15), we obtain the first-order equation

$$\text{Rate} = \frac{d[\mathrm{B}]}{dt} = k_2K_1[\mathrm{A}] = \frac{k_2k_1}{k_1'}[\mathrm{A}] \qquad (13.4\text{-}20)$$

which is the same as Eq. (13.4-14) if the k_2 term in the denominator of the expression in Eq. (13.4-14) is deleted. This deletion corresponds to the case in which the forward rate of the second step is much smaller than the reverse rate of the first step (the second step is rate-limiting).

b. The rate law is second order in the case that $k_2 \gg k_1'[\mathrm{A}]$:

$$\text{Rate} = -\frac{d[\mathrm{A}]}{dt} = k_1[\mathrm{A}]^2 \qquad (13.4\text{-}21)$$

For the Lindemann mechanism, the steady-state approximation is more general than the rate-limiting step approximation, since the result of the rate-limiting step approximation is a special case of the steady-state result.

Gaseous unimolecular processes generally proceed by mechanisms like that of Eq. (13.4-13) and are therefore not truly elementary and are not strictly first order.[12] However, most unimolecular processes are observed in the first-order (high-pressure) region, and we will continue to assume first-order kinetics for unimolecular steps in multistep mechanisms. There are not very many reactions known to be unimolecular. The first one 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 mechanisms consists of three steps, three independent simultaneous differential equations can be written. Either the rate-limiting step approximation or the steady-state approximation can be applied to obtain a single rate law. If the third step is rate-limiting, algebraic equations are written for the equilibria of the first two steps, and these equations are used to eliminate the concentrations of reactive intermediates from the differential equation for the rate-limiting step. If the steady-state approximation is

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[12] K. J. Laidler, *op. cit.*, pp. 150ff (Note 3).

[13] K. J. Laidler, *op. cit.*, pp. 150ff (Note 3).

applied, two differential equations are replaced by algebraic equations. In either case, we retain only one differential equation.

EXAMPLE 13.10

The approximation schemes can be applied to liquid-phase reactions as well as to gas-phase reactions. Find the rate law for the liquid-phase mechanism:[14]

$$\begin{array}{llll} (1) & H^+ + HNO_2 + NO_3^- \rightleftharpoons N_2O_4 + H_2O & \text{(fast)} & (13.4\text{-}22a) \\ (2) & N_2O_4 \rightleftharpoons 2NO_2 & \text{(fast)} & (13.4\text{-}22b) \\ (3) & NO_2 + Fe(CN)_6^{3-} \rightarrow \text{further intermediates} & \text{(slow)} & (13.4\text{-}22c) \end{array}$$

using the rate-limiting step approximation.

Solution

Since the third step is the rate-limiting step, we must write chemical equilibrium expressions for both steps 1 and 2. These equations must be solved simultaneously to obtain expressions for concentrations that can be substituted into the rate differential equation for step 3.

$$K_1 = \frac{k_1}{k_1'} = \frac{[N_2O_4][H_2O]}{[H^+][HNO_2][NO_3^-]} \qquad (13.4\text{-}23)$$

$$K_2 = \frac{k_2}{k_2'} = \frac{[NO_2]^2}{[N_2O_4]} \qquad (13.4\text{-}24)$$

The rate differential equation for the third step is

$$\text{Rate} = k_3[NO_2][\text{fer}] \qquad (13.4\text{-}25)$$

where [fer] stands for the concentration of the $Fe(CN)_6^{3-}$ ion. Equation (13.4-24) is solved to give the concentration of NO_2,

$$[NO_2] = (K_2[N_2O_4])^{1/2} \qquad (13.4\text{-}26)$$

However, this equation still contains the concentration of N_2O_4, which is also a reactive intermediate. We solve Eq. (13.4-23) to obtain

$$[N_2O_4] = \frac{K_1[H^+][HNO_2][NO_3^-]}{[H_2O]} \qquad (13.4\text{-}27)$$

Equation (13.4-27) is substituted into Eq. (13.4-26) and the resulting equation is substituted into Eq. (13.4-25). The result is

$$\begin{aligned} \text{Rate} &= \left(\frac{k_3 K_2 K_1 [H^+][HNO_2][NO_3^-]}{[H_2O]}\right)^{1/2} [\text{fer}] \\ &= k_{\text{app}}[H^+]^{1/2}[HNO_2]^{1/2}[NO_3^-]^{1/2}[\text{fer}] \qquad (13.4\text{-}28) \end{aligned}$$

We have incorporated the concentration of H_2O into k_{app}, the apparent rate constant, since the concentration of water is nearly constant in aqueous solution.

Exercise 13.13

Apply the steady-state approximation to the mechanism of Example 13.10.

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[14] M. V. Twigg, *Mechanisms of Inorganic and Organometallic Reactions*, Plenum Press, New York, 1983, p. 39.

EXAMPLE 13.11

The following is a famous gas-phase reaction, with a mechanism proposed by Ogg.[15]

Stoichiometry: $$2N_2O_5 \rightarrow 4NO_2 + O_2 \qquad (13.4\text{-}29)$$

Mechanism:

(1) $$N_2O_5 \rightleftharpoons NO_2 + NO_3 \qquad (13.4\text{-}30a)$$

(2) $$NO_2 + NO_3 \rightarrow NO + O_2 + NO_2 \qquad (13.4\text{-}30b)$$

(3) $$NO + NO_3 \rightarrow 2NO_2 \qquad (13.4\text{-}30c)$$

Find the rate law using the steady-state approximation.

Solution

We write the three differential equations and impose the steady-state approximation on the reactive intermediates NO_3 and NO.

$$\text{Rate} = -\frac{d[N_2O_5]}{dt} = k_1[N_2O_5] - k_1'[NO_2][NO_3] \qquad (13.4\text{-}31)$$

$$\frac{d[NO_3]}{dt} = k_1[N_2O_5] - k_1'[NO_2][NO_3] - k_2[NO_2][NO_3] - k_3[NO][NO_3] \approx 0 \qquad (13.4\text{-}32a)$$

$$\frac{d[NO]}{dt} = k_2[NO_2][NO_3] - k_3[NO][NO_3] \approx 0 \qquad (13.4\text{-}32b)$$

The second equalities in Eqs. (13.4-32a) and (13.4-32b) give two simultaneous algebraic equations, which can be solved for $[NO_3]$ and [NO]. The results are

$$[NO] = \frac{k_2[NO_2]}{k_3} \qquad (13.4\text{-}33a)$$

and

$$[NO_3] = \frac{k_1[N_2O_5]}{[(k_1' + 2k_2)[NO_2]} \qquad (13.4\text{-}33b)$$

When these two equations are substituted into Eq. (13.4-31), we obtain

$$\text{Rate} = \frac{2k_2k_2}{k_1' + 2k_2}[N_2O_5] = k_{\text{app}}[N_2O_5] \qquad (13.4\text{-}34)$$

so that the reaction is first order.

Exercise 13.14

a. Verify Eq. (13.4-34).

b. Add a back reaction in the second step of the mechanism of Example 13.11 and assume that the third step is rate-limiting. Find the rate law for the reaction. An equilibrium expression must be written for each of the first two steps.

c. What assumptions will cause the steady-state result to become the same as the result of part (b)?

The examples of this section have illustrated the fact that it is often possible to deduce a rate law from a proposed mechanism using either the rate-limiting step approximation or the steady-state approximation. It is not always a routine matter to

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[15] R. A. Ogg, Jr., *J. Chem. Phys.*, **15**, 337, 613 (1947).

decide what mechanism to propose. However, inspection of the experimental rate law can provide some guidance.[16] If in the experimental rate law there is a denominator with two or more terms, one should attempt to find a mechanism to which the steady-state approximation applies. If the rate law shows definite orders, one should first attempt to find a mechanism to which the rate-limiting step approximation applies.

In order to propose a reasonable mechanism to which the rate-limiting step approximation can be applied, one can use some of the following rules:

1. 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.
2. If no products appear in the rate law for the forward reaction, a possible mechanism is that the rate-limiting step is the first step.
3. If negative orders or fractional orders occur in the rate law, the rate-limiting step cannot be the first step.
4. 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.
5. Reactive intermediates must occur in the left-hand side of one step equation and on the right-hand side of a later step equation.
6. Let the chemistry guide the choice of an assumed mechanism. For example, consider the breaking of a weak bond in preference to the breaking of a strong bond.

Let us examine a few hypothetical cases: If the stoichiometry of the reaction is

$$a\mathrm{A} + b\mathrm{B} \rightarrow c\mathrm{C} + d\mathrm{D} \qquad (13.4\text{-}35)$$

and if the rate law is

$$\text{Rate} = k_1[\mathrm{A}]^a[\mathrm{B}]^b \qquad (13.4\text{-}36)$$

then the mechanism could be

$$\begin{array}{lll} (1) & a\mathrm{A} + b\mathrm{B} \rightarrow \text{reactive intermediates} & (\text{slow, rate-limiting}) \\ (2) & \text{reactive intermediates} \rightarrow c\mathrm{C} + d\mathrm{D} & (\text{fast}) \end{array}$$

If the stoichiometry of a reaction is

$$\mathrm{B} + \mathrm{F} \rightarrow \mathrm{D} + \text{other products} \qquad (13.4\text{-}37)$$

and the rate law is

$$\text{Rate} = k_{\text{app}}[\mathrm{B}]^{a+b}[\mathrm{F}]^a[\mathrm{D}]^{-a}$$

then the first step in the mechanism cannot be rate-limiting. The following mechanism can produce this rate law:

$$\begin{array}{llll} (1) & \mathrm{B} + \mathrm{F} \rightleftharpoons \mathrm{A} + \mathrm{D} & (\text{fast in both directions}) & (13.4\text{-}38a) \\ (2) & a\mathrm{A} + b\mathrm{B} \rightarrow \text{products} & (\text{slow, rate-limiting}) & (13.4\text{-}38b) \end{array}$$

The equilibrium approximation applied to the first step gives

$$[\mathrm{A}] = \mathrm{K}_1 \frac{[\mathrm{B}][\mathrm{F}]}{[\mathrm{D}]}$$

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[16] J. O. Edwards, E. F. Greene, and J. Ross, *J. Chem. Educ.*, **45**, 381 (1968).

so that the rate expression is

$$\text{Rate} = k_2\left(K_1\frac{[\text{B}][\text{F}]}{[\text{D}]}\right)^a[\text{B}]^b = k_{\text{app}}[\text{B}]^{a+b}[\text{F}]^a[\text{D}]^{-a} \qquad (13.4\text{-}39)$$

If the stoichiometry of a reaction is

$$b\text{B} + 2\text{F} + \text{H} \rightarrow \text{D} + \text{other products}$$

and the rate law is

$$\text{Rate} = k_{\text{app}}[\text{B}][\text{F}]^2[\text{H}][\text{D}]^{-1}$$

then the first step cannot be rate-limiting because of the presence of [D] in the rate law. The following three-step mechanism corresponds to this rate law if the third step is rate-limiting:

$$\begin{array}{llll} (1) & \text{B} + \text{F} \rightleftharpoons \text{A} + \text{D} & \text{(fast)} & (13.4\text{-}40\text{a}) \\ (2) & \text{F} + \text{H} \rightleftharpoons \text{G} & \text{(fast)} & (13.4\text{-}40\text{b}) \\ (3) & \text{A} + \text{G} \rightarrow \text{products} & \text{(slow)} & (13.4\text{-}40\text{c}) \end{array}$$

This mechanism leads to the rate law

$$\text{Rate} = k_3([K_1[\text{B}][\text{F}][\text{D}]^{-1})(K_2[\text{F}][\text{H}]) \qquad (13.4\text{-}41)$$

in agreement with the given rate law.

Exercise 13.15

Verify Eq. (13.4-41).

EXAMPLE 13.12

For the gaseous reaction

$$4\text{HNO}_3 \rightarrow 4\text{NO}_2 + 2\text{H}_2\text{O} + \text{O}_2 \qquad (13.4\text{-}42)$$

the rate law is found to be

$$\text{Rate} = k_{\text{app}}[\text{HNO}_3]^2[\text{NO}_2]^{-1} \qquad (13.4\text{-}43)$$

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

$$\begin{array}{llll} (1) & \text{HNO}_3 \rightleftharpoons \text{HO} + \text{NO}_2 & \text{(fast)} & (13.4\text{-}44\text{a}) \\ (2) & \text{HO} + \text{HNO}_3 \rightarrow \text{further intermediates/products} & \text{(slow)} & (13.4\text{-}44\text{b}) \end{array}$$

with step 2 assumed to be rate-limiting. Other steps following step 2 do not affect the rate law.

Exercise 13.16

a. Show that the proposed mechanism in Example 13.12 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. (13.4-31).

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. (13.4-4) is given by Eq. (13.4-7):

$$\text{Rate} = \frac{1}{3}\left(\frac{d[O_2]}{dt}\right) = k_{\text{app}}\frac{[O_3]^2}{[O_2]} = k_2K_1\frac{[O_3]^2}{[O_2]} = k_2\frac{k_1}{k_1'}\frac{[O_3]^2}{[O_2]} \tag{13.4-45}$$

If each of the elementary rate constants is governed by the Arrhenius formula, Eq. (13.3-2),

$$k = Ae^{-E_a/RT} \tag{13.4-46}$$

then the temperature dependence of the overall rate constant, k_{app}, is given by

$$\begin{aligned} k_{\text{app}} &= \frac{A_2A_1}{A_{-1}}\,\frac{e^{-E_{a2}/RT}e^{-E_{a1}/RT}}{e^{-E_{a1'}/RT}} = A_{\text{app}}\exp\left(-\frac{E_{a2}+E_{a1}-E_{a1'}}{RT}\right) \\ &= A_{\text{app}}\exp\left(-\frac{E_{a,\text{app}}}{RT}\right) \end{aligned} \tag{13.4-47}$$

The relationship of the overall activation energy, $E_{a,\text{app}}$, to the activation energies of the individual rate constants is shown in this equation. Since the ratio k_1/k_1' is equal to an equilibrium constant, we can rewrite this Eq. (13.4-47) as

$$k_{\text{app}} = A_2\exp\left(-\frac{E_{a2}+\Delta G_1^\circ}{RT}\right) \tag{13.4-48}$$

It is even possible that the apparent activation energy of a reaction with a multistep mechanism is negative, so that the reaction is slower at higher temperature. This occurs in the recombination of iodine atoms to form I_2.

*Exercise 13.17

The temperature dependence of a rate law corresponding to a steady-state approximation is more complicated. Write the temperature dependence of the apparent first-order rate constant for the decomposition of N_2O_5 given in Eq. (13.4-34).

13.5 Some Additional Mechanisms, Including Chain and Photochemical Mechanisms. Competing Mechanisms

In this section, we complete our brief introduction to reaction mechanisms with discussion of three specialized categories of mechanisms.

Chain Reactions

Chain reactions are characterized by a mechanism in which one or more steps produce reactive intermediates (**chain carriers**) in addition to products. The chain carriers react further, producing more products and still more chain carriers, which react further, and so forth. A chain mechanism usually contains the following steps: an **initiation step**, in which chain carriers are formed; one or two **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.

A thoroughly studied chain reaction is the gas-phase reaction:

$$H_2 + Br_2 \rightarrow 2HBr \tag{13.5-1}$$

The empirical rate law for the foward reaction in the presence of some HBr is

$$-\frac{d[H_2]}{dt} = \frac{k_a[H_2][Br_2]^{1/2}}{1 + k_b[HBr]/[Br_2]} \tag{13.5-2}$$

where k_a and k_b are temperature-dependent parameters. The accepted mechanism for the forward reaction is[17]

$$(1) \qquad Br_2 \rightleftharpoons 2Br \tag{13.5-3a}$$

$$(2) \qquad Br + H_2 \rightleftharpoons HBr + H \tag{13.5-3b}$$

$$(3) \qquad H + Br_2 \rightarrow HBr + Br \tag{13.5-3c}$$

The reverse reaction of step 3 is omitted because its rate is small in the initial stages of the reaction. The forward reaction of step 1 is the initiation step, which produces Br, one of the two chain carriers. 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**. Once Br atoms are formed in the initiation step, the reaction can proceed almost indefinitely 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 intiation 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 average number of molecules of product for each initiation step is equal to 4 times the chain length.

We obtain the rate law by use of the steady-state approximation. We write differential equations for the time derivatives of the concentrations of H_2, H and Br. It is better to

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[17] K. J. Laidler, *op. cit.*, pp. 291ff (Note 3).

choose H_2 instead of Br_2 because H_2 occurs in only one step of the mechanism and will give a simpler differential equation. We obtain the simultaneous equations:

$$-\frac{d[H_2]}{dt} = k_2[Br][H_2] - k'_2[HBr][H] \tag{13.5-4a}$$

$$\frac{d[Br]}{dt} = 2k_1[Br_2] - k_2[Br][H_2] + k_3[H][Br_2] + k'_2[HBr][H] - 2k'_1[Br]^2 = 0 \tag{13.5-4b}$$

$$\frac{d[H]}{dt} = k_2[Br][H_2] - k'_2[HBr][H] - k_3[H][Br_2] = 0 \tag{13.5-4c}$$

where we have applied the steady-state approximation and set the time derivatives of the concentration of the chain carriers equal to zero. To solve the algebraic versions of Eqs. (13.5-4b) and (13.5-4c), we add Eqs. (13.5-4b) and (13.5-4c) to give

$$k_1[Br_2] - k'_1[Br]^2 = 0 \tag{13.5-5a}$$

which is the same as

$$[Br] = \left(\frac{k_1}{k'_1}\right)^{1/2}[Br_2]^{1/2} \tag{13.5-5b}$$

Equation (13.5-5b) is the same equation that would result from assuming that step 1 is at equilibrium. The relation of Eq. (13.5-5b) is substituted into Eq. (13.5-4b) or Eq. (13.5-4c) to obtain (after several steps of algebra)

$$[H] = \frac{k_2(k_1/k'_1)^{1/2}[H_2][Br_2]^{1/2}}{k_3[Br_2]^{1/2} + k'_2[HBr]} \tag{13.5-6}$$

We now simplify Eq. (13.5-4a) by noticing that the first two terms in Eq. (13.5-4c) are the same as the two terms on the right-hand side of Eq. (13.5-4a), so that

$$-\frac{d[H_2]}{dt} = k_3[H][HBr_2]$$

When Eq. (13.5-6) is substituted into this equation, we have

$$-\frac{d[H_2]}{dt} = \frac{k_2(k_1/k'_1)^{1/2}[H_2][Br_2]^{1/2}}{1 + \dfrac{k'_2[HBr]}{k_3[Br_2]}} \tag{13.5-7}$$

which reproduces the empirical rate law with the following expressions for the empirical parameters:

$$k_a = k_2\left(\frac{k_1}{k'_1}\right)^{1/2} \tag{13.5-8}$$

$$k_b = \frac{k'_2}{k_3} \tag{13.5-9}$$

Exercise 13.18

Verify Eqs. (13.5-6) and (13.5-7).

Photochemical Chain Reactions

The initiation step of the chain mechanism of Eq. (13.5-3) requires 194 kJ mol^{-1} to break the Br–Br bond. This energy can be supplied by ultraviolet light instead of by inelastic molecular collisions.

*Exercise 13.19

Calculate the minimum frequency and maximum wavelength of light with sufficient energy per photon to break a Br–Br bond.

The accepted mechanism for the photochemically initiated reaction is

$$\text{(1)} \quad Br_2 + h\nu \rightarrow 2Br \qquad (13.5\text{-}10a)$$

$$\text{(1}'\text{)} \quad 2Br \rightarrow Br_2 \qquad (13.5\text{-}10b)$$

$$\text{(2)} \quad Br + H_2 \rightleftharpoons HBr + H \qquad (13.5\text{-}10c)$$

$$\text{(3)} \quad H + Br_2 \rightarrow HBr + Br \qquad (13.5\text{-}10d)$$

where we use the expression for the energy of a photon, $h\nu$, as a symbol for the photon itself. The mechanism is just as in Eq. (13.5-3) except for replacing process 1 by the photochemical process. The termination reaction is the same as before and is labeled 1$'$.

Photochemical reactions are described by two empirical laws. The first is the **Grotthuss–Draper law**, which states that only the 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.[18]

The hydrogen–bromine reaction conforms to the laws of photochemistry, so that the rate of the initiation step of Eq. (13.5-10a) is proportional to the rate at which photons are absorbed. By measurement of incident and transmitted intensities of light, one can measure the amount of radiation absorbed in the range of wavelengths that can produce Br atoms. We let J be the average rate of absorption of light, measured in einsteins per unit volume per second (one einstein is one mole 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

$$\begin{aligned}\frac{d[\mathrm{Br}]}{dt} &= 2J - k_2[\mathrm{Br}][\mathrm{H_2}] + k_3[\mathrm{H}][\mathrm{Br_2}] + k_2'[\mathrm{HBr}][\mathrm{H}] - 2k_1'[\mathrm{Br}]^2 \\ &= 0 \end{aligned} \qquad (13.5\text{-}11)$$

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. (13.5-4c). When this equation is added to Eq. (13.5-11), we obtain

$$J - k_1'[\mathrm{Br}]^2 = 0 \qquad (13.5\text{-}12)$$

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[18] See, for example, L. Li, M. Wu, and P. M. Johnson, *J. Chem. Phys.*, **86**, 1131 (1987).

Equation (13.5-12) is combined with Eq. (13.5-5) and substituted into Eq. (13.5-7) to obtain

$$-\frac{d[\mathrm{H_2}]}{dt}=\frac{k_2(2/k_1')^{1/2}[\mathrm{H_2}]\,J^{1/2}}{1+\dfrac{k_2'}{k_3}\dfrac{[\mathrm{HBr}]}{[\mathrm{Br_2}]}} \tag{13.5-13}$$

which agrees with experiment. Note that [Br] does not occur in the numerator of the rate law, as it did in Eq. (13.5-7).

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 range from nearly zero to about 10^6. Quantum yields greater than unity ordinarily indicate a chain reaction. The quantum yield of the photochemical hydrogen–bromine reaction is equal to four times the chain length, and therefore can greatly exceed unity.

Hydrogen reacts in the gas phase with chlorine or with iodine much as with bromine, but there are differences between the three reactions. The first difference is the fact that it is inhibited by the presence of oxygen. An approximate empirical rate law for the photochemical reaction is[19]

$$\frac{d[\mathrm{HCl}]}{dt}=\frac{k_aJ[\mathrm{H_2}][\mathrm{Cl_2}]}{k_b[\mathrm{Cl_2}]+[\mathrm{O_2}]([\mathrm{H_2}]+k_c[\mathrm{Cl_2}])} \tag{13.5-14}$$

where k_a, k_b, and k_c are temperature-dependent parameters. In the complete absence of oxygen, the 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. (13.5-10) is unimportant, while termination of chains by combination of chlorine atoms with the surface of the reaction vessel and with other molecules (such as oxygen) is important. 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 hydrogen–iodine reaction was mentioned at the beginning of the previous section:

$$\mathrm{H_2}+\mathrm{I_2}\rightarrow 2\mathrm{HI} \tag{13.5-15}$$

It is different from both of the other reactions since it is not primarily a chain reaction, except at high temperatures. The reaction obeys second-order kinetics and was thought at one time to be a bimolecular elementary reaction. It is now thought that several mechanisms compete, including the elementary mechanism, and that under different conditions of temperature and pressure different mechanisms dominate. The chain mechanism analogous to Eq. (13.5-3) is dominant above 750 K but is unimportant

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[19] K. L. Laidler, *op. cit.*, pp. 295ff (Note 3).

below 600 K. The following nonchain mechanism appears to be dominant below 600 K:[20]

$$\begin{array}{llll} (1) & I_2 \rightleftharpoons 2I & \text{(fast)} & (13.5\text{-}16a) \\ (2) & 2I + H_2 \rightarrow 2HI & \text{(slow)} & (13.5\text{-}16b) \end{array}$$

***Exercise 13.20**

a. Find the rate law for the mechanism of Eq. (13.5-16) using the rate-limiting step approximation.

b. Find the rate law for the mechanism of Eq. (13.5-16) using the steady-state approximation.

The Principle of Detailed Balance

For any reaction that proceeds by two competing mechanisms, there is a fundamental physical principle that governs the rate constants for the two mechanisms. This principle is called the **principle of detailed balance:** *All 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.* Consider the elementary gas-phase mechanism at some high temperature:

$$(1a) \qquad H_2 + I_2 \rightleftharpoons 2HI \qquad (13.5\text{-}17)$$

Consider also the mechanism of Eq. (13.5-16) with inclusion of a reverse reaction in step 2. Figure 13.2 shows the two pathways. Since both mechanisms must separately be at equilibrium, it is not possible for the forward reaction of one mechanism to be canceled by the reverse reaction of the other mechanism. If this were possible, the laws of thermodynamics could be violated. Let us assume that equilibrium of the reaction of Figure 13.2 corresponds to a large forward rate of the two-step mechanism and a large reverse step 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 absorbs iodine atoms, insertion of a sample 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 might 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, in violation of the laws of thermodynamics.

From Eq. (12.4-7), the equilibrium constant for reaction (1a) is given by

$$K_{1a} = \frac{k_{1a}}{k'_{1a}} \qquad (13.5\text{-}18)$$

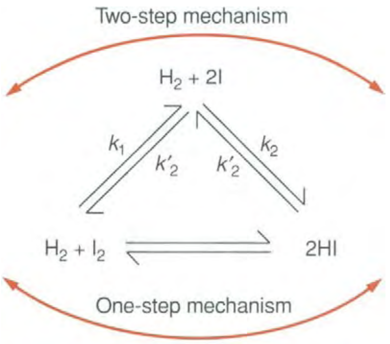

Figure 13.2. Two Mechanisms for the $H_2 + I_2$ Reaction. Since both mechanics lead from the same reactants to the same products, the equilibrium constants for the two mechanisms must be equal.

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[20] K. L. Laidler, *op. cit.*, pp. 295ff (Note 3). See also J. H. Sullivan, *J. Chem. Phys.*, **46**, 73 (1967).

By analogy with Eq. (12.5-16), the equilibrium constant for the mechanism of Eq. (13.5-16) is

$$K = \frac{k_1 k_2}{k_1' k_2'} \tag{13.5-19}$$

Since both equilibrium constants refer to the same reaction, they must be equal:

$$\frac{k_1 k_2}{k_1' k_2'} = \frac{k_{1a}}{k_{1a}'} \tag{13.5-20}$$

The statement about time reversibility is correct for classical mechanics. In quantum mechanics, other transformations must be carried out in addition to time-reversal, but the overall situation is much the same.

The principle of detailed balance follows from a more fundamental principle, the **principle of microscopic reversibility**, which states that all 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 seem to apply if the movie were run backward. This would not be the case if the principle of detailed balance were not valid.

Irreversible macroscopic processes do not obey time reversibility. A movie of a macroscopic diffusion process or a chemical reaction run backward would appear to violate the second law of thermodynamics, and the entropy of the universe would seem to decrease. However, a microscopic movie of the molecular motions during the process would appear normal if run backwards. One of the most interesting tasks of science is to answer the question: How can irreversible macroscopic processes result from time-reversible molecular processes? Although much progress has been made in understanding how to average over microstates to represent a macrostate, the question is not yet completely answered.

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[21]

(1)	$H_2 + \text{wall} \rightarrow \text{H(adsorbed)} + H$	(initiation)
(2)	$H + O_2 \rightarrow OH + O$	(branching)
(3)	$O + H_2 \rightarrow OH + H$	(branching)
(4)	$OH + H_2 \rightarrow H_2O + H$	(propagation)
(5)	$H + O_2 + M \rightarrow HO_2 + M$	(termination)
(6)	$H + \text{wall} \rightarrow \text{stable species}$	(termination)
(7)	$HO + \text{wall} \rightarrow \text{stable species}$	(termination)
(8)	$HO_2 + \text{wall} \rightarrow \text{stable species}$	(termination)

In step 5, M represents any molecule that can collide with the H and O_2. This could be an H_2 or an O_2 molecule, but could be an impurity molecule if one is present. Steps 2 and 3 consume one chain carrier but provide two chain carriers, so that as these steps

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[21] S. W. Benson, *The Foundations of Chemical Kinetics*, McGraw-Hill, New York, 1990, p. 454ff.

occur the reaction rate is accelerated 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, as are the temperature and pressure, in determining whether an explosion will occur.

13.6 Catalysis

A substance that increases the rate of a chemical reaction but does not appear in the chemical equation for the reaction is a **catalyst**. This term was coined in 1836 by Berzelius from the Greek words "kata" (wholly) and "lyein" (to loosen).[22] 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 (the catalyst is usually a solid). **Enzyme catalysis** can be considered to be a separate class. A catalyst generally provides an alternative mechanism that competes with the uncatalyzed mechanism. If the catalyzed mechanism is faster than the uncatalyzed mechanism, the observed rate of the reaction is due mostly to the catalyzed mechanism, although the reaction is also still proceeding by the uncatalyzed mechanism.

Heterogeneous Catalysis

In this type of catalysis reacting molecules are adsorbed from a gas or liquid phase onto the surface of a solid catalyst. Consider an uncatalyzed unimolecular process:

$$\text{A(gas)} \rightarrow \text{products or intermediates} \tag{13.6-1}$$

and a competing catalyzed process:

$$\text{A(gas)} + \text{surface site} \rightarrow \text{A(adsorbed)} \tag{13.6-2}$$

$$\text{A(adsorbed)} \rightarrow \text{same products or intermediates} \tag{13.6-3}$$

The rate of the first process depends on the concentration of substance A in the gas phase, while the rate of the second process depends on the amount of substance A adsorbed on the solid surface.

The Langmuir Theory of Adsorption

Irving Langmuir, 1881–1957, was an American industrial chemist who won the 1932 Nobel Prize in chemistry for his work on surface chemistry.

The study of adsorption was pioneered by Langmuir, who derived an expression for the equilibrium fraction of a solid surface covered by an adsorbed substance as a function of the concentration of the substance in the gas or liquid phase. The adsorption process is represented by

$$\text{A} + \text{surface site} \rightleftharpoons \text{A(adsorbed)} \tag{13.6-4}$$

It is assumed that the surface contains a set of sites at which molecules of A can be adsorbed, and that only a single layer of molecules (a **monolayer**) can be adsorbed on the surface. The 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

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[22] K. J. Laidler, *op. cit.*, p. 229 (Note 3).

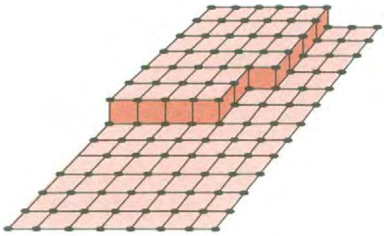

Figure 13.3. Idealized Sites on a Solid Surface. A real crystal surface is not a perfect plane of molecules, but contains imperfections such as the step imperfection shown in this figure. The adsorption probably takes place primarily at the imperfections.

depicted in Figure 13.3. The fraction of the surface sites occupied by adsorbed A molecules is denoted by θ.

The adsorption process is assumed to be an elementary process so that the rate of adsorption is first order in the concentration of A in the fluid phase and is also proportional to $1-\theta$, the fraction of surface sites available for adsorption:

$$\text{Rate of adsorption} = k_1[\text{A}](1-\theta) \tag{13.6-5}$$

The desorption is also assumed to be an elementary process, so that

$$\text{Rate of desorption} = k_1'\theta \tag{13.6-6}$$

At equilibrium, the rate of desorption equals the rate of adsorption, and we can write

$$k_1'\theta = k_1[\text{A}](1-\theta) \tag{13.6-7}$$

This equation can be solved for θ to give the **Langmuir isotherm**:

$$\theta = \frac{k_1[\text{A}]}{k_1' + k_1[\text{A}]} = \frac{K[\text{A}]}{1+K[\text{A}]} \tag{13.6-8}$$

where K is a type of equilibrium constant, and has the units of reciprocal concentration (L mol^{-1} or $\text{m}^3\,\text{mol}^{-1}$).

$$K = \frac{k_1}{k_1'} \tag{13.6-9}$$

The name "isotherm" is used because the formula gives the fraction of the surface covered as a function of the concentration of A at a fixed temperature.

Figure 13.4 schematically depicts the Langmuir isotherm for a hypothetical system. The value of K can be determined from a graph of the Langmuir isotherm by determining the value of the concentration of A corresponding to $\theta = \frac{1}{2}$.

Exercise 13.21

Show that $1/K$ equals the value of [A] corresponding to $\theta = \frac{1}{2}$.

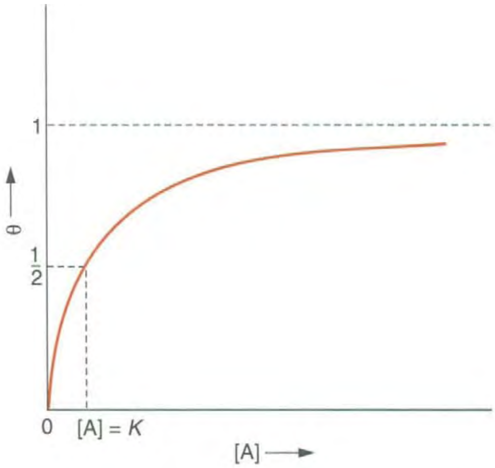

Figure 13.4. The Langmuir Isotherm. This curve has the property that when [A] = K, the surface adsorption sites are half occupied. The asymptote corresponds to full occupation.

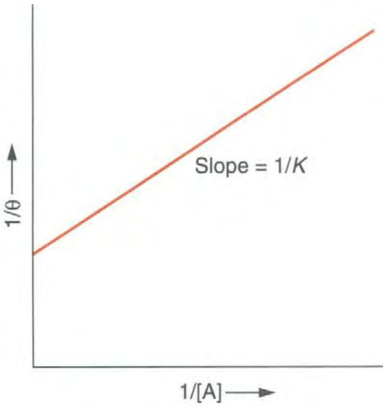

Figure 13.5. Linear Plot of the Langmuir Isotherm. The plot of $1/\theta$ against $1/[\mathrm{A}]$ is linear according to the Langmuir isotherm.

Since the total area of an adsorbing surface and the area occupied by an adsorbed molecule will probably not be known, the value of θ is not directly measurable. 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 13.4; the location of the asymptote corresponds to $\theta = 1$, allowing one to determine where $\theta = \frac{1}{2}$ is located on the graph. Accurately locating an asymptote on a graph is difficult if the data suffer from experimental errors, so it is desirable to make a linear plot, as shown in Figure 13.5. In this graph, $1/\theta$ is plotted as a function of $1/[\mathrm{A}]$, corresponding to the version of Eq. (13.6-8):

$$\frac{1}{\theta} = \frac{1 + K[\mathrm{A}]}{K[\mathrm{A}]} = \frac{1}{K[\mathrm{A}]} + 1 \qquad (13.6\text{-}10)$$

In practice, a plot of the reciprocal of the mass adsorbed is plotted, 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 plot. A linear least-squares procedure can be used as an alternative to graphing.

Exercise 13.22

Show that Eq. (13.6-10) is correct.

EXAMPLE 13.13

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/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 area of the sample of charcoal.

Solution

a. Since m, the mass absorbed, is proportional to θ, we write

$$\frac{1}{m} = \frac{B}{\theta} = \frac{B}{K[\mathrm{A}]} + B \qquad (13.6\text{-}11)$$

where B is a proportionality constant that we evaluate from the data. For each data point, we calculate $1/m$ and $1/[\mathrm{A}]$, using grams as the unit of mass and $\mathrm{mol\,L^{-1}}$ as the unit of concentration:

$\dfrac{1}{m/\mathrm{g}}$	0.333	0.263	0.233	0.213	0.208
$\dfrac{1}{[\mathrm{A}]/\mathrm{mol\,L^{-1}}}$	855	340	170	85.5	56.8

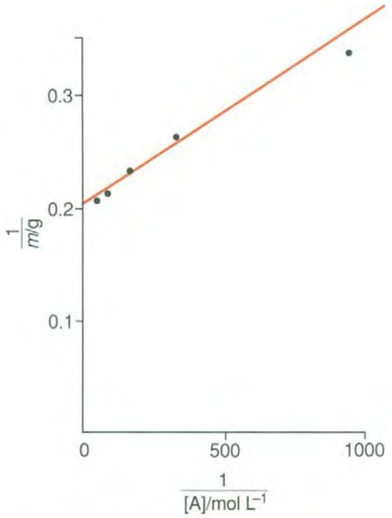

Figure 13.6. Plot of $1/m$ vs. $1/[A]$. The value of the Langmuir constant K and of the total surface area are deduced from fitting these data to a straight line.

Figure 13.6 shows a graph of $1/m$ as a function of $1/[A]$, with the linear least-squares line drawn in. The slope of this line is equal to 1.55×10^{-4} mol L^{-1} g^{-1} and its intercept is equal to 0.203 g^{-1}. The parameter B is therefore equal to 0.203 g^{-1}, and the value of K is equal to $0.203\ \text{g}^{-1}/1.55 \times 10^{-4}\ \text{mol L}^{-1}\ \text{g}^{-1} = 1310\ \text{L mol}^{-1}$. 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 g mol^{-1}, the asymptotic amount adsorbed is equal to 0.0764 mol. The area is

$$A = (0.260\ \text{nm}^2\ \text{molecule}^{-1})(6.022 \times 10^{23}\ \text{molecule mol}^{-1})(0.0764\ \text{mol})$$
$$= 1.20 \times 10^{22}\ \text{nm}^2 = 1.20 \times 10^4\ \text{m}^2$$

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.

Adsorption processes are divided into two classes: **physical adsorption** and **chemical adsorption** (**chemisorption**). In physical adsorption, the binding forces are London dispersion forces, dipole–dipole attractions, etc. In chemisorption, 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 so long as only a monolayer of atoms or molecules can be adsorbed on the surface, and so long as the adsorbed molecules do not dissociate. There are other isotherms that apply to the case of multiple layers.[23]

In some cases of chemisorption, the molecules of the adsorbed substance dissociate and are bonded to the surface as atoms or as free radicals. For example, when hydrogen is adsorbed on platinum it dissociates into individual hydrogen atoms that are chemically bonded to platinum atoms on the surface. Platinum is an effective surface for a hydrogen electrode and an effective catalyst for hydrogenation reactions for this reason. In this case a different isotherm from that of Eq. (13.6-8) applies. If a substance A_2 dissociates to form two A atoms, it occupies two sites on the surface and we write

$$A_2(g) + 2\ \text{surface sites} \rightleftharpoons 2A(\text{adsorbed}) \qquad (13.6\text{-}12)$$

If the adsorption is an elementary process,

$$\text{Rate of adsorption} = k_1[A_2](1-\theta)^2 \qquad (13.6\text{-}13)$$

The rate of desorption is proportional to the square of the number of adsorbed atoms per unit area and thus to θ^2:

$$\text{Rate of desorption} = k_1'\theta^2 \qquad (13.6\text{-}14)$$

The rates of adsorption and desorption are equated to obtain the equilibrium isotherm:

$$\theta = \frac{K^{1/2}[A_2]^{1/2}}{1 + K^{1/2}[A_2]^{1/2}} \qquad (13.6\text{-}15)$$

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[23] K. J. Laidler, *op. cit.*, p. 234 (Note 3).

The Rate of a Heterogeneously Catalyzed Reaction

Consider the mechanism:

(1) $A + \text{surface site} \rightleftharpoons \text{A(adsorbed)}$ (fast) (13.6-16a)
(2) $\text{A(adsorbed)} \rightarrow$ further intermediates or products (slow) (13.6-16b)

If the second step is rate-limiting the rate is proportional to θ. We assume the first step to be at equilibrium so that θ is given by Eq. (13.6-8) and the rate is given by

$$\text{Rate} = k_2\theta = \frac{k_2K[\text{A}]}{1 + K[\text{A}]} \tag{13.6-17}$$

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 amount of surface sites and not by the concentration of A.

Exercise 13.23

Derive an expression for the rate of the reaction of Eq. (13.6-16) assuming the steady-state approximation instead of the rate-limiting step approximation.

*Exercise 13.24

The catalyzed reaction of a substance that dissociates upon adsorption can also be studied. Find the rate law for the forward rate of the catalyzed reaction

$$A_2 \rightarrow \text{products}$$

with the assumed mechanism

(1) $A_2 + 2$ surface sites $\rightleftharpoons 2\,\text{A(adsorbed)}$ (fast)
(2) $\text{A(adsorbed)} \rightarrow$ further intermediates or products (slow)

Assume that the second step is rate-limiting.

For the case of two different substances reacting 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) $A + \text{surface site} \rightleftharpoons \text{A(adsorbed)}$ (13.6-18a)
(2) $\text{A(adsorbed)} + \text{B} \rightarrow$ further intermediates or products (13.6-18b)

Since molecules must collide to react this mechanism means that the B molecules from the fluid phase must collide with the adsorbed A molecules. If the second step is rate-limiting, the rate law is

$$\text{Rate} = \frac{k_2K_1[\text{B}][\text{A}]}{1 + K_1[\text{A}]} \tag{13.6-19}$$

This mechanism is thought to be quite improbable.

Exercise 13.25

Derive Eq. (13.6-19).

If both of the reacting molecules are adsorbed and if at least one of them can move around on the surface, the reaction between two adsorbed molecules can occur. This mechanism is called the **Langmuir–Hinshelwood mechanism**, and occurs more commonly than the Langmuir–Rideal mechanism. It can be represented by

(1) $\mathrm{A} + \text{surface site} \rightleftharpoons \mathrm{A(adsorbed)}$ (13.6-20a)

(2) $\mathrm{B} + \text{surface site} \rightleftharpoons \mathrm{B(adsorbed)}$ (13.6-20b)

(3) $\mathrm{A(adsorbed)} + \mathrm{B(adsorbed)} \rightarrow$ further intermediates or products (13.6-20c)

We assume both substances adsorb on the same set of sites so that 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:

$$\text{Rate of adsorption of A} = k_1[\mathrm{A}](1-\theta_A-\theta_B) \qquad (13.6\text{-}21)$$

$$\text{Rate of adsorption of B} = k_2[\mathrm{B}](1-\theta_A-\theta_B) \qquad (13.6\text{-}22)$$

The rates of desorption are

$$\text{Rate of desorption of A} = k_1'\theta_A \qquad (13.6\text{-}23)$$

$$\text{Rate of desorption of B} = k_2'\theta_B \qquad (13.6\text{-}24)$$

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 get the equilibrium relations:

$$\theta_A = \frac{K_1[\mathrm{A}]}{1+K_1[\mathrm{A}]+K_2[\mathrm{B}]} \qquad (13.6\text{-}25)$$

$$\theta_B = \frac{K_2[\mathrm{B}]}{1+K_1[\mathrm{A}]+K_2[\mathrm{B}]} \qquad (13.6\text{-}26)$$

Exercise 13.26

Verify Eqs. (13.6-25) and (13.6-26).

If step 3 in the Langmuir–Hinshelwood mechanism is rate-limiting, both absorption processes will be assumed to be at equilibrium, and the rate law is

$$\text{Rate} = k_3\theta_A\theta_B = \frac{k_3K_1K_2[\mathrm{A}][\mathrm{B}]}{(1+K_1[\mathrm{A}]+K_2[\mathrm{B}])^2} \qquad (13.6\text{-}27)$$

Figure 13.7 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 $K_1[\mathrm{A}]$ that is larger than the other two terms in the denominator, so that the denominator becomes proportional to $[\mathrm{A}]^2$. The 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 CO is bonded much more strongly on the catalyst surface than is the O_2, and the rate is inversely proportional to [CO] for nearly all cases,[24] corresponding to the case that $K_1[\mathrm{CO}]$ is much larger than the other terms in the denominator.

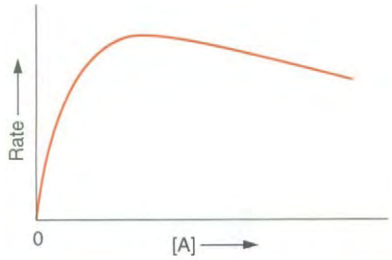

Figure 13.7. Schematic Plot of the Rate of a Catalyzed Reaction A + B → Products as a Function of [A] with fixed [B]. The decrease in the rate comes from the fact that most of the adsorption sites are occupied by A molecules, and there are too few B molecules adsorbed to sustain the maximum rate or the reaction.

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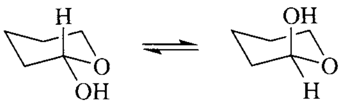
[24] K. J. Laidler, *op. cit.*, p. 249 (Note 3).

Homogeneous Catalysis

This class of catalysis occurs in a gas or a liquid phase. One subclass of homogeneous catalysis in aqueous solutions is acid or base catalysis. One type of acid catalysis is called **general acid catalysis**, defined as catalysis depending on the concentration of undissociated weak acid. If the catalysis depends on the concentration of hydrogen ions, irrespective of the strong or weak acid from which the hydrogen ions come, it is called **specific hydrogen-ion catalysis**. Acid and base catalysis are illustrated by an example,[25] the isomerization of α-D-glucose to β-D-glucose (or vice versa). This was one of the first reactions shown to exhibit generalized acid catalysis. It is sometimes called the "mutarotation" of glucose because of the change in optical rotation of the solution as the reaction proceeds. The reaction is



(13.6-28)

where the structural formulas are abbreviated by omission of some Hs and OHs.

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 forward reaction of the alpha isomer is

$$\text{Forward rate} = k_0[\alpha] \tag{13.6-29}$$

where [α] stands for the concentration of the alpha isomer. The rate constant k_0 has the value of $0.0054\,\mathrm{min}^{-1}$ at 18°C. In the presence of a strong acid, the rate law is

$$\text{Forward rate} = k_0[\alpha] + k_{\mathrm{H}^+}[\mathrm{H}^+][\alpha] \tag{13.6-30}$$

where k_0 has the same value as before and where k_{H^+} is equal to $0.0040\,\mathrm{L\,mol^{-1}\,min^{-1}}$ at 18°C. The uncatalyzed mechanism gives rise to the first term and the catalyzed mechanism gives rise to the second term, showing the competition between the two mechanisms. The second term corresponds to specific hydrogen ion catalysis, since hydrogen ions from any strong acid give the same contribution to the rate.

The reaction also exhibits **base catalysis**, so that the rate law with both catalyzed mechanisms included is:

$$\text{Forward rate} = k_0[\alpha] + k_{\mathrm{H}^+}[\mathrm{H}^+][\alpha] + k_{\mathrm{OH}^-}[\mathrm{OH}^-][\alpha] \tag{13.6-31}$$

where $k_{\mathrm{OH}^-} = 3800\ \mathrm{L\,mol^{-1}\,min^{-1}}$ at 18°C. In basic solution the concentration of hydrogen ions will be small and in acidic solution the concentration of hydroxide ions will be small, so that only one of the last two terms will make an important contribution in a given case. However, both terms are still present because introducing another mechanism does not shut down an existing mechanism.

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. The mechanism for forming the open-chain form is thought to be the following for general acid catalysis:[26]

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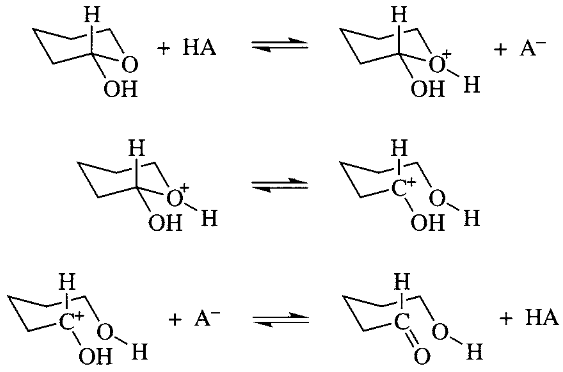
[25] S. W. Benson, *op. cit.*, pp. 558ff (Note 21).

[26] S. W. Benson, *op. cit.*, pp. 558ff (Note 21).



(13.6-32)

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 acid HA:

$$\text{Rate} = k_1[\alpha][\text{HA}] \tag{13.6-33}$$

Other examples of homogeneous catalysis also correspond to mechanisms that contain steps involving the catalyst. For example, the gas-phase decomposition of ozone

$$2\text{O}_3 \rightarrow 3\text{O}_2 \tag{13.6-34}$$

is catalyzed by N_2O_5. The proposed mechanism is[27]

$$(1) \quad \text{N}_2\text{O}_5 \rightarrow \text{NO}_3 + \text{NO}_2 \tag{13.6-35a}$$

$$(2) \quad \text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2 \tag{13.6-35b}$$

$$(3) \quad 2\text{NO}_3 \rightarrow 2\text{NO}_2 + \text{O}_2 \tag{13.6-35c}$$

$$(4) \quad \text{NO}_3 + \text{NO}_2 \rightarrow \text{N}_2\text{O}_5 \tag{13.6-35d}$$

Step 1 is the same as the first step of the mechanism of Example 13.11. Step 4 is the reverse of step 1. We have written it separately to emphasize that the N_2O_5 is regenerated. Step 2 must be doubled for the equations of the mechanism to add up to the stoichiometric equation.

EXAMPLE 13.14

Find the rate law for the forward reaction of the O_3 decomposition according to the above mechanism.

Solution

We write differential equations for the rate of change of $[O_3]$, which gives the rate, and for the rates of change of $[NO_3]$ and $[NO_2]$, which are the reactive intermediates whose concentrations can be considered to be constant in the steady-state approximation:

$$\text{Rate} = -\frac{1}{2}\frac{d[\text{O}_3]}{dt} = k_2[\text{NO}_2][\text{O}_3] \tag{13.6-36a}$$

$$\frac{d[\text{NO}_2]}{dt} = k_1[\text{N}_2\text{O}_5] - k_1'[\text{NO}_3][\text{NO}_2] + 2k_3[\text{NO}_3]^2 - k_2[\text{NO}_2][\text{O}_3] = 0 \tag{13.6-36b}$$

$$d[\text{NO}_3]/dt = k_1[\text{N}_2\text{O}_5] - k_1'[\text{NO}_3][\text{NO}_2] - 2k_3[\text{NO}_3]^2 + k_2[\text{NO}_2][\text{O}_3] = 0 \tag{13.6-36c}$$

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[27] H. S. Johnston, *Gas Phase Reaction Rate Theory*, Ronald Press, New York, 1966.

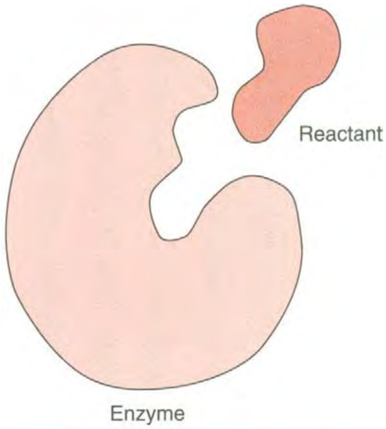

Figure 13.8. The Active Site on a Hypothetical Enzyme. The reactant molecule fits into the active site in such way that a bond is stretched or compressed, or the molecule is made more reactive when it is combined with the active site.

Subtraction of Eq. (13.6-36c) from Eq. (13.6-36b) gives an equation that is solved to obtain

$$[\mathrm{NO_2}] = \frac{2k_3[\mathrm{NO_3}]^2}{k_2[\mathrm{O_3}]} \tag{13.6-37}$$

Adding Eqs. (13.6-36b) and (13.6-36c) gives an equation that is combined with Eq. (13.6-37) and solved to give

$$[\mathrm{NO_3}] = \left(\frac{k_1}{2k_1'k_3}[\mathrm{N_2O_5}][\mathrm{O_3}]\right)^{1/3} \tag{13.6-38}$$

Equation (13.6-38) is substituted into Eq. (13.6-37), which is substituted into Eq. (13.6-20a) to give our solution:

$$\text{Rate} = -\frac{1}{2}\frac{d[\mathrm{O_3}]}{dt} = k_2k_3\left(\frac{k_1}{2k_1'k_3}[\mathrm{N_2O_5}][\mathrm{O_3}]\right)^{2/3} = k_{\mathrm{app}}[\mathrm{N_2O_5}]^{2/3}[\mathrm{O_3}]^{2/3} \tag{13.6-39}$$

The rate depends on both the concentration of the reactant and that of the catalyst, as expected.

Enzyme Catalysis

In cellular biological organisms nearly all reactions are catalyzed by enzymes. Enzymes are usually given trivial names by adding the ending "ase" to the name of the reactant or the reaction that is catalyzed. The enzyme urease catalyzes the hydrolysis of urea and a protease catalyzes the hydrolysis of proteins. Most enzymes are proteins, although some ribonucleic acids have been found to exhibit catalytic activity.[28] Enzymes generally exhibit **specificity**. 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 will catalyze 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 13.8. Once situated in the active site, the reactant molecule is rendered more reactive. Through conformational changes or polarizations produced by interaction with the enzyme, it is put into a state of greater reactivity, often into a conformation similar to a transition state. The first accepted mechanism for enzyme catalysis was proposed by Michaelis and Menten.[29] For the case of a single reactant R and a single product P, this mechanism is

Many biochemistry textbooks denote the reactant S *(for substrate) and its concentration by* [S] *instead of* [R].

$$(1) \qquad \mathrm{E} + \mathrm{R} \rightleftharpoons \mathrm{ER} \tag{13.6-40a}$$

$$(2) \qquad \mathrm{ER} \rightarrow \mathrm{E} + \mathrm{P} \tag{13.6-40b}$$

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[28] T. R. Cech, *Science*, **236**, 1532 (1987).

[29] L. Michaelis and M. L. Menten, *Biochem. Z.*, **49**, 333 (1913).

where E stands for the enzyme, R stands for the reactant, ER stands for the enzyme–reactant complex, and P stands for the product. In addition to this mechanism there is presumably an uncatalyzed mechanism proceeding at the same time but with a smaller rate, so that the catalyzed mechanism dominates.

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.[30] The two differential rate equations are

$$\frac{d[\mathrm{ER}]}{dt} = k_1[\mathrm{E}][\mathrm{R}] - k_1'[\mathrm{ER}] - k_2[\mathrm{ER}] \tag{13.6-41a}$$

$$\frac{d[\mathrm{P}]}{dt} = k_2[\mathrm{ER}] \tag{13.6-41b}$$

The steady-state approximation is invoked by setting the right-hand side of Eq. (13.6-41a) equal to zero. This equation can be solved for [ER] and the expression for [ER] can be substituted into Eq. (13.6-41b). However, in a typical case [E], the concentration of uncombined enzyme, is not known. 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 enzyme, given by $[\mathrm{E}]_{\mathrm{total}} = [\mathrm{E}] + [\mathrm{ER}]$. However, since the concentration of reactant is much larger than the enzyme concentration and is thus much larger than [ER], [R] can be considered to be approximately equal to both the total concentration of reactant and to the concentration of uncombined reactant.

When we substitute $[\mathrm{E}]_{\mathrm{total}} - [\mathrm{ER}]$ into the right-hand side of Eq. (13.6-41a) in place of [E], set the result equal to zero, and solve for [ER], we obtain

$$[\mathrm{ER}] = \frac{k_1[\mathrm{E}]_{\mathrm{total}}[\mathrm{R}]}{k_1' + k_2 + k_1[\mathrm{R}]} \tag{13.6-42}$$

The rate law is obtained by substituting Eq. (13.6-42) into Eq. (13.6-41b). Since we have not included a reverse reaction for the second step, we obtain the rate law for the forward reaction. This rate law is called the **Michaelis–Menten equation**:

$$\mathrm{Rate} = \frac{d[\mathrm{P}]}{dt} = \frac{k_2[\mathrm{E}]_{\mathrm{total}}[\mathrm{R}]}{K_{\mathrm{m}} + [\mathrm{R}]} \tag{13.6-43}$$

where

$$K_{\mathrm{m}} = \frac{k_1' + k_2}{k_1} \tag{13.6-44}$$

The parameter K_{m} is called the **Michaelis–Menten constant** or the **Michaelis constant**. Since it is a combination of rate constants it is a constant only at constant temperature. An extended version can be derived with a reverse reaction for step 2, which applies near equilibrium and can be related to the equilibrium constant for the reaction. (See Problem 13.57.) The Michaelis–Menten mechanism has also been studied without use of the steady-state approximation.[31]

Since Eq. (13.6-43) is not easily integrated, the method of initial rates is commonly used to apply it. A number of experiments with the same concentration of enzyme, but with different concentrations of reactant, are carried out and the initial rate in each case is determined. Figure 13.9 shows the initial rate given by Eq. (13.6-43) as a function of

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[30] G. E. Briggs and J. B. S. Haldane, *Biochem. J.*, **19**, 338 (1925).

[31] N. Sundaram and P. Wankat, *J. Phys. Chem.*, **102**, 717 (1988).

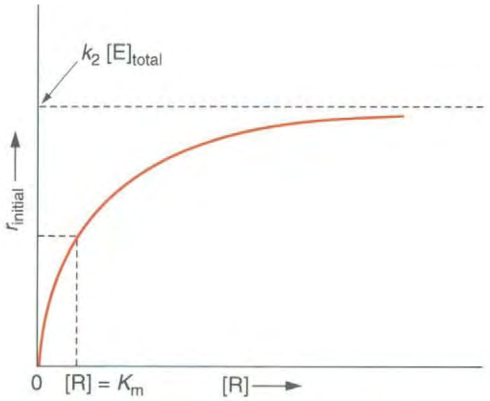

Figure 13.9. The Initial Rate as a Function of Reactant Concentration for the Michaelis–Menten Mechanism. Compare this graph with the graph of the Langmuir isotherm in Figure 13.4.

reactant concentration. Note the resemblance of Eq. (13.6-43) to Eq. (13.6-17), and the resemblance of Figure 13.9 to Figure 13.4. The initial rate increases monotonically as the reactant concentration is increased, approaching the value $k_2[\mathrm{E}]_{\mathrm{total}}$ 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 $10^6\,\mathrm{s}^{-1}$.

Exercise 13.27

a. Show that the initial rate approaches the value $k_2[\mathrm{E}]_{\mathrm{total}}$ 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.

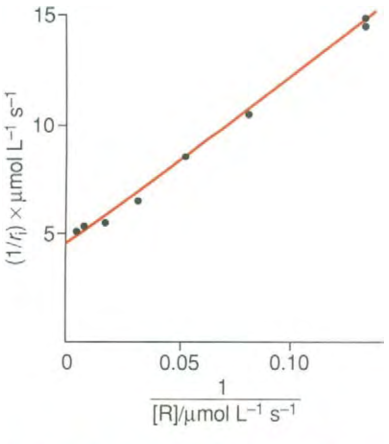

Figure 13.10. The Lineweaver–Burk Plot. Compare this plot with the linear plot in Figure 13.5.

Just as with Eq. (13.6-8), the accurate location of the asymptote in Figure 13.9 from experimental data on initial rates is difficult if there is considerable experimental error. To avoid this problem, plots of initial rate data analogous to that of Figure 13.5 can be made. If (13.6-44) is solved for the reciprocal of the initial rate the result is the **Lineweaver-Burk equation**.[32]

$$\frac{1}{r_{\mathrm{i}}} = \frac{K_{\mathrm{m}}}{k_2[\mathrm{E}]_{\mathrm{total}}[\mathrm{R}]} + \frac{1}{k_2[\mathrm{E}]_{\mathrm{total}}} \tag{13.6-45}$$

where $r_{\mathrm{i}} = (d[\mathrm{P}]/dt)_{\mathrm{initial}}$ is the initial rate. Data on initial rates should give a straight line when $1/r_{\mathrm{i}}$ is plotted as a function of $1/[\mathrm{R}]$, as in Figure 13.10. The slope of the line is equal to $K_{\mathrm{m}}/k_2[\mathrm{E}]_{\mathrm{total}}$, 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 $-1/K_{\mathrm{m}}$.

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[32] H. Lineweaver and D. Burk, *J. Am. Chem. Soc.*, **56**, 658 (1934).

EXAMPLE 13.15

The following data were gathered for the myosin-catalyzed hydrolysis of ATP at 25°C and pH 7.0:

[ATP]/μmol L^{-1}	Initial rate/μmol 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–Burke plot of the data is shown in Figure 13.10. The line drawn in the figure is the line determined by an unweighted linear least-squares procedure. The slope of this line is equal to 76.58 s, and the intercept on the vertical axis is equal to 4.547 L μmol^{-1} s. The correlation coefficient for the least-squares fit is equal to 0.9975. The intercept on the horizontal axis is equal to 0.0595 L μmol^{-1}, so that the Michaelis–Menten constant is equal to 16.8 μmol L^{-1}. In this solution an unweighted least-squares fit was used. If the experimental errors in the initial rates are all nearly equal, the experimental errors in the reciprocals will not be equal, and a weighted least-squares procedure would be preferable.

*Exercise 13.28

An alternative linear plot is the **Eadie plot**,[33] for which Eq. (13.6-43) is put into the form

$$\frac{r_i}{[R]} = \frac{r_i}{K_m} + \frac{k_2[E]_{\text{total}}}{K_m} \tag{13.6-46}$$

Use the data of Example 13.15 to make a plot or a linear least-squares fit of $r_i/[R]$ as a function of r_i. Find the value of the Michaelis–Menten constant for the reaction of Example 13.15 and compare it with the value from the Lineweaver–Burk equation of Example 13.15.

Many enzyme-catalyzed reactions are subject to **inhibition**. That is, the rate of the process is decreased by the presence of some substance. The **degree of inhibition** is defined as

$$i = 1 - \frac{r}{r_0} \tag{13.6-47}$$

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**

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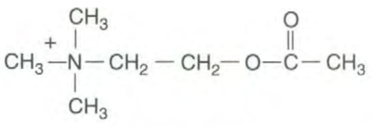
[33] G. S. Eadie, *J. Biol. Chem.*, **146**, 85 (1942).

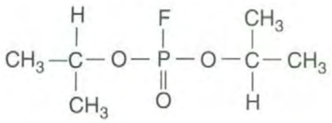
inhibitor is one for which the degree of inhibition increases if the concentration of the reactant is increased.

The accepted mechanism for competitive inhibition is that the inhibitor can occupy the same active site as the reactant. Acetylcholine is a neurotransmitter, or 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 interrupted by lowering the concentration of acetylcholine. Diisopropyl fluorophosphate is a competitive inhibitor for this hydrolysis. Figure 13.11 shows the structural formulas of acetylcholine and of diisopropyl fluorophosphate. 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. 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 it can still bind to the reactant.



$$\mathrm{CH_3-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{\overset{+}{N}}}-CH_2-CH_2-O-\overset{\overset{\textstyle O}{\|}}{C}-CH_3}$$

Acetylcholine



$$\mathrm{CH_3-\overset{\overset{\textstyle H}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-O-\overset{\overset{\textstyle F}{|}}{\underset{\underset{\textstyle O}{\|}}{P}}-O-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle H}{|}}{C}}-CH_3}$$

Diisopropyl fluorophosphate

Figure 13.11. The Structural Formulas of Acetylcholine and Diisopropyl Fluorophosphate. Diisopropyl fluorophosphate is a competitive inhibitor for cholinesterase, the enzyme that catalyzes the reaction of acetylcholine. It is apparent that both molecules might fit into the same enzyme active site.

13.7 Experimental Molecular Study of Chemical Reactions

The "classical" study of chemical reaction rates involves determination of concentrations of reactants or products, and delivers only macroscopic information. Such information cannot lead directly to knowledge of a reaction mechanism. However, there exist techniques that deliver molecular information about a reaction mechanism.

Observation of Reaction 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. An early example of spectroscopic detection of a reactive intermediate was a study of the decomposition of N_2O_5.[34] According to the mechanism of Example 13.11, 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 tube 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. Schott and Davidson were able to determine the concentration of NO_3 as a function of time and to calculate values for the

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[34] 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).

elementary rate constants in the mechanism of Example 13.11. They found that the preexponential factor in k_2 is equal to 1.66×10^8 L mol^{-1} s^{-1} and that the activation energy is approximately equal to 16 kJ mol^{-1} over the temperature range from 300 K to 820 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 electric field, attaining a speed depending on their charge/mass ratio. They are then passed through electric 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 of the original substance can often be deduced, not only from its molecular mass but also from its fragmentation pattern. To employ mass spectrometric detection of reactive intermediates, one carries out a gas-phase reaction in a vessel that adjoins the ionization chamber of a mass spectrometer. The total pressure in the ionization chamber is around 10^{-4} torr. A small aperture allows the reacting gases to pass into the ionization chamber of the mass spectrometer. The mass spectrum of a reactive intermediate can sometimes be found in the mass spectrum of the reacting mixture of reactants, intermediates, and products. An advantage of the mass spectrometric method of detecting reactive intermediates comes fom the fact that the pressure in the mass spectrometer is very small, both in the analyzing chamber and in the ionizing chamber. The low pressure in both chambers lowers the collision rate of reactive intermediates, prolonging their lifetimes and making it easier to detect short-lived species.

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 trap.[35] 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. At room temperature equilibrium H_2 consists of 75% ortho-H_2 and 25% para-H_2, while at low temperatures the equilibrium mixture is nearly 100% para-H_2. (Ortho-H_2 has its two nuclear spins parallel, and para-H_2 has its two nuclear spins antiparallel. See Section 19.2 for more information.) If para-H_2 prepared at low temperature is brought into 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.

A final technique is the use of isotopic substitution. For example, the decomposition of acetaldehyde

$$CH_3CHO \rightarrow CH_4 + CO \tag{13.7-1}$$

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[35] S. W. Benson, *op. cit.*, p. 101, gives a table of free radicals and metals that had been studied as of the 1950s (Note 21).

was thought to proceed by the mechanism

$$\begin{aligned} &(1) \quad CH_3CHO \rightarrow CH_3 + CHO && (13.7\text{-}2a) \\ &(2) \quad CH_3 + CH_3CHO \rightarrow CH_4 + CH_3CO && (13.7\text{-}2b) \\ &(3) \quad CH_3CO \rightarrow CH_3 + CO && (13.7\text{-}2c) \end{aligned}$$

A mixture of CH_3CHO and CD_3CDO was reacted, where D stands for deuterium (^2H).[36] The product mixture contained 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.

Molecular Beam Reactions

In this technique the reaction is carried out by forming beams of reactants in an otherwise evacuated chamber ("beams instead of bulbs"). Figure 13.12 shows schematically an apparatus for generating a molecular beam from a solid or liquid material. 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 chamber that is evacuated to even lower pressure. The molecules then pass into a third chamber in which the beam can be observed or reacted with a second beam. Only those molecules moving in nearly the same direction can pass through both barriers, producing a nearly unidirectional (collimated) beam. It is also possible to collimate the beam further by a third barrier with a small hole.

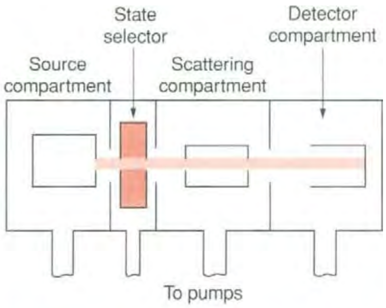

Figure 13.12. An Apparatus for Generating a Molecular Beam (Schematic). The molecule beam is generated thermally in one compartment, and passed through a velocity selector in the second compartment before impinging on another substance in a third compartment.

If it is desirable to select only those molecules in a narrow range of speeds, a velocity selector can be used. Figure 13.13 shows schematically one type of velocity selector. The rotating disks have slots through which molecules can pass. When the set of disks is rotating, it allows molecules to pass only if their speed is such that they reach the second disk when one of its slots is in the beam position and reach the third disk when one of its slots is in the beam position, etc. Varying the speed of rotation of the disks allows different speeds to be selected.

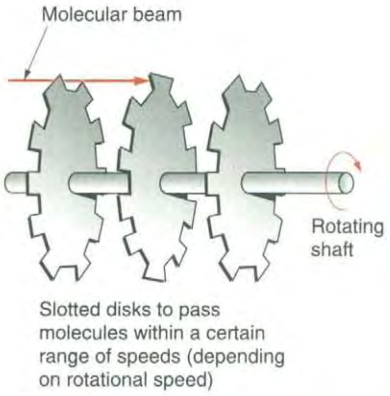

Figure 13.13. A Velocity-selecting Apparatus (Schematic). Such a rotating apparatus will allow molecules to pass only if they have a speed in a fairly narrow range. The speed of the molecules selected depends on the rate of rotation.

Chemical reactions can be carried out with two crossed molecular beams, as schematically depicted in Figure 13.14. The beams are generally brought together at right angles and the product molecules that are scattered away from the collision region are detected by a movable detector, allowing the angular distribution of products to be determined. Since the product molecules are scattered away from the reaction region into a region where further collisions are unlikely, reactive intermediates can be detected and identified. The detector is usually a mass spectrometer, but molecules containing alkali metal atoms can be detected by a surface ionization detector.[37]

It is also possible to carry out a reaction by bringing a beam of molecules into a stationary gaseous sample. The **reaction cross section** is equal to the collision cross section times the reaction probability, and 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

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[36] S. W. Benson, *op. cit.*, p. 108 (Note 21).

[37] G. G. Hammes, *Principles of Chemical Kinetics*, Academic Press, New York, 1978, pp. 113ff.

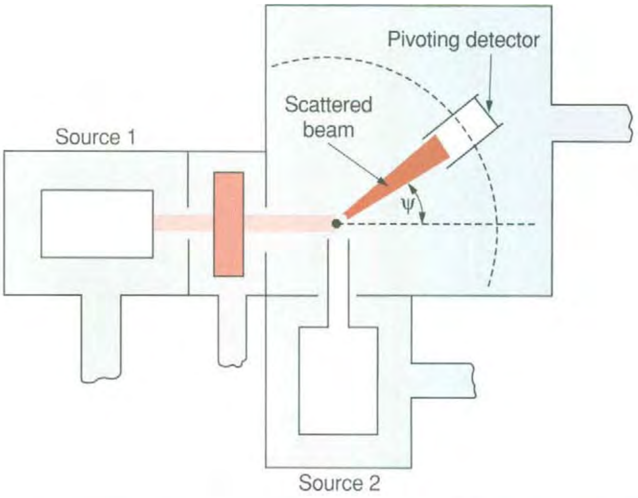

Figure 13.14. An Apparatus for Carrying Out a Chemical Reaction in Crossed Molecular Beams. In this type of apparatus, two molecular beams impinge on each other in the reaction chamber. A movable detector allows the products to be determined as a function of scattering angle.

different states of the reactants, the angular distribution of products (the angle relative to the original molecular beam at which the product molecules leave the collision region), 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 types of molecular beam experiments that are used to obtain molecular kinetic information are:[38]

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 radiation of the same wavelength is emitted (see Chapter 20). 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:

$$(1)\qquad CF_3I \xrightarrow{\text{UV flash}} F + CF_2I \qquad (13.7\text{-}3a)$$

$$(2)\qquad F + H_2 \rightarrow H + HF^* \qquad (13.7\text{-}3b)$$

$$(3)\qquad HF^* \xrightarrow{\text{stimulated emission}} HF + h\nu \qquad (13.7\text{-}3c)$$

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[38] G. G. Hammes, *op. cit.*, pp. 210ff (Note 37).

Incident radiation of the proper frequency can cause emission of radiation from the excited HF molecules. Figure 13.15 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.
4. Crossed molecular beams. This method is illustrated in Figure 13.16, which shows an apparatus for the reaction of chlorine atoms with molecules of the other halogens. The detector is a mass spectrometer that can be moved to different angles so that the angular distribution of the products can be studied. The TOF (time-of-flight) chopper allows for determination of the velocity distribution of the products, giving information on the distribution of energy between translational and internal degrees of freedom. By the use of chemiluminescence or laser

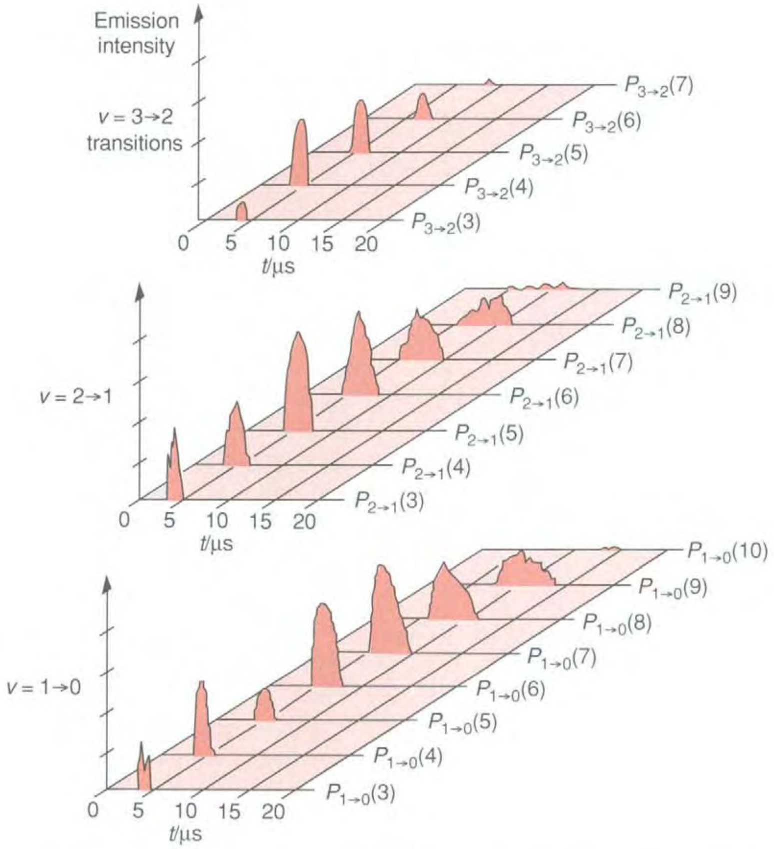

Figure 13.15. Intensity of Laser Pulses as a Function of Time for Excited HF Molecules. In each plot, the vertical axis represents the intensity of a laser pulse corresponding to emission from HF formed in a flash-initiated reaction. The horizontal axis represents time measured in microseconds. Each 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, 1989, p. 213.

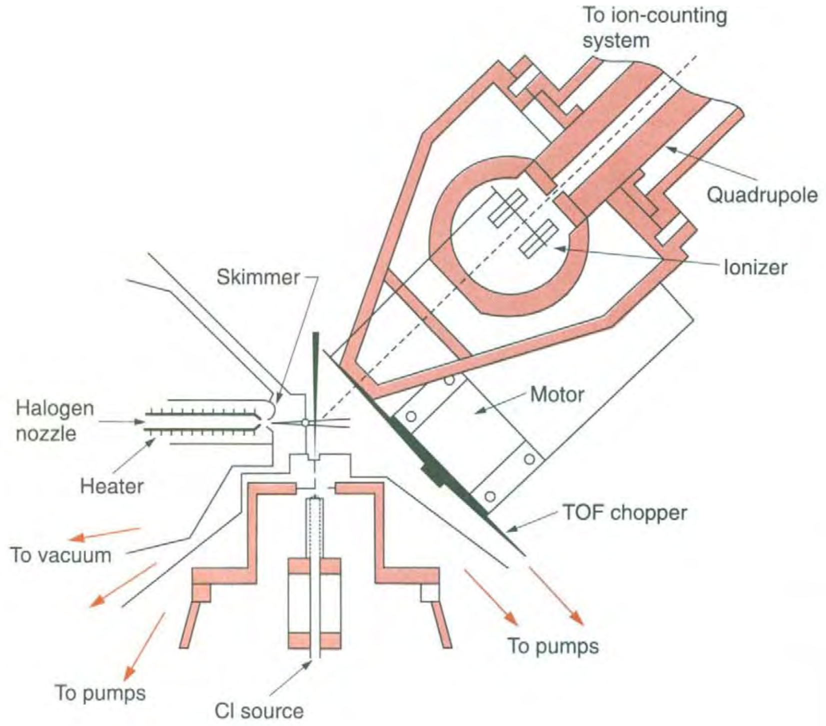

Figure 13.16. A Crossed Molecular Beam Apparatus (Schematic). From R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity*, Oxford University Press, New York, 1987, p. 234.

excitation fluorescence, the vibrational and rotational state distribution can be determined, giving the distribution of energy among the translational, rotational, and vibrational degrees of freedom.

Summary of the Chapter

This chapter has focused on chemical reaction mechanisms, which are the sequences of elementary steps that make up chemical reactions. An elementary step is one that cannot be divided into simpler steps. A gas-phase elementary process involves a single molecular collision. A liquid-phase "elementary" process is actually preceded and followed by diffusion 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. 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 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 approximation schemes are used to deduce a rate law corresponding to a given mechanism. Example mechanisms were studied, including chain reactions, in which propagation steps are included in the mechanism.

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 various techniques for direct detection of reaction intermediates. These techniques included direct observation of the reaction intermediates and study of their effects.

PROBLEMS

Problems for Section 13.2

***13.29.** The reaction

$$2\mathrm{I} \rightarrow \mathrm{I}_2$$

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 Exercise 13.9 and from viscosities in Table A.18 of Appendix A.

13.30. **a.** The reaction

$$2\mathrm{CH}_3 \rightarrow \mathrm{C}_2\mathrm{H}_6$$

in toluene is diffusion-controlled. The viscosity of toluene at 30°C is equal to 5.236×10^{-4} 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 5.9×10^{-4} 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.

***13.31.** Compute the reaction diameter d_{12} for the reaction

$$\mathrm{CH}_3\mathrm{CO}_2^- + \mathrm{H}^+ \rightarrow \mathrm{CH}_3\mathrm{CO}_2\mathrm{H}$$

for which $k = 4.5 \times 10^{10}$ L mol^{-1} s^{-1}. Use the values of the ion mobilities from Table A.20 of Appendix A.

13.32. For the reaction at 25.00°C in methanol,

$$\mathrm{CH}_3\mathrm{Br} + \mathrm{I}^- \rightarrow \mathrm{CH}_3\mathrm{I} + \mathrm{Br}^-$$

the rate constant is equal to 9.48×10^{-4} L mol^{-1} s^{-1}. The viscosity of methanol at this temperature is 5.47×10^{-4} 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 lead to reaction?

***13.33.** For the reaction of $\mathrm{C}_2\mathrm{H}_5\mathrm{Br}$ and $(\mathrm{C}_2\mathrm{H}_5)_2\mathrm{S}$ at 20.00°C in benzyl alcohol, the rate constant is equal to 1.44×10^{-8} L mol^{-1} s^{-1}. The viscosity of benzyl alcohol at this temperature is 5.8×10^{-3} 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 lead to reaction?

Problems for Section 13.3

13.34. The first-order rate constant for the thermal decomposition of 3-methylcyclobutanone has the values:[39]

T/K	552.24	561.81	570.41	579.35	589.05	596.96	606.14
$k/10^{-4}\ \mathrm{s}^{-1}$	0.4259	0.8936	1.707	3.207	6.459	11.201	20.83

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.

***13.35.** The gas-phase decomposition of acetaldehyde, CH_3CHO, obeys second-order kinetics. Some values of the rate constant are:

T/K	k/L mol^{-1} s^{-1}	T/K	k/L mol^{-1} 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.

13.36. For the reaction of I_2 and $N_2CHCO_2C_2H_5$ in CCl_4 at 298.15 K, $k = 3.28 \times 10^{-4}$ L mol^{-1} s^{-1}, and at 323.15 K, $k = 4.60 \times 10^{-3}$ L mol^{-1} 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.

***13.37. a.** The rate constant for the bimolecular elementary gaseous reaction

$$CO + O_2 \rightarrow CO_2 + O$$

is equal to 1.22×10^5 L mol^{-1} s^{-1} at 2500 K, and is equal to 3.66×10^5 L mol^{-1} 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.

Problems for Section 13.4

13.38. The formation of phosgene

$$CO + Cl_2 \rightleftharpoons COCl_2$$

is thought to proceed by the mechanism:[40]

$$\begin{aligned} &(1) \quad Cl_2 \rightleftharpoons 2Cl \\ &(2) \quad Cl + CO \rightleftharpoons COCl \\ &(3) \quad COCl + Cl_2 \rightleftharpoons COCl_2 + Cl \end{aligned}$$

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.

13.39. An alternative mechanism for the reaction of the previous problem is

$$\begin{aligned} &(1) \quad Cl_2 \rightleftharpoons 2Cl \\ &(2) \quad Cl + Cl_2 \rightleftharpoons Cl_3 \\ &(3) \quad Cl_3 + CO \rightleftharpoons COCl_2 + Cl \end{aligned}$$

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.

Compare your results with the results of the previous problem.

13.40. Another plausible mechanism for the reaction of H_2 and I_2, in addition to that of Eq. (13.5-16) is[41]

$$\begin{aligned} &(1) \quad I_2 \rightleftharpoons 2I \\ &(2) \quad H_2 + I \rightleftharpoons H_2I \\ &(3) \quad H_2I + I \rightleftharpoons 2HI \end{aligned}$$

a. Obtain the rate law for the forward reaction for this mechanism using the steady-state approximation (omit the

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[39] H. M. Frey, H. P. Watts, and I. D. R. Stevens, *J. Chem. Soc., Faraday Trans. 2*, **83**, 601 (1987).

[40] K. J. Laidler, *op. cit.*, p. 301ff (Note 3).

[41] Sullivan, *J. Chem. Phys.*, **46**, 73 (1967).

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.

13.41. Obtain the rate law for the forward reaction for the mechanism of the previous problem assuming that step 3 is rate-limiting.

13.42. The reaction equation for the nitration of an aromatic compound in a strong acid (usually sulfuric acid) can be written

$$\mathrm{ArH} + \mathrm{HNO_3} \rightarrow \mathrm{ArNO_2} + \mathrm{H_2O}$$

where Ar stands for an aromatic group such as the phenyl group, C_6H_5. A proposed mechanism is[42]

$$\begin{array}{ll} (1) & \mathrm{HNO_3} + \mathrm{HA} \rightleftharpoons \mathrm{H_2NO_3^+} + \mathrm{A^-} \\ (2) & \mathrm{H_2NO_3^+} \rightleftharpoons \mathrm{H_2O} + \mathrm{NO_2^+} \\ (3) & \mathrm{NO_2^+} + \mathrm{ArH} \rightarrow \mathrm{ArNO_2H^+} \\ (4) & \mathrm{ArNO_2H^+} + \mathrm{A^-} \rightarrow \mathrm{ArNO_2} + \mathrm{HA} \end{array}$$

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.

13.43. For the reaction

$$2\mathrm{ICl} + \mathrm{H_2} \rightarrow \mathrm{I_2} + 2\mathrm{HCl}$$

the forward rate law is found to be

$$\text{Rate} = \frac{d[\mathrm{I_2}]}{dt} = k[\mathrm{ICl}][\mathrm{H_2}]$$

Propose a mechanism that predicts this rate law.

13.44. The reaction

$$\mathrm{H_2O_2} + 3\mathrm{I^-} + 2\mathrm{H^+} \rightarrow 2\mathrm{H_2O} + \mathrm{I_3^-}$$

obeys the rate law[43]

$$-\frac{d[\mathrm{H_2O_2}]}{dt} = k_1[\mathrm{H_2O_2}][\mathrm{I^-}] + k_2[\mathrm{H_2O_2}][\mathrm{I^-}][\mathrm{H^+}]$$

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.

13.45. The hypothetical reaction

$$2\mathrm{A} \rightarrow 2\mathrm{B} + \mathrm{C}$$

obeys the rate law

$$\text{Rate} = \frac{d[\mathrm{C}]}{dt} = k\frac{[\mathrm{A}]^2}{[\mathrm{B}]}$$

Propose a mechanism consistent with this rate law.

Problems for Section 13.5

13.46. The chain mechanism for the $H_2 + I_2$ reaction is

$$\begin{array}{ll} (1) & \mathrm{I_2} \rightleftharpoons 2\mathrm{I} \\ (2) & \mathrm{I} + \mathrm{H_2} \rightleftharpoons \mathrm{HI} + \mathrm{H} \\ (3) & \mathrm{H} + \mathrm{I_2} \rightarrow \mathrm{HI} + \mathrm{I} \end{array}$$

Note that no reverse reaction is included in step 3.

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?

13.47. Insert a reverse reaction as step 3′ in the previous problem. 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 in Section 13.5, using the principle of detailed balance.

13.48. The thermal decomposition of acetaldehyde follows the reaction equation

$$\mathrm{CH_3CHO} \rightarrow \mathrm{CH_4} + \mathrm{CO}$$

The following mechanism is proposed:[44]

$$\begin{array}{ll} (1) & \mathrm{CH_3CHO} \rightarrow \mathrm{CH_3} + \mathrm{CHO} \\ (2) & \mathrm{CH_3CHO} + \mathrm{CH_3} \rightarrow \mathrm{CH_4} + \mathrm{CO} + \mathrm{CH_3} \end{array}$$

with the following termination steps, which make only traces of C_2H_6 and H_2, and are not included in the stoichiometric

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[42] R. J. Gillespie, E. D. Hughes, C. K. Ingold, and R. I. Reed, *Nature*, **163**, 599 (1949).

[43] D. Benson, *Mechanisms of Inorganic Reactions in Solution*, McGraw-Hill, New York, 1968, pp. 6ff.

[44] J. L. Latham, *Elementary Reaction Kinetics*, 2d ed., Butterworths, London, 1969, p. 128.

equation:

$$\begin{array}{ll} (3) & 2CH_3 \rightarrow C_2H_6 \\ (4) & 2CHO \rightarrow 2CO + H_2 \end{array}$$

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 approxiamation.

c. Johnston[45] gives a mechanism in which step 2 is replaced by the steps

$$\begin{array}{ll} (2a) & CH_3 + CH_3CHO \rightarrow CH_3CO + CH_4 \\ (2b) & CH_3CO \rightarrow CH_3 + CO \end{array}$$

Repeat the steady-state solution using this mechanism, again ignoring the termination steps. What must be assumed to bring the two results into agreement?

Problems for Section 13.6

13.49. **a.** The hydrogenation of ethylene on copper appears to follow the Langmuir–Hinshelwood mechanism, with the rate law

$$\text{Rate} = \frac{k_a[H_2][C_2H_4]}{(1 + k_b[C_2H_4])^2}$$

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.

13.50. Apply the steady-state approximation to obtain a rate law for the reaction of Exercise 13.24:

$$A_2 \rightarrow \text{products}$$

with the assumed mechanism

$$\begin{array}{ll} (1) & A_2 + 2 \text{ surface sites} \rightleftharpoons 2\,A(\text{adsorbed}) \\ (2) & A(\text{adsorbed}) \rightarrow \text{further intermediates or products} \end{array}$$

What condition would make this rate law coincide with that of Exercise 13.24?

***13.51.** **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.

13.52. 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

$$\text{Rate} = \frac{aP(N_2O)}{1 + b(P_0(N_2O) - P(N_2O))} = \frac{aP(N_2O)}{1 + bP(O_2)}$$

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 $P_0 = P_0(NO_2)/2$ and where $x = P(O_2)$.

c. Following are data of Hinshelwood and Pritchard for this reaction at 741°C and for an initial pressure of N_2O equal to 95 torr.

x/torr	315	750	1400	2250	3450	5150
t/s	10	20	30	40	50	60

Using a graphical or a least-squares method, fit these data to the integrated rate law and determine the values of a and b. How well does the formula fit the data points?

13.53. The platinum-catalyzed oxidation of methanol apparently proceeds through formation of formaldehyde and then carbon monoxide.[46] The following mechanism is proposed for the oxidation of the carbon monoxide:

$$\begin{array}{ll} (1) & CO(g) + \text{surface site} \rightleftharpoons CO(\text{adsorbed}) \\ (2) & O_2 + \text{surface site} \rightleftharpoons O_2(\text{adsorbed}) \\ (3) & O_2(\text{adsorbed}) + \text{surface site} \rightarrow 2O(\text{adsorbed}) \\ (4) & CO(\text{adsorbed}) + O(\text{adsorbed}) \rightarrow CO_2(g) \end{array}$$

Use the steady-state approximation, assuming that the rates of change of θ_{CO}, θ_{CO_2}, and θ_O are negligible. Find the rate law

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[45] H. S. Johnston, *op. cit.*, p. 36 (Note 27).

[46] R. W. McCabe and D. F. McCready, *J. Phys. Chem.*, **90**, 1428 (1986).

for the oxidation of CO. Assume that

$$1 - \theta_{CO} - \theta_{O_2} - \theta_O \approx 1 - \theta_{CO}$$

and neglect k_2' compared with $k_3(1 - \theta_{CO})\theta_{O_2}$.

13.54. The gas-phase thermal decomposition of acetaldehyde is catalyzed by iodine. The proposed mechanism is[47]

$$\begin{aligned} &(1) \qquad CH_3CHO + I_2 \rightleftharpoons CH_3I + HI + CO \\ &(2) \qquad CH_3I + HI \rightarrow CH_4 + I_2 \end{aligned}$$

a. Find the rate law, assuming 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. Tell how you would decide which assumption is preferable.

13.55. An **autocatalytic reaction** is one in which a product acts as a catalyst. Assume that the reaction

$$A \rightarrow B$$

has the rate law

$$-\frac{d[A]}{dt} = k[A][B]$$

***a.** Let $[A]_0$ be the initial concentration of A and $[B]_0$ be the initial concentration of B (not equal to 0). Derive the integrated rate law.

***b.** If $[A]_0 = 0.500$ mol L^{-1}, $[B]_0 = 0.010$ mol L^{-1}, and $k = 0.100$ L mol^{-1} min^{-1}, find [A] at $t = 10.00$ min.

c. Construct a graph of [A] as a function of time for the values of part (b).

13.56. Obtain the rate law for the simple Michaelis–Menten mechanism of Eq. (13.6-40), assuming the second step to be rate-limiting instead of assuming the steady-state approximation.

13.57. a. Add the reverse reaction to the second step of the Michaelis–Menten mechanism of Eq. (13.6-40) 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.

13.58. Derive the rate law for the forward rate of the enzyme-catalyzed reaction with the mechanism

$$\begin{aligned} &(1) \qquad E + R \rightleftharpoons ER \\ &(2) \qquad ER \rightarrow ER' + P_1 \\ &(3) \qquad ER' \rightarrow E + P_2 \end{aligned}$$

where P_1 and P_2 are two different products. Comment on the relationship of your answer to the ordinary Michaelis–Menten formula.

General Problems

***13.59.** For the reaction

$$H_2 + I_2 \rightarrow 2HI$$

the value of ΔU is -8.2 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.

13.60. The decomposition of ethyl bromide, C_2H_5Br, in the gas phase is observed to be a first-order reaction.

a. Write the steps of the mechanism, assuming the Lindemann 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 equal to 0.0361 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 s. Neglect any reverse reaction.

d. The rate constant is equal to 1.410 s^{-1} at 627°C. Find the value of the Arrhenius activation energy and of the preexponential factor for the reaction.

13.61. The gas-phase recombination of iodine atoms proceeds in the presence of a second substance, M:

$$I + I + M \rightarrow I_2 + M$$

Two mechanisms are proposed.[48] The first is

$$\begin{aligned} &(1) \qquad I + I \rightleftharpoons I_2^* \\ &(2) \qquad I_2^* + M \rightarrow I_2 + M \end{aligned}$$

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[47] J. L. Latham, *op. cit.*, p. 108 (Note 44).

[48] H. S. Johnston, *op. cit.*, pp. 253ff (Note 27).

where I_2^* represents a high-energy molecule. The second mechanism is

$$(1) \qquad I + M + M \rightleftharpoons IM + M$$

$$(2) \qquad IM + I \rightarrow I_2 + M$$

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 is argon, $k = 8.3 \times 10^{-33}\ \mathrm{cm^6\ s^{-1}}$ 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 $\mathrm{cm^{-3}}$ 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.

13.62. 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.

***13.63.** 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 follow each other sequentially.

d. In a typical gas-phase chemical reaction, only a small fraction of molecular collisions lead to reaction.

e. Termolecular steps are relatively rare in chemical reaction mechanisms.

f. One way to verify a reaction mechanism is to observe the presence of reactive intermediates.

g. Diffusion-limited reactions are rapid because diffusion is an inherently rapid process.

h. Only mechanisms with branching chains can lead to explosions.

i. An inhibitor for an enzyme-catalyzed reaction must compete with a reactant for an active site.

j. A reaction can be catalyzed heterogeneously if only one of the reactants is adsorbed.

14

The Principles of Quantum Mechanics. I. Classical Waves and the Schrödinger Equation

OBJECTIVES

After studying this chapter, a student should:

1. understand the solution of classical equations of motion;
2. understand the classical wave equation and its solutions and be able to solve problems involving classical wave phenomena;
3. understand the way in which quantization is introduced in the old quantum theory, and be able to solve problems related to that theory;
4. understand the relation of the Schrödinger equation to the classical wave equation and understand the boundary conditions imposed on its solutions;
5. understand and be able to use the method of separation of variables to solve a class of differential equations;
6. be able to solve problems related to the Schrödinger equation.

PRINCIPAL FACTS AND IDEAS

1. Classical mechanics ascribes exact trajectories to particles.
2. The old quantum theory contained quantization as hypotheses but was based on classical mechanics.
3. The "matter waves" of de Broglie led to quantum mechanics.
4. The Schrödinger equation describes the waves that correspond to states of systems.
5. Quantum mechanics contains the concept of wave–particle duality: objects can exhibit wavelike properties as well as particlelike properties.
6. The time-independent Schrödinger equation can be solved for some example systems, and produces quantization as a natural part of the solution.

14.1

Classical Mechanics

Classical mechanics is based on the laws of motion discovered by Sir Isaac Newton, and is also called Newtonian mechanics. Appendix D presents a brief survey of classical mechanics, which is now known to be accurate only for objects of relatively large mass and for relatively high energies.

The Classical Mechanical Analysis of the Harmonic Oscillator

The harmonic oscillator is a model system that represents a mass suspended from a stationary object by a spring as shown in Figure 14.1. Let the vertical coordinate z of the mass equal zero at its equilibrium position and be positive if the mass is above this position and negative below it. The force on a mass suspended by a spring is described for fairly small values of z by **Hooke's law**:

Hooke's law is named for Robert Hooke, 1635–1703, one of Newton's contemporaries and rivals.

$$F_z = -kz \tag{14.1-1}$$

where k is called the **force constant**. The larger the force constant, the stiffer the spring.

The harmonic oscillator obeys Hooke's law exactly for all values of the z coordinate. The mass of the spring suspending the oscillator is assumed to be negligible. From Newton's second law, Eq. (D-1) of Appendix D, the force on an object equals its mass times its acceleration. This gives the **equation of motion** of the harmonic oscillator:

$$-kz = m\frac{d^2z}{dt^2} \tag{14.1-2}$$

This differential equation is called **linear** because the variable z enters only to the first power and is called **second order** because its highest-order derivative is the second derivative.

The **general solution** of a differential equation is a family of functions that includes nearly every solution of the equation. The general solution for Eq. (14.1-2) must contain two arbitrary constants, since this is a property of linear differential equations of second order. A general solution can be written as

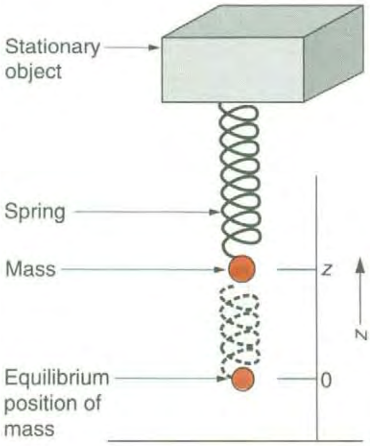


Figure 14.1. A System Represented by a Harmonic Oscillator. This system is a mass on a spring.

$$z(t) = A\sin\left(\sqrt{\frac{k}{m}}t\right) + B\cos\left(\sqrt{\frac{k}{m}}t\right) \tag{14.1-3}$$

where A and B are arbitrary constants. The velocity can also be found from Eq. (14.1-3):

$$v_z(t) = \frac{dz}{dt} = \sqrt{\frac{k}{m}}\left[A\cos\left(\sqrt{\frac{k}{m}}t\right) - B\sin\left(\sqrt{\frac{k}{m}}t\right)\right] \tag{14.1-4}$$

To make the general solution apply to a specific case, we apply **initial conditions**. Since there are two arbitrary constants, we require two initial conditions. These conditions can be that at time $t = 0$

$$z(0) = z_0, \qquad v_z(0) = 0 \tag{14.1-5}$$

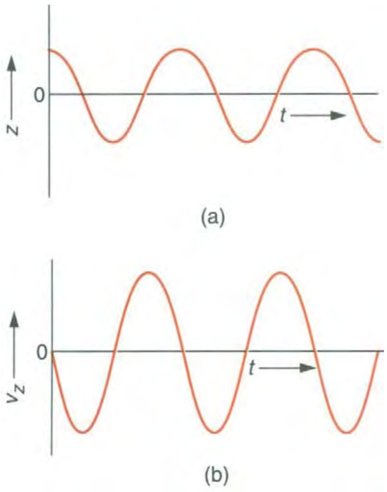


Figure 14.2. The Behavior of a Harmonic Oscillator. (a) **The position as a function of time according to classical mechanics.** (b) **The velocity as a function of time according to classical mechanics.** This motion is called uniform harmonic motion. The position and velocity both vary sinusoidally.

where z_0 is a constant initial displacement. Since $\sin(0) = 0$ and $\cos(0) = 1$, then $v_z(0) = 0$ only if $A = 0$ and $z(0) = z_0$ only if $B = z_0$. The solution that applies to the initial conditions shown in Eq. (14.1-5) is

$$z(t) = z_0 \cos\left(\sqrt{\frac{k}{m}}\,t\right) \tag{14.1-6}$$

$$v_z(t) = -\sqrt{\frac{k}{m}}\,z_0 \sin\left(\sqrt{\frac{k}{m}}\,t\right) \tag{14.1-7}$$

Figure 14.2a shows the position 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. The constant z_0 is the largest magnitude that z attains and is called the maximum **amplitude** of the oscillation.

The length of time required for the oscillator to go from a certain position and velocity to the next repetition of that position and velocity is called the **period** of the oscillation and is denoted by τ. It is the length of time required for the argument of the sine function in Eq. (14.1-6) or the cosine function in Eq. (14.1-7) to change by 2π:

$$\sqrt{\frac{k}{m}}\,\tau = 2\pi \tag{14.1-8}$$

or

$$\tau = 2\pi\sqrt{\frac{m}{k}} \tag{14.1-9}$$

The **frequency** ν of the oscillation is the reciprocal of the period, or the number of oscillations per second:

$$\nu = \frac{1}{\tau} = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \tag{14.1-10}$$

The frequency is larger if the force constant is larger and smaller if the mass is larger.

EXAMPLE 14.1

An object of mass 0.250 kg is suspended from a spring with $k = 5.55\,\mathrm{N\,m^{-1}}$. Find the period and the frequency.

Solution

$$\tau = (2\pi)\sqrt{\frac{0.250\,\mathrm{kg}}{5.55\,\mathrm{N\,m^{-1}}}} = 1.33\,\mathrm{s}$$

$$\nu = \frac{1}{1.33\,\mathrm{s}} = 0.750\,\mathrm{s^{-1}} = 0.750\,\mathrm{Hz}$$

The unit of frequency is the reciprocal second, properly called the hertz (Hz).

EXAMPLE 14.2

A typical chemical bond is similar to a spring with a force constant near $500\,\mathrm{N\,m^{-1}}$. 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 typical of vibrational frequencies of molecules.

The kinetic energy of a harmonic oscillator is a state function of the velocity. For our initial conditions,

$$\mathcal{K} = \frac{1}{2}mv^2 = \frac{1}{2}m\frac{k}{m}z_0^2\left[\sin\left(\sqrt{\frac{k}{m}}t\right)\right]^2 = \frac{k}{2}z_0^2\sin^2\left(\sqrt{\frac{k}{m}}t\right) \qquad (14.1\text{-}11)$$

Equation (D-5) of Appendix D relates the potential energy $\mathcal{V}$ and the corresponding force:

$$F_z = -\frac{d\mathcal{V}}{dz} \qquad (14.1\text{-}12)$$

The potential energy of the harmonic oscillator is

$$\mathcal{V}(z) = \frac{1}{2}kz^2 + \text{constant} \qquad (14.1\text{-}13)$$

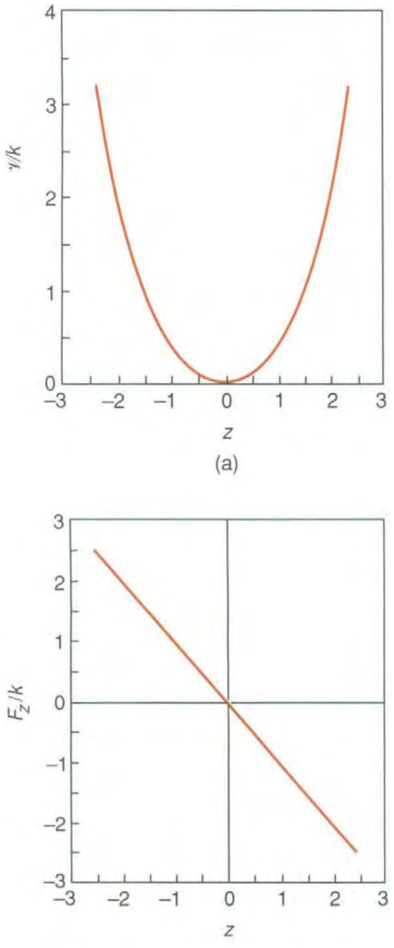


Figure 14.3. Mechanical Variables of a Harmonic Oscillator. (a) **The potential energy.** (b) **The force on the oscillator.** The force is given as the negative derivative of the potential energy.

An arbitrary constant can be added to a potential energy without any physical effect, since it does not change the forces. We set the constant in Eq. (14.1-13) equal to zero so that $\mathcal{V}0) = 0$. Figure 14.3a shows the potential energy for the harmonic oscillator as a function of z, 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

$$\mathcal{V} = \frac{k}{2}z_0^2\cos^2\left(\sqrt{\frac{k}{m}}t\right) \qquad (14.1\text{-}14)$$

The total energy, E, is given by

$$E = \mathcal{K} + \mathcal{V} = \frac{1}{2}kz_0^2\left[\sin^2\left(\sqrt{\frac{k}{m}}t\right) + \cos^2\left(\sqrt{\frac{k}{m}}t\right)\right] = \frac{1}{2}kz_0^2 \qquad (14.1\text{-}15)$$

since $\sin^2(x) + \cos^2(x) = 1$ for all values of x. The total energy does not change during the oscillation, corresponding to **conservation of energy**.

The kinetic energy becomes equal to zero at the extreme of an oscillation (the **turning point**) as the object changes direction, so the total energy equals the potential energy:

$$E = \mathcal{V}(z_t) = \frac{1}{2}kz_t^2 \qquad (14.1\text{-}16)$$

The displacement at the turning point is denoted by z_t,

$$z_t = \sqrt{\frac{2E}{k}} \qquad (14.1\text{-}17)$$

For our initial conditions, $z_t = z_0$.

The harmonic oscillator is used as a model for a vibrating diatomic molecule. Since both nuclei move, the model oscillator consists of two movable masses connected by a spring, as depicted in Figure 14.4. As shown in Appendix D, it is necessary to replace the mass in the harmonic oscillator formulas by the **reduced mass** μ:

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \tag{14.1-18}$$

where m_1 and m_2 are the masses of the two nuclei. The frequency of oscillation of a diatomic molecule is given by

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{14.1-19}$$

14.2 Classical Waves

There are various wave phenomena that are adequately described by classical mechanics. These include sound waves, light waves, waves on the surface of bodies of water, and vibrations of the strings in musical instruments. A wave consists of an oscillating displacement. In a water wave the displacement is the distance to a point on the surface from the equilibrium position of this part of the surface. 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**. Most waves are periodic waves, with a number of crests and troughs having the same shape. The distance from one crest to the next is called the **wavelength** λ. The **period** of a wave is the time for the first return of the oscillating object to an initial state. The **frequency** is the reciprocal of the period, or the number of oscillations per unit time, and it is denoted by ν. A wave is inherently delocalized (cannot exist at a single point in space).

There are two principal types of waves. A **traveling wave** propagates (moves along) like the 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. It shows how the traveling wave in Figure 14.5a moves to the right without changing shape, while the standing wave in Figure 14.5b oscillates between stationary nodes.

One important property of waves is **interference**. When two waves 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**. Constructive and destructive interference are qualitatively depicted in Figure 14.6a, which shows the sum of two waves of different wavelengths.

A property that arises from interference is **diffraction**. If a water wave encounters a post, there will be a reflected wave that moves out in all directions with crests that are circles or arcs of circles. The reflected waves from a row of equally spaced posts can interfere to produce a diffracted wave with straight crests, which travels in a direction different from that of the incident wave. Figure 14.6b illustrates diffraction by a set of equally spaced scattering centers. The broken straight lines 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 distance from the scattering centers that is large compared to a wavelength, these crests combine to produce a diffracted

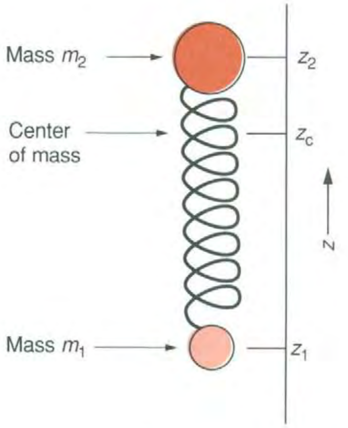


Figure 14.4. A Second System Represented by a Harmonic Oscillator. This system consists of two masses connected by a spring.

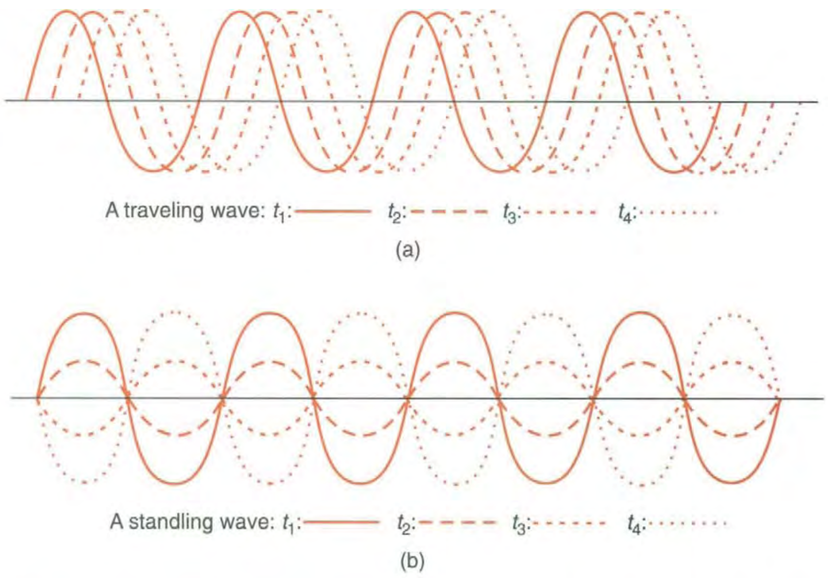


Figure 14.5. Traveling and Standing Waves. (a) **A traveling wave at times $t_1 < t_2 < t_3 < t_4$.** The nodes of the traveling wave move along (from left to right in this diagram). (b) **A standing wave at times $t_1 < t_2 < t_3 < t_4$.** The nodes of the standing wave remain at fixed positions.

plane wave. The wave nature of light was established experimentally when interference and diffraction of light were observed.

Waves in a Flexible String

The flexible string is a model system that represents a real vibrating string. It is defined to be uniform (all parts have the same mass per unit length, denoted by ρ); there is a tension force of magnitude T pulling at each end of the string; the string is perfectly

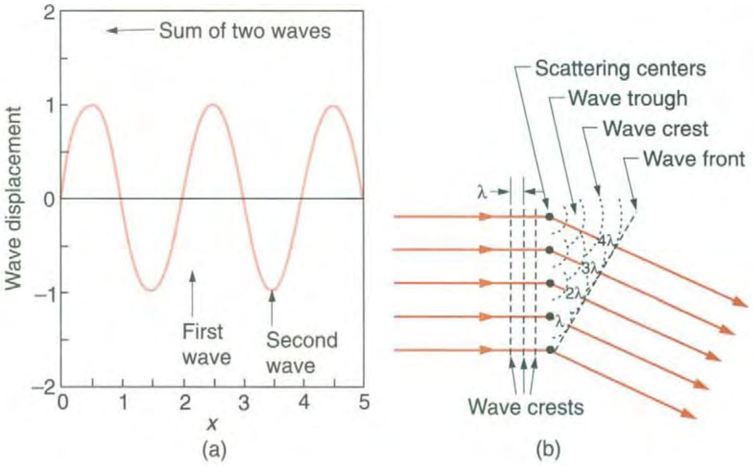


Figure 14.6. (a) **The superposition of two waves of different wavelengths.** This figure illustrates constructive and destructive interference at one time. (b) **The diffraction of a wave by a row of scattering centers.** The direction of the diffracted wave depends on the wavelength.

flexible; there is no friction; the string undergoes only small displacements, so that the total length of the string remains nearly constant and the magnitude of the tension force T is nearly constant; the equilibrium position of the string is a straight line segment on the x axis, with its ends fixed on the x axis at $x = 0$ and $x = L$.

At some initial time the string is displaced into some position in the x–z plane and released to vibrate freely in this plane. The state of the string is specified by giving the displacement and velocity at each point of the string as a function of t:

$$z = z(x, t) \tag{14.2-1}$$

$$v_z = v_z(x, t) = \frac{\partial z}{\partial t} \tag{14.2-2}$$

The classical wave equation of the string is derived from Newton's second law in Appendix D. Equation (D-9) of Appendix D is

$$\frac{\partial^2 z}{\partial x^2} = \frac{\rho}{T}\frac{\partial^2 z}{\partial t^2} = \frac{1}{c^2}\frac{\partial^2 z}{\partial t^2} \tag{14.2-3}$$

where $c^2 = T/\rho$. We will show later that c is equal to the speed of propagation of the wave in the string.

Standing Waves in a Flexible String

Equation (14.2-3) is a partial differential equation whose solution is a function of x and t. We begin by seeking a solution that represents a standing wave by separating the variables.

1. The first step in the separation of variables is to assume a **trial solution** that is a product of functions of one independent variable:

$$z(x, t) = \psi(x)\zeta(t) \tag{14.2-4}$$

2. The second step of the method is to substitute the trial solution into the differential equation and to perform whatever algebraic operations that result in an equation with terms that are functions of only one independent variable. We substitute the trial function of Eq. (14.2-4) into Eq. (14.2-3):

$$\zeta\frac{d^2\psi}{dx^2} = \frac{1}{c^2}\psi\frac{d^2\zeta}{dt^2} \tag{14.2-5}$$

The derivatives are ordinary derivatives since ζ and ψ each depends on a single variable. We divide Eq. (14.2-5) by $\psi\zeta$:

$$\frac{1}{\psi(x)}\frac{d^2\psi}{dx^2} = \frac{1}{c^2\zeta(t)}\frac{d^2\zeta}{dt^2} \tag{14.2-6}$$

Each term depends on only one independent variable, so the variables are separated.

3. The third step in the method is to set each side of the equation equal to a constant since each side is a function of a different independent variable. This gives the two equations:

$$\frac{1}{\psi(x)}\frac{d^2\psi}{dx^2} = \text{constant} = -\kappa^2 \tag{14.2-7}$$

$$\frac{1}{c^2\zeta(t)}\frac{d^2\zeta}{dt^2} = -\kappa^2 \tag{14.2-8}$$

The constant must be negative to give an oscillatory solution. We denote it by $-\kappa^2$ so that κ will be a real quantity.

Multiplying Eq. (14.2-7) by ψ and Eq. (14.2-8) by $c^2\zeta$ gives

$$\frac{d^2\psi}{dx^2} + \kappa^2\psi(x) = 0 \tag{14.2-9}$$

$$\frac{d^2\zeta}{dt^2} + \kappa^2c^2\zeta(t) = 0 \tag{14.2-10}$$

These equations have the same form as Eq. (14.1-2). The general solutions are obtained by transcribing the solution to that equation with appropriate changes in symbols:

$$\psi(x) = B\cos(\kappa x) + D\sin(\kappa x) \tag{14.2-11}$$

$$\zeta(t) = F\cos(\kappa ct) + G\sin(\kappa ct) \tag{14.2-12}$$

where B, D, F, and G are arbitrary constants. The product of these two functions is a wave function that satisfies the wave equation, Eq. (14.2-3).

However, the solution does not yet apply to a string with fixed ends. It must obey the **boundary conditions** that z vanishes at $x = 0$ and at $x = L$. The function ψ must vanish at these points, since it contains all of the x dependence of z. The condition that $\psi(0) = 0$ requires that $B = 0$, since $\sin(0) = 0$ and $\cos(0) = 1$. The sine function vanishes if its argument is an integral multiple of π, so that

$$\kappa L = n\pi \tag{14.2-13}$$

where n is an integer. We have the values of B and κ, and can write

$$\psi(x) = D\sin\left(\frac{n\pi x}{L}\right) \tag{14.2-14}$$

Now that we have satisfied the boundary conditions, the constants D, F, and G are chosen to match **initial conditions**. A classical equation of motion generally requires two initial conditions, one related to the initial position and one related to the initial velocity. We specify the first initial condition that the string is passing through its equilibrium position ($z = 0$ for all x) at the time $t = 0$. This requires that $F = 0$, since $\sin(0) = 0$ and $\cos(0) = 1$. The solution can now be written as

$$\begin{aligned} z(x, t) = \psi(x)\zeta(t) &= DG\sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi ct}{L}\right) \\ &= A\sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi ct}{L}\right) \end{aligned} \tag{14.2-15}$$

We have replaced the product DG by a constant A.

We now choose as the second initial condition that the maximum value that z achieves is equal to z_0. We call z_0 the maximum displacement or **amplitude** of the wave. This condition determines the initial velocity of the string. The solution now contains no unknown constants:

$$z(x, t) = z_0\sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi ct}{L}\right) \tag{14.2-16}$$

The velocity of any point of the string is

$$v_z = \frac{\partial z}{\partial t} = z_0\left(\frac{n\pi c}{L}\right)\sin\left(\frac{n\pi x}{L}\right)\cos\left(\frac{n\pi ct}{L}\right) \tag{14.2-17}$$

The velocity at $t = 0$ is

$$v_z(0) = z_0\left(\frac{n\pi c}{L}\right)\sin\left(\frac{n\pi x}{L}\right) \tag{14.2-18}$$

The function $z(x, t)$ is a **wave function** that represents the motion of the flexible string for all values of x and t.

Exercise 14.1

a. Show by substitution that Eq. (14.2-15) satisfies Eq. (14.2-3).
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 relationship between L and the wavelength λ for a standing wave is

$$n\lambda = 2L \qquad \text{or} \qquad \lambda = \frac{2L}{n} = \frac{2\pi}{\kappa} \tag{14.2-19}$$

The **period** τ of the motion is the time for the string to return to an initial state. It is the time necessary for the argument of $\sin(n\pi ct/L)$ to change by 2π, so that

$$2\pi = \frac{n\pi c\tau}{L} \qquad \text{or} \qquad \tau = \frac{2L}{nc} \tag{14.2-20}$$

The **frequency** ν is the number of oscillations per unit time or the reciprocal of the period:

$$\nu = \frac{nc}{2L} = \frac{n}{2L}\sqrt{\frac{T}{\rho}} \tag{14.2-21}$$

A different frequency results for each value of n. For a fixed value of n, the frequency can be increased by increasing the tension force, by decreasing the length of the string, or decreasing the mass per unit length of the string.

The wave function shown in Eq. (14.2-15) represents a different standing wave for each value of n, so there is a set of wave functions. Figure 14.7 represents the wave functions for several values of n. Each wave function corresponds to a different frequency and wavelength. The frequencies and wavelengths are **quantized** (take on values from a discrete set). 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** to the **second harmonic** and so on. A string does not usually move as described by a single harmonic. A **linear combination** (sum with coefficients) of harmonics can satisfy the wave equation, and such a linear combination represents a typical motion of a flexible string:

$$z(x, t) = \sum_{n=1}^{\infty} a_n(t)\sin\left(\frac{n\pi x}{L}\right) \tag{14.2-22}$$

The Fourier series is named for Jean Baptiste Joseph Fourier, 1768–1830, famous French mathematician and physicist.

The fact that a linear combination of solutions can be a solution to the wave equation is called the **principle of superposition**. The sum shown in Eq. (14.2-22) is called a **Fourier sine series**. Fourier cosine series also exist, which are linear combinations of cosine functions, and a more general Fourier series contains both sine and cosine terms.

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 $t = 0$, the following sum is a solution:

$$z(x, t) = \sum_{n=1}^{\infty} A_n \sin\left(\frac{n\pi x}{L}\right)\sin\left(\frac{n\pi ct}{L}\right) \tag{14.2-23}$$

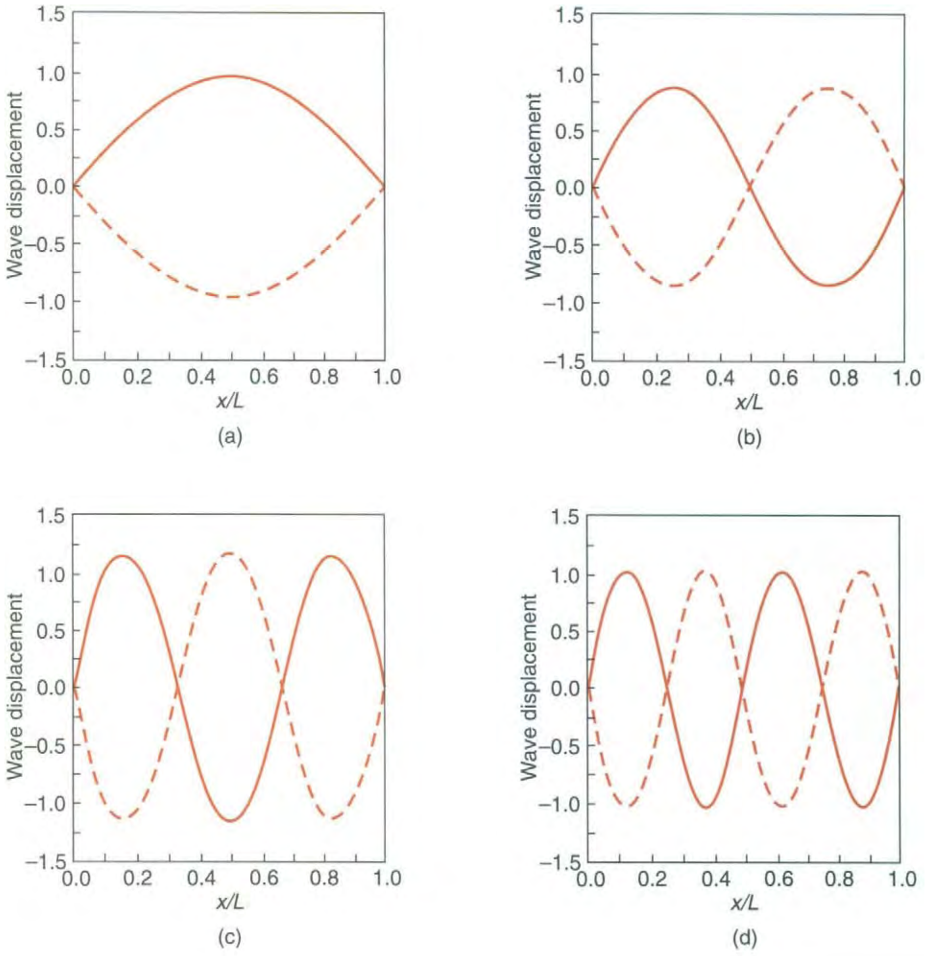


Figure 14.7. Standing Waves in a Flexible String. (a) **The wave function for $n = 1$.** (b) **The wave function for $n = 2$.** (c) **The wave function for $n = 3$.** (d) **The wave function for $n = 4$.** These are the first few standing waves which satisfy the condition that the ends of the string are fixed. The nodes are fixed. Between the nodes the string oscillates.

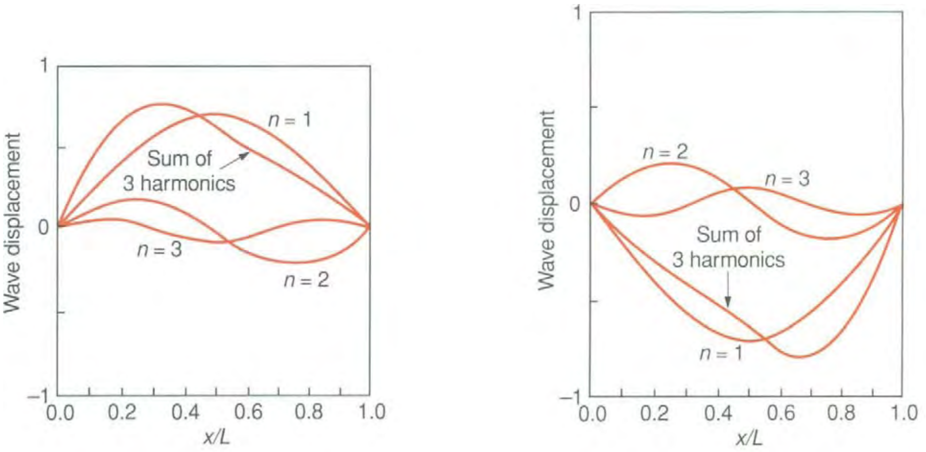
Exercise 14.2

Show by substitution that the series in Eq. (14.2-23) satisfies Eq. (14.2-3).

The constants $A_1, A_2, \ldots,$ can have any values. Any harmonic whose coefficient does not vanish makes a contribution to the motion of the string, with constructive and destructive interference that continually changes 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, stationary nodes are required at the ends of the string, which prevents the occurrence of traveling waves. Traveling waves can occur in an infinitely



(a)

(b)

Figure 14.8. The Superposition of Three Harmonics of a Flexible String. (a) **At time $t = L/(4c)$.** (b) **At time $t = 3L/(4c)$.** By the principle of superposition, a sum of the three harmonics satisfies the wave equation. Constructive and destructive interference produces waves that are not sinusoidal and do not maintain a fixed shape.

long string. A wave function that satisfies Eq. (14.2-3) and corresponds to a traveling wave is

$$z(x, t) = a\sin(\kappa x - \kappa ct) \tag{14.2-24}$$

Exercise 14.3

Show by substitution that the function in Eq. (14.2-24) satisfies Eq. (14.2-3).

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 at $x = 0$. As time passes this node will be located at the point where $x - ct = 0$. Thus

$$x(\text{node}) = ct \tag{14.2-25}$$

The node is moving toward the positive end of the x axis with a speed equal to c, as stated earlier. Since $c = \sqrt{T/\rho}$, increasing the mass per unit length decreases the speed and increasing the tension force increases the speed.

*Exercise 14.4

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. (14.2-24) is replaced by

$$z(x, t) = A\sin(\kappa x + \kappa ct) \tag{14.2-26}$$

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. (14.3-24).

Exercise 14.5

a. Show that the function of Eq. (14.2-26) satisfies Eq. (14.2-3).
b. Show that the speed of the wave is equal to c.

In one wavelength, the argument of the sine function changes by 2π for fixed t, so that the same relationship occurs as in Eq. (14.2-19) for a standing wave:

$$\kappa = \frac{2\pi}{\lambda} \tag{14.2-27}$$

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

$$\text{Length} = ct$$

where c is the speed. The number of wavelengths in this wave train is equal to

$$\text{Number} = \frac{ct}{\lambda}$$

In time t, the number of oscillations is equal to

$$\text{Number} = \nu t$$

so that $\nu t = ct/\lambda$, or

$$\nu = \frac{c}{\lambda} \tag{14.2-28}$$

Equation (14.2-28) is the general relation between wavelength and frequency. This important equation holds for all kinds of waves, including sound waves and electromagnetic waves.

*Exercise 14.6

The speed of sound in air at sea level and room temperature is approximately equal to $338\ \mathrm{m\,s^{-1}}$. 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 a musical scale.)

Two traveling waves moving in opposite directions can interfere to produce a standing wave. The two waves

$$z_R(x, t) = A\sin(\kappa x - \kappa ct) \tag{14.2-29a}$$

and

$$z_L(x, t) = A\sin(\kappa x + \kappa ct) \tag{14.2-29b}$$

interfere to give

$$z(x, t) = A[\sin(\kappa x + \kappa ct) + \sin(\kappa x - \kappa ct) \tag{14.2-30}$$

which is the same as

$$z(x, t) = 2A\sin(\kappa x)\cos(\kappa ct) \tag{14.2-31}$$

Exercise 14.7

Use trigonometric identities to obtain Eq. (14.2-31) from Eq. (14.2-30).

The Classical Wave Theory of Light

James Clerk Maxwell, 1831–1879, made fundamental contributions to electrodynamics, gas kinetic theory and thermodynamics.

In 1865, Maxwell developed a mathematical theory of electromagnetism. In this theory, there are four important vector quantities, the electric field $\mathscr{E}$, the electric displacement **D**, the magnetic field strength $\mathscr{H}$, and the magnetic induction **B**. 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. Example of such radiation are visible light, infrared radiation, ultraviolet radiation, X-rays, radio waves, microwaves, etc., which differ from each other only in having different wavelengths and frequencies. At first 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 light and other electromagnetic waves as oscillations that do not require any supporting medium.

Albert A. Michelson, 1852–1931, was an American physicist who was the first American to win a Nobel Prize in science (in 1907) and Edward W. Morley, 1838–1923, was an American chemist.

A **plane polarized** wave traveling in the y direction can have an electric field that oscillates in the y–z plane and a magnetic field that oscillates in the x–y 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.[1]

$$\frac{\partial^2 \mathscr{E}_z}{\partial y^2} - \frac{1}{c^2}\frac{\partial^2 \mathscr{E}_z}{\partial t^2} = 0 \qquad (14.2\text{-}32)$$

$$\frac{\partial^2 \mathscr{H}_x}{\partial y^2} - \frac{1}{c^2}\frac{\partial^2 \mathscr{H}_x}{\partial t^2} = 0 \qquad (14.2\text{-}33)$$

where

$$c = \frac{1}{\sqrt{\varepsilon\mu}} \qquad (14.2\text{-}34)$$

and where ε is called the **permittivity** of the medium and μ is called the **permeability** of the medium. The values of these quantities for a vacuum are denoted by ε_0 and μ_0. In SI units, the permeability of a vacuum has the value

$$\begin{aligned} \mu_0 &= 4\pi \times 10^{-7}\,\mathrm{N\,A^{-2}} \quad \text{(exact value by definition)} \\ &= 12.566370614\ldots \times 10^{-7}\,\mathrm{N\,A^{-2}} \end{aligned} \qquad (14.2\text{-}35a)$$

and the permittivity of a vacuum is

$$\varepsilon_0 = 8.8542 \times 10^{-12}\,\mathrm{C^2\,N^{-1}\,m^{-2}} \qquad (14.2\text{-}35b)$$

There is an additional condition from Maxwell's equations that makes Eqs. (14.2-32) and (14.2-33) interdependent:

$$\frac{\mathscr{E}_z}{\mathscr{H}_x = \pm\sqrt{\frac{\mu}{\varepsilon}}} \qquad (14.2\text{-}36)$$

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[1] See J. C. Slater and N. H. Frank, *Electromagnetism*, McGraw-Hill, New York, 1947, pp 90ff, or any other textbook on electricity and magnetism.

The electric field cannot oscillate without oscillation of the magnetic field, and vice versa. Equations (14.2-32) and (14.2-33) have the same form as Eq. (14.2-3), in which c is the speed of propagation of the wave. The theory of Maxwell correctly predicts the value of the speed of light.

EXAMPLE 14.3

Use the value of the permittivity of the vacuum and the permeability of the vacuum to show that Eq. (14.2-34) gives a value for the speed of light in a vacuum that agrees with experiment.

Solution

$$c_{\text{vacuum}} = \frac{1}{\sqrt{(8.8542\times 10^{-12}\,\mathrm{C^2\,N^{-1}\,m^{-2}})(4\pi\times 10^{-7}\,\mathrm{N\,A^{-2}})}}$$

$$= 2.9979\times 10^{8}\,\mathrm{m\,s^{-1}}$$

Exercise 14.8

Show that the units in Eq. (14.2-34) are correct, using the fact that an ampere (A) is the same as a coulomb per second.

A traveling-wave solution to Eqs. (14.2-32) and (14.2-33) is

$$\mathscr{E}_z(y,t) = \mathscr{E}_0 \sin[2\pi(y-ct)/\lambda] \tag{14.2-37}$$

$$\mathscr{H}_x(y,t) = \mathscr{H}_0 \sin[2\pi(y-ct)/\lambda] \tag{14.2-38}$$

where $\mathscr{E}_0$ and $\mathscr{H}_0$ are constants that obey Eq. (14.2-36). The wavelength λ can take on any real value.

Figure 14.9 shows $\mathscr{E}$ and $\mathscr{H}$ as functions of y at time $t = 0$ with $\mathscr{E}$ and $\mathscr{H}$ plotted in the directions in which they point. As time passes, the traveling wave moves to the right without changing its shape or wavelength. Since oscillating electric and magnetic fields put oscillating forces on charged particles such as the electrons and nuclei in molecules,

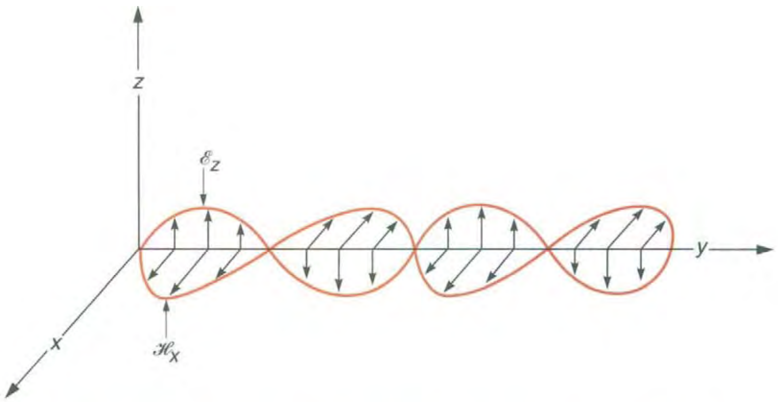

Figure 14.9. The Electric and Magnetic Fields in an Electromagnetic Wave. The wave is propagating to the right in the y direction. The electric field is oscillating in the z direction, and the magnetic field is oscillating in the x direction. The nodes of the electric field and those of the magnetic field coincide.

molecules can absorb electromagnetic radiation. The converse is also true. According to Maxwell's equations, oscillating electric charges emit electromagnetic radiation.

An electromagnetic wave cannot penetrate a perfect conductor. Therefore, 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.

14.3

The Old Quantum Theory

Near the end of the nineteenth century, several important phenomena were discovered that classical physics was unable to explain. Three of these were explained early in the twentieth century by new theories: Planck's theory of blackbody radiation, Einstein's theory of the photoelectric effect, and Bohr's theory of the hydrogen atom. These theories are the major parts of what is called the "old quantum theory." They were based on assumptions of **quantization**, which is the idea that the value of a physical quantity can equal one of a discrete set of values, but not any of the values between those in the discrete set. We will discuss these theories for historical perspective, and this section can be skipped without loss of continuity.

Planck's Theory of Blackbody Radiation

If an object has a temperature of 1000°C, it glows with a red color, 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. At any temperature an object with a lower reflectivity glows more intensely at every wavelength, so that 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 a hollow box. If the inside of the box (the "cavity") is made fairly nonreflective, 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 such a 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 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 750 nm, is labeled in the figure.

At 2000 K, only the red part of the visible spectrum (around 650 to 750 nm) is represented, but at higher temperature the other visible wavelengths are also represented. At around 6000 K the maximum in the curve is in the middle (green) portion of the visible region, and black-body radiation of this temperature is similar to sunlight. Near room temperature, almost all of the radiation is in the infrared region. It is this radiation from the surface of the earth that is involved in the greenhouse effect in the earth's atmosphere, which is the absorption in the upper atmosphere of infrared radiation emitted by the earth. It is principally due to CO_2, H_2O, CH_4, and various chlorofluorocarbons.

The total radiant emittance (emission per unit area per unit time, summed over all wavelengths) is equal to the area under the curve. The **Stefan–Boltzmann law** is an

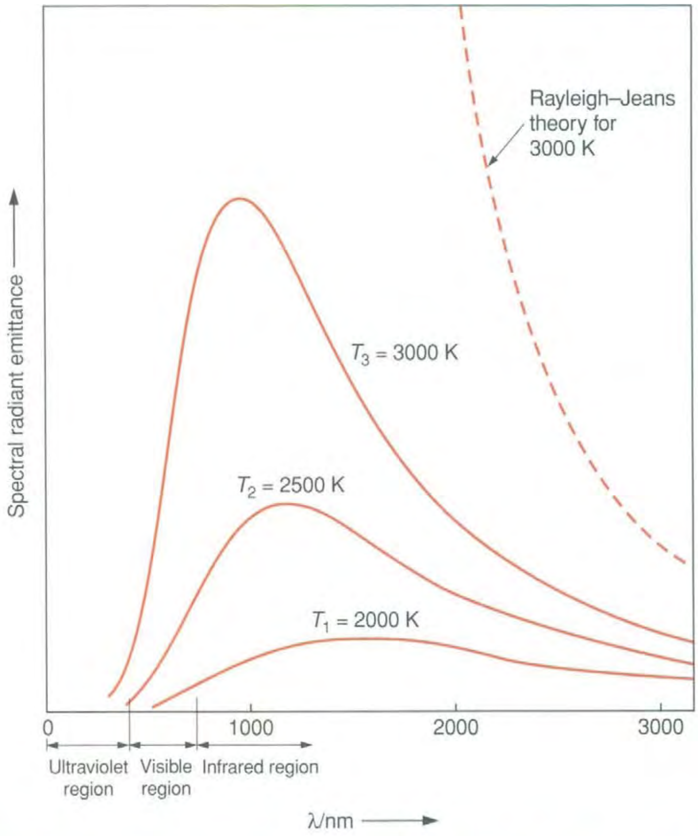

Figure 14.10. The Spectral Radiant Emittance of a Black Body for $T_1 = 2000$ K, $T_2 = 2500$ K, and $T_3 = 3000$ K. The maximum in the curve shifts to shorter wavelengths as the temperature is raised. The Rayleigh–Jeans curve and the experimental curve coincide for sufficiently long wavelengths.

empirical law that relates the total radiant emittance to the absolute temperature of the black body:

$$(\text{Total radiant emittance}) = \sigma T^4 \tag{14.3-1}$$

The **Stefan–Boltzmann constant** σ has the value

$$\sigma = 5.67051 \times 10^{-8}\,\mathrm{J\,m^{-2}\,s^{-1}\,K^{-4}} = 5.67051 \times 10^{-8}\,\mathrm{W\,m^{-2}\,K^{-4}} \tag{14.3-2}$$

John William Strutt, third Baron Rayleigh, 1842–1919, was the 1904 Nobel Prize winner in physics, and Sir James Jeans, 1877–1946, was a British astronomer and physicist.

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 cavity. For a rectangular cavity, they counted the possible standing waves of various wavelengths that could exist in the cavity with nodes at the walls and computed the average energy of each standing wave as a function of temperature using statistical mechanics (see Chapters 21 and 22). Their result was

$$\eta(\lambda)\,d\lambda = \frac{2\pi c k_\mathrm{B} T}{\lambda^4}\,d\lambda \tag{14.3-3}$$

where c is the speed of light, k_B is Boltzmann's constant, and T is the absolute temperature.

Max Planck, 1858–1947, received the Nobel Prize in physics in 1918 for this theory, although at first most other physicists were reluctant to believe that it was correct.

Equation (14.3-3) agrees well with experiment for large values of the wavelength (much larger than visible wavelengths), but predicts that the spectral radiant emittance becomes large without bound in the limit of short wavelength. This failure of the Rayleigh–Jeans theory was called the "ultraviolet catastrophe." In 1900, Planck devised a new theory of black-body radiation that eliminated the ultraviolet catastrophe. Although he was working to obtain a result in agreement with experimental data, his theory is based on assumptions (hypotheses) that at the outset had no direct evidence to support them. The following statements are a simplified version of assumptions that lead to his result:[2]

1. In the walls of the cavity there exist oscillating electric charges. Each such oscillator has a characteristic fixed frequency of oscillation, but many oscillators are present and every frequency is represented.
2. The standing waves in the cavity are equilibrated with the oscillators in such a way that the average energy of standing waves of a given frequency equals the average energy of the oscillators of the same frequency.
3. The energy of a wall oscillator is **quantized**. That is, it is capable of assuming only one of the values

   $$E = 0, h\nu, 2h\nu, 3h\nu, 4h\nu, \ldots, nh\nu, \ldots \qquad (14.3\text{-}4)$$

   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 nonnegative integral value, is called a **quantum number**. A quantum number is an integer or some other value that can be used to specify which state occurs from a set of possible states. Figure 14.11 schematically shows this energy quantization. Quantization has been compared to 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. (14.3-4), but no value between these values.
4. The probability of any energy is given by the Boltzmann probability distribution, Eq. (1.8-25).

The result of Planck's derivation is that the spectral radiant emittance is given by

$$\eta(\lambda)\,d\lambda = \frac{2\pi hc^2}{\lambda^5\left(e^{hc/\lambda k_B T} - 1\right)}\,d\lambda \qquad (14.3\text{-}5)$$

This formula agrees accurately with experimental measurements of blackbody radiation at all temperatures and wavelengths if an optimum value of the constant h is taken. By fitting data available at the time, Planck was able to get a value of h approximately equal to the presently accepted value, 6.62608×10^{-34} J s. Planck's formula agrees with an empirical law known as Wien's law, with the result of Rayleigh and Jeans for large wavelengths and with the Stefan–Boltzmann law.

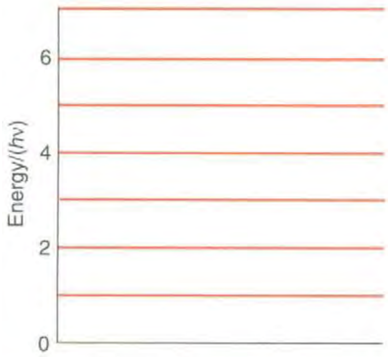

Figure 14.11. The Quantized Energies of an Oscillator as Postulated by Planck. The horizontal line segments are plotted at the heights of the assumed energy values, 0, $h\nu$, $3h\nu$, $4h\nu$, $5h\nu$, $6h\nu$, $7h\nu$, etc.

EXAMPLE 14.4

Find the relation of the wavelength of maximum spectral radiant emittance to the temperature.

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[2] M. Jammer, *The Conceptual Development of Quantum Mechanics*, McGraw-Hill, New York, 1966, pp. 10ff.

Solution

We set the derivative of the function of Eq. (14.3-5) equal to zero:

$$\frac{d\eta}{d\lambda} = 2\pi hc^2 \frac{(hc/\lambda k_B T)e^{hc/\lambda k_B T} - 5(e^{hc/\lambda k_B T} - 1)}{\lambda^6[e^{hc/\lambda k_B T} - 1]} = 0$$

This expression can vanish only if the numerator vanishes, which is equivalent to

$$\frac{hc}{\lambda_{\mathrm{max}} k_B T} = 5(1 - e^{-hc/\lambda_{\mathrm{max}} k_B T})$$

This equation must be solved by numerical approximation. The result is the Wien displacement law,

$$\lambda_{\mathrm{max}} = (0.2014)\frac{hc}{k_B T} = \frac{2.898 \times 10^{-3}\ \mathrm{m\,K}}{T} \tag{14.3-6}$$

***Exercise 14.9**

Find the temperature that corresponds to a wavelength of maximum spectral emittance in the red part of the visible spectrum at 650. nm.

Exercise 14.10

Show that in the limit as $\lambda \to \infty$, Eq. (14.3-5) agrees with Eq. (14.3-3).

***Exercise 14.11**

Use the definite integral

$$\int_0^\infty \frac{x^3}{e^x - 1}\, dx = \frac{\pi^4}{15} \tag{14.3-7}$$

to derive the Stefan–Boltzmann law, Eq. (14.3-1). Calculate the theoretical value of the Stefan–Boltzmann constant.

Einstein's Theory of the Photoelectric Effect

When a metal plate inside an evacuated glass tube is illuminated with light of sufficiently short wavelength, it emits electrons. Electrons are not ejected unless the wavelength of the incident light is at least as small as a threshold wavelength, and the maximum energy of the ejected electrons depends only on the wavelength. There was no explanation for this behavior until 1905, when Einstein published a theory for the photoelectric effect. 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 twentieth century and made fundamental contributions in almost every area of theoretical physics.

$$E = h\nu = \frac{hc}{\lambda} \tag{14.3-8}$$

where h is Planck's constant and c is the speed of light. Equation (14.3-8) is known as the **Planck–Einstein relation**. The quanta of light are called **photons**.

Einstein obtained the quantitative explanation for the photoelectric effect from Eq. (14.3-8). 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 energy is

$$E_{\max}(\text{electron}) = h\nu - W = \frac{hc}{\lambda} - W \tag{14.3-9}$$

Robert A. Millikan, 1868–1953, was an American physicist who received the Nobel Prize in physics in 1923 for his measurement of the charge on the electron.

In 1916 Millikan made accurate measurements of the photoelectric effect that agreed well with Eq. (14.3-9).

Since light exhibits a particlelike nature in some experiments and wavelike properties in other experiments, we say that it has a **wave–particle duality**. This terminology means that light appears in some circumstances to act like a wave and in other circumstances to act like a particle. We cannot adequately answer the question: "What is light *really* like?" We use the wave description when it explains the observations of a particular experiment, and use the particle description when it explains the observations of another experiment.

***Exercise 14.12**

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.

Bohr's Theory of the Hydrogen Atom

Excited hydrogen atoms emit light when electrons in higher energy states drop to lower energies. However, only certain wavelengths are emitted. Four wavelengths are present in the visible light 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 spectroscope, resembling a line segment. Such a set of separated lines is called a **line spectrum** and the slit images are called **spectral lines**.

Johannes Robert Rydberg, 1854–1919, was a Swedish physicist.

Rydberg was able to represent the wavelengths of all of the spectral lines of hydrogen atoms with a single empirical formula:

$$\frac{1}{\lambda} = \mathfrak{R}_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{14.3-10}$$

where n_1 and n_2 are two positive integers and $\mathfrak{R}_H$ is a constant known as **Rydberg's constant** for the hydrogen atom, equal to $1.09677581 \times 10^7\ \text{m}^{-1}$. Using classical physics, no explanation for this relationship could be found.

Ernest Rutherford, first Baron Rutherford of Nelson, 1871–1937, was a British physicist originally from New Zealand who won the 1908 Nobel Prize in chemistry, and who coined the terms α, β, and γ radiation.

In 1911, Rutherford scattered α-particles from a thin piece of gold foil. From the way in which the α-particles were scattered, he concluded that atoms contained a very small positive nucleus containing almost all of the mass of the atom, with the negative electrons orbiting around the nucleus. However, according to the electrodynamics of Maxwell, an orbiting electron would emit electromagnetic radiation, losing energy and falling onto the nucleus and collapsing the atom. Classical physics was unable to explain either the line spectrum of the hydrogen atom or its continuing existence.

Niels Henrik David Bohr, 1885–1962, was a Danish physicist who received the Nobel Prize in physics in 1922 for this work. He was 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.

In 1913, Bohr published a theory of the hydrogen atom, based on unproven assumptions. 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 D) of the electron is quantized: its magnitude can take on one of the values $h/2\pi$, $2h/2\pi$, $3h/2\pi$, $4h/2\pi$, etc., where h is Planck's constant. No other values are possible. 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 sudden 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. (14.3-8), 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.

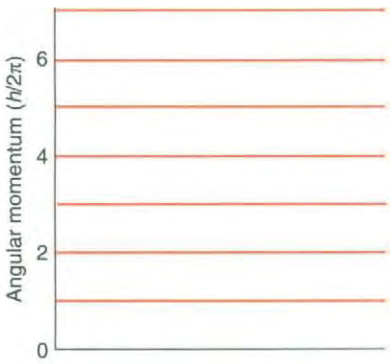

Figure 14.12. The Quantized Angular Momentum Values of Electronic Motion in a Hydrogen Atom as Postulated by Bohr. The horizontal line segments are plotted at the heights of the assumed angular momentum values, $h/2\pi$, $2h/2\pi$, $3h/2\pi$, $4h/2\pi$, $5h/2\pi$, $6h/2\pi$, $7h/2\pi$, etc.

We now derive the consequences of Bohr's assumptions. For simplicity, we assume that the electron orbits around a stationary nucleus. This is a good approximation, but it can be removed if desired by replacing the mass of the orbiting electron by the reduced mass of the electron and the nucleus (see Appendix D). To maintain a circular orbit, there must be a centripetal force on the electron:

$$F_r = -\frac{mv^2}{r} \tag{14.3-11}$$

where v is the speed of the electron, m is its mass, and r is its distance from the nucleus (see Eq. (D-13) of Appendix D).

*Exercise 14.13

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 2.50 m and the time required for one orbit is 1.00 s (a speed of 9.43 m s^{-1}).

The centripetal force is provided by the electrostatic attraction of the positive nucleus for the negative electron:

$$\frac{mv^2}{r} = \frac{e^2}{4\pi\varepsilon_0 r^2} \tag{14.3-12}$$

where ε_0 is the permittivity of the vacuum.

The angular momentum of the electron in a circular orbit is given by Eq. (D-15) of Appendix D. It is quantized, according to assumption 2:

$$L = rmv = \frac{nh}{2\pi} \tag{14.3-13}$$

where the **quantum number** n is a positive integer.

Equation (14.3-13) is solved for the speed v and the result is substituted into Eq. (14.3-12). The resulting equation is solved for r to give

$$r = \frac{h^2 4\pi\varepsilon_0}{4\pi^2 me^2} n^2 = a_0 n^2 \tag{14.3-14}$$

where a_0 is equal to 5.29×10^{-11} m 52.9 pm and is called the **Bohr radius**. Figure 14.13 depicts the first few Bohr orbits.

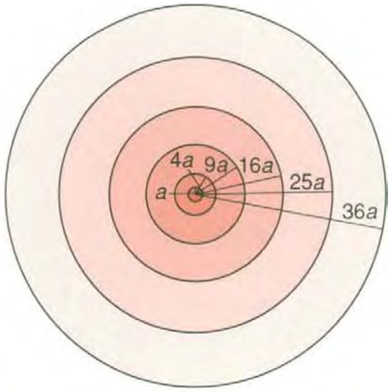

Figure 14.13. The Quantized Bohr Orbits. The radius of an electron orbit can take on only the values a, $4a, \ldots, n^2a, \ldots$ where n is a positive integer.

Exercise 14.14

a. Obtain Eq. (14.3-14) from Eqs. (14.3-12) and (14.3-13).

b. Using the accepted values of the physical constants, verify the value of the Bohr radius.

The energy of the electron is also quantized. The potential energy for an electron of charge $-e$ in an orbit of radius r around a nucleus of charge e is

$$\mathscr{V} = -\frac{e^2}{4\pi\varepsilon_0 r} \tag{14.3-15}$$

where we choose a value of zero for the potential energy at $r \to \infty$.

Exercise 14.15

Using Eq. (D-6) of Appendix D and Eq. (B-41) of Appendix B, show that the potential energy of Eq. (14.3-15) leads to the force expression of Eq. (14.3-12).

The kinetic energy is given by

$$\mathscr{K} = \frac{1}{2}mv^2 = \frac{1}{2}\frac{e^2}{4\pi\varepsilon_0 r} = \frac{1}{2}|\mathscr{V}| \tag{14.3-16}$$

where Eq. (14.3-12) 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 that holds for any system acted upon only by electrostatic forces.[3]

The total energy of the hydrogen atom is

$$E = E_n = \mathscr{K} + \mathscr{V} = -\frac{2\pi m e^4}{(4\pi\varepsilon_0)^2 h^2 n^2} \tag{14.3-17}$$

where we have used Eq. (14.3-14) for the value of r. The energy is determined by the value of the quantum number, n. Figure 14.14 depicts the first few energy levels. Each horizontal line segment is placed at a height proportional to the energy value.

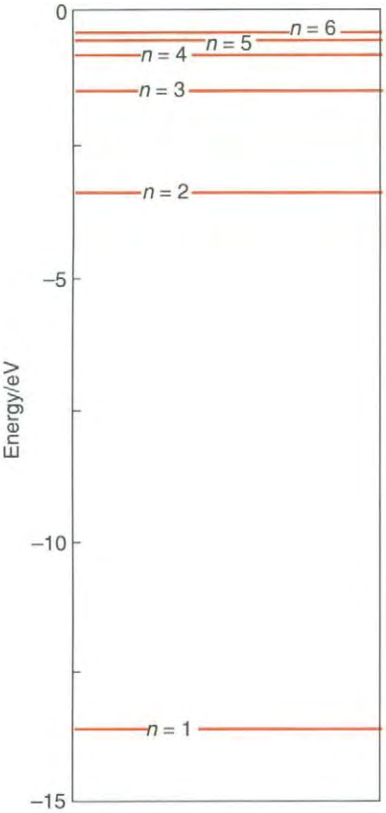

Figure 14.14. The Quantized Electron Energies by the Bohr Theory. The energy values are all negative, since an energy value of zero corresponds to enough energy barely to remove the electron from the atom.

The energy of an emitted or absorbed photon is equal to the difference between two quantized energies of the atom:

$$E_{(\text{photon})} = E_{n_2} - E_{n_1} = \frac{2\pi m e^4}{(4\pi\varepsilon_0)^2 h^2}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{14.3-18}$$

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. (14.3-8),

$$\frac{1}{\lambda} = \frac{E_{n_2} - E_{n_1}}{hc} = \frac{2\pi m e^4}{(4\pi\varepsilon_0)^2 h^3 c}\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right) \tag{14.3-19}$$

This is the formula of Rydberg, Eq. (14.3-10), with the constant $\mathfrak{R}$ given by the expression in front of the bracket. The first set of transitions shown in Figure 14.15, in which the lower-energy state (n_1 state) is the $n = 1$ state, corresponds to the series of spectral lines known as the Lyman series. The second set of transitions, in which

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[3] Ira N. Levine, *Quantum Chemistry*, 4th ed., Prentice-Hall, Englewood Cliffs, N.J., 1991, pp. 434ff.

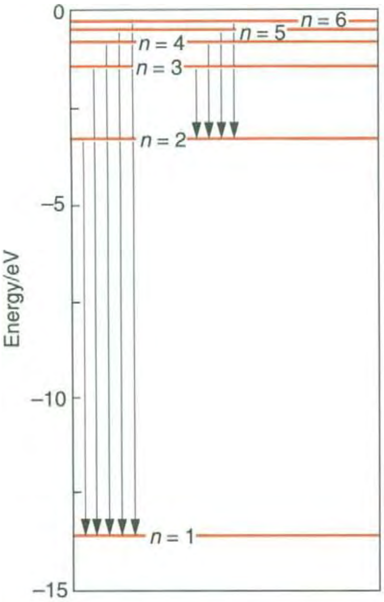

Figure 14.15. The Transitions between Bohr Theory Energies for the Hydrogen Atom. These are some of the transitions that lead to the wavelengths given by the Rydberg formula.

$n_1 = 2$, is the Balmer series. The next series, which is not shown, is the Paschen series. When the values of the physical constants are substituted into Eq. (14.3-19), we get

$$\mathfrak{R}_\infty = 1.097373 \times 10^7\,\mathrm{m}^{-1} \tag{14.3-20}$$

This value is labeled with the subscript ∞, corresponding to the assumption that the nucleus is stationary, as it would be if infinitely heavy. if we replace the mass of the electron by the reduced mass of the electron and proton to correct for the actual motion of the nucleus as in Eq. (D-27) of Appendix D, we get

$$\mathfrak{R}_\mathrm{H} = 1.09678 \times 10^7\,\mathrm{m}^{-1} \tag{14.3-21}$$

which is in agreement with the experimental value. This value of Rydberg's constant is for wavelengths measured in a vacuum. Wavelengths measured in air are slightly shorter than vacuum wavelengths, so the value of $\mathfrak{R}$ in air is larger by a factor of 1.00027, the refractive index of air for visible wavelengths.

Exercise 14.16

a. Substitute the values of the constants into the expression of Eq. (14.3-19) to verify the value of $\mathfrak{R}_\infty$.

b. Use the value of the reduced mass of the proton and electron to calculate the value of $\mathfrak{R}_\mathrm{H}$ from the value of $\mathfrak{R}_\infty$.

***c.** Calculate the wavelength and frequency of the light emitted when n changes from 4 to 2. What color does this correspond to?

14.4

De Broglie Waves and the Schrödinger Equation

Even though the Bohr theory gave the correct values for the energies of the hydrogen atom, it failed when applied to any other atoms or to any molecule. The theories of Planck, Einstein, and Bohr are now known as the "old quantum theory," and have been supplanted by the quantum theory of Schrödinger and Heisenberg, based on the "matter waves" of de Broglie.

De Broglie Waves

Prince Louis Victor de Broglie, 1892–1977, was a graduate student in 1923 and won the Nobel Prize in physics in 1929 for this work.

In 1923 de Broglie was trying to find a physical justification for Bohr's hypothesis of quantization of angular momentum. In classical physics, one thing that is quantized is the wavelength of standing waves, given for example by Eq. (14.2-19). De Broglie sought a way to relate this to Bohr's theory of the hydrogen atom, and came up with the idea that a moving particle such as an electron might somehow be accompanied by a "fictitious wave."[4]

According to Einstein's theory of relativity, a photon of energy E has a mass m such that

$$E = mc^2 \tag{14.4-1}$$

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[4] Jammer, *op. cit.*, pp. 243ff (Note 2).

where c is the speed of light, even though it has no rest-mass. If the Planck–Einstein relation, Eq. (14.3-8), is used for the energy and if mc is replaced by the momentum p, Eq. (14.4-1) becomes

$$\frac{hc}{\lambda} = pc \qquad \text{or} \qquad \lambda = \frac{h}{p} \tag{14.4-2}$$

where λ is the wavelength. De Broglie deduced that the velocity of the wave accompanying a particle was the same as the velocity of the particle if the wavelength is given by Eq. (14.4-2).

$$\boxed{\lambda = \frac{h}{p} = \frac{h}{mv}} \tag{14.4-3}$$

We omit most of de Broglie's argument, which is more complicated than simply saying that Eq. (14.4-3) is analogous to Eq. (14.4-2).

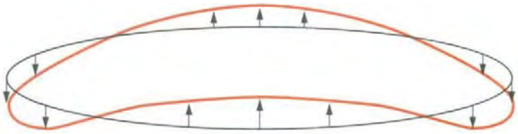
The quantization assumption of Bohr's theory arises naturally from Eq. (14.4-3) if one assumes that the circumference of a circular electron orbit in a hydrogen atom is equal to an integral number of wavelengths. This assumption means that the wave repeats itself with the same phase (with crests in the same positions) on each trip around the orbit, as depicted in Figure 14.16a. The situation depicted in Figure 14.16b is assumed not to occur. For a circular orbit

$$2\pi r = n\lambda = \frac{nh}{mv} \tag{14.4-4}$$

This equation is the same as Eq. (14.3-13), the hypothesis of Bohr.

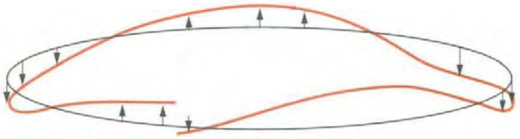
$$mvr = \frac{nh}{2\pi} \tag{14.4-5}$$

Although he had established his wave–particle relation only for the motion of electrons in the hydrogen atom, de Broglie hypothesized this relation to hold for any motion of any particle. This proposal of **matter waves** was revolutionary. When



As assumed by de Broglie

(a)



Mismatch–contrary to assumption

(b)

Figure 14.16. De Broglie Waves around a Closed Orbit. (a) **An integral number of wavelengths on the circumference.** Only if the circumference is an integral multiple of the wavelength. (b) **Not an integral number of wavelengths on the circumference.** In this case, a unique point occurs at which there is a discontinuity in the wave.

de Broglie presented his doctoral thesis containing this proposal, the examining committee refused to believe that it might correspond to physical reality.

EXAMPLE 14.5

Calculate the de Broglie wavelength of a baseball of mass 5.1 ounces thrown at 95 miles per hour.

Solution

$$\lambda = \frac{6.6261 \times 10^{-34}\,\mathrm{J\,s}}{(5.1\,\mathrm{oz})(59\,\mathrm{mi/h})}\left(\frac{16\,\mathrm{oz}}{1\,\mathrm{lb}}\right)\left(\frac{1\,\mathrm{lb}}{0.4536\,\mathrm{kg}}\right)\left(\frac{3600\,\mathrm{s}}{1\,\mathrm{h}}\right)\left(\frac{1\,\mathrm{mi}}{1609\,\mathrm{m}}\right)$$

$$= 1.1 \times 10^{-34}\,\mathrm{m}$$

This value suggests why matter waves are not observed for objects of ordinary size.

De Broglie suggested at his final oral examination that electron diffraction by crystals could verify his theory. In 1927, Davisson and Germer[5] accidentally grew a single crystal while heating a piece of nickel. When they irradiated this piece of nickel with a beam of electrons, they observed diffraction effects, verifying the existence of de Broglie's matter waves.

*Exercise 14.17

Find the speed of electrons with a de Broglie wavelength equal to 2.15×10^{-10} m, the lattice spacing in a nickel crystal.

The notion of a wave moving along with a particle as it traces out a classical trajectory has been abandoned. We now speak of a wave–particle duality for electrons and other particles, with the wavelike properties inherently belonging to the object and not to an accompanying wave. This wave–particle duality is illustrated by a hypothetical experiment.[6] A beam of electrons, all with the same speed, is allowed to stream toward a partition with two slits in it, as depicted in Figure 14.17a. At some distance from 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 an intense beam of electrons is passed through the slits. This pattern is schematically depicted in Figure 14.17b, where the intensity of the glow is plotted as a function of position on the screen. The pattern is explained by the constructive and destructive interference of waves appearing to pass through the two slits, since the waves are diffracted by the slits and produce waves moving in various directions from the slits. 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.

If the intensity of the source is decreased so that electrons pass through the slits one at a time, it can be observed that each electron lands at a single point on the screen. There is a tiny localized flash when each electron arrives. If the flashes are recorded and summed up, exactly the same pattern of diffraction bands appears as with an intense

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[5] C. J. Davisson and L. H. Germer, *Phys. Rev.* **30**, 705 (1927).

[6] R. P. Feynman, R. B. Leighton, and M. Sands, *The Feynman Lectures on Physics*, Vol. 3, Addison-Wesley, Reading Mass. 1965, Ch. 1.

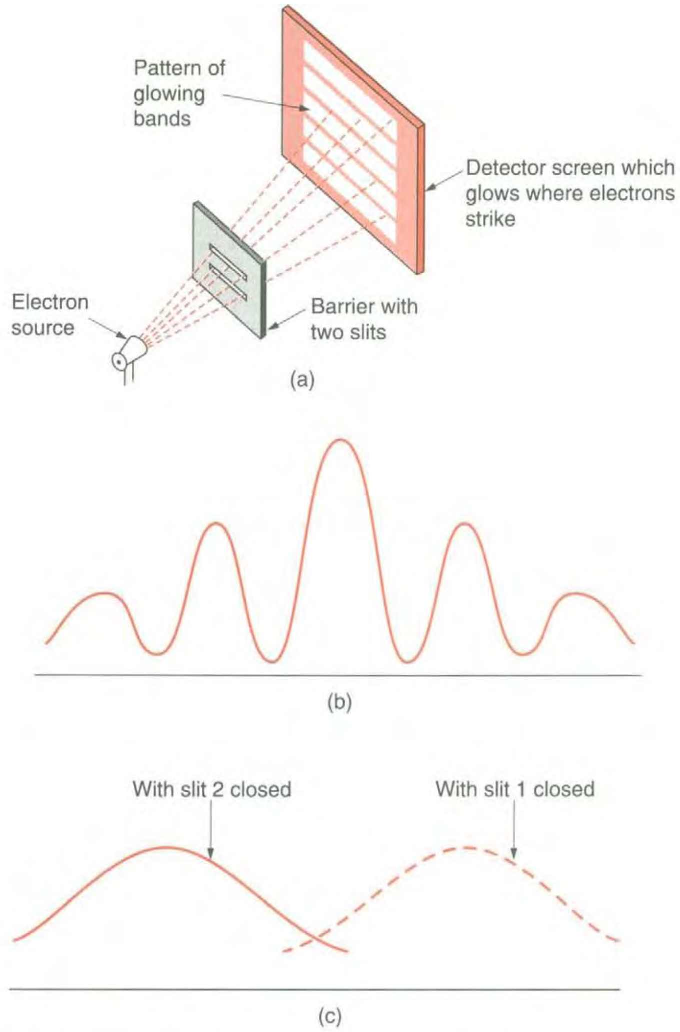

Figure 14.17. A Hypothetical Experiment with Electrons Passing through Two Slits. (a) **The apparatus.** (b) **The intensity of the glow due to electrons arriving at the screen in (a) with both slits open.** This diagram shows the diffraction pattern that proves that the particles have a wavelike character. (c) **The intensity of the glow due to electrons arriving at the screen in (a) with one slit open at a time.** If only one slit is open at a time, no diffraction pattern occurs.

beam of electrons. If one slit is covered while the electrons continue to pass through the second slit, there is a single band distributed 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 14.17c.

Our observations are interpreted as follows: The path of any electron from the source to the screen cannot be specified when no attempt is made to detect its location along the path. The position of the electron can be determined only by doing something to it such as stopping it with a screen. Only when the screen is placed at the slits is it possible to say which slit the electron passes through. When the screen is some distance from the slits, there is no way to say whether the electron went through slit 1 or slit 2, and wavelike interference properties are observed as though the electron passed through both slits in a delocalized wavelike fashion.

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.

In 1926, Schrödinger published a series of four papers containing a wave equation for de Broglie waves. The first three papers presented the time-independent version of the Schrödinger 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 paper at the end of 1926.[7]

Nonrigorous Derivation of the 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 wave along the x axis, the classical coordinate wave equation of Eq. (14.2-9) is

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{\lambda^2}\psi = 0 \tag{14.4-6}$$

where we have used Eq. (14.2-19) to replace the wave constant κ in terms of the wavelength λ. Use of the de Broglie relation, Eq. (14.4-3), to replace λ gives

$$\frac{d^2\psi}{dx^2} + \frac{4\pi^2}{h^2}m^2v^2\psi = 0 \tag{14.4-7}$$

This equation now represents a matter wave moving along the x axis.

We eliminate the speed v from our equation, using the relation

$$E = \mathcal{K} + \mathcal{V} = \tfrac{1}{2}mv^2 + \mathcal{V}(x) \tag{14.4-8}$$

where $\mathcal{K}$ is the kinetic energy, $\mathcal{V}(x)$ is the potential energy, and E is the total energy. The result is the **time-independent Schrödinger equation** for one-dimensional motion:

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \mathcal{V}(x)\psi = E\psi \tag{14.4-9}$$

where ψ is the coordinate wave function or time-independent wave function. We introduce the symbol $\hbar$ ("h-bar"):

$$\hbar = \frac{h}{2\pi} \tag{14.4-10}$$

Exercise 14.18

Carry out the algebra to obtain Eq. (14.4-9) from Eq. (14.4-7).

The left-hand side of Eq. (14.4-9) can be abbreviated by

$$\hat{H} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \mathcal{V}(x) \tag{14.4-11}$$

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[7] The time-independent equations are presented in *Ann. Physik*, **79**, 361 (1926), **79**, 489 (1926), and **80**, 437 (1926), and the time-dependent equation is presented in *Ann. Physik*, **81**, 109 (1926).

so that

$$\hat{H}\psi = E\psi \qquad (14.4\text{-}12)$$

The quantity $\hat{H}$ is a **mathematical operator**, since it stands for the carrying out of mathematical operations. It is called the **Hamiltonian operator**. Mathematical operators will be discussed in Chapter 15.

The Time-Dependent Schrödinger Equation

For motion in the x direction, the time-dependent Schrödinger equation is postulated to be

$$\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t} \qquad (14.4\text{-}13)$$

where i is the imaginary unit

$$i = \sqrt{-1} \qquad (14.4\text{-}14)$$

There is no way to construct the time-dependent Schrödinger equation from the classical wave equation because that wave equation is second order in time while the Schrödinger equation is first order in time. A first-order differential equation requires one initial condition to apply a general solution to a specific case, while a second-order differential equation requires two initial conditions. Equation (14.2-12) required one initial condition related to the position of the string and one related to its velocity in order to assign values to the two constants F and G. The uncertainty principle of quantum mechanics (to be discussed later) implies that positions and velocities cannot be specified simultaneously to 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 must occur in the equation in order for oscillatory solutions to exist. The function Ψ is the **time-dependent wave function**, or the displacement of the matter 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 wave function.

The time-independent Schrödinger equation, Eq. (14.4-12), can be obtained from the time-dependent equation by separation of variables. We assume a trial solution of the same type as with the classical wave function:

$$\Psi(x, t) = \psi(x)\zeta(t) \qquad (14.4\text{-}15)$$

We use the same symbols as for the factors in the classical wave function, Eq. (14.2-4), but do not mean to imply that they are the same functions. We substitute (14.4-15) into Eq. (14.4-13) and divide by $\psi(x)\zeta(t)$, obtaining

$$\frac{1}{\psi}\hat{H}\psi = \frac{i\hbar}{\zeta}\frac{d\zeta}{dt} \qquad (14.4\text{-}16)$$

The variables x and t are separated in this equation. Each side is equal to the same constant, which we denote by E:

$$\frac{1}{\psi}\hat{H}\psi = E \qquad (14.4\text{-}17)$$

and

$$\frac{i\hbar}{\zeta}\frac{d\zeta}{dt} = E \tag{14.4-18}$$

Multiplication of the first equation by ψ and of the second equation by $\zeta/i\hbar$ gives

$$\hat{H}\psi = E\psi \tag{14.4-19}$$

and

$$\frac{d\zeta}{dt} = \frac{E}{i\hbar}\zeta \tag{14.4-20}$$

Equation (14.4-19) is the same as the time-independent Schrödinger equation, Eq. (14.4-12), so ψ is the same coordinate wave function as in that equation and E is the constant energy of the system. Equation (14.4-20) has the solution

$$\zeta(t) = Ce^{Et/i\hbar} = Ce^{-iEt/\hbar} \tag{14.4-21}$$

where C is a constant. Since the Schrödinger equation is satisfied for any value of C, we take $C = 1$ and the complete wave function is

$$\Psi(x, t) = \psi(x)e^{-iEt/\hbar} \tag{14.4-22}$$

If we have a solution to the time-independent Schrödinger equation, including knowledge of the value of the energy E, we can immediately write a solution to the time-dependent equation by multiplying the coordinate wave function by the function ζ. This type of solution, with the coordinate and time dependence in separate factors, corresponds to a standing wave, as in the classical wave. There are also solutions of the time-dependent Schrödinger equation that correspond to traveling waves, and the time-independent Schrödinger equation does not necessarily apply to such solutions. The time-dependent equation applies to all cases.

The coordinate wave function can in many cases be chosen to be a real function. The function ζ is always complex, and can be written as a real part plus an imaginary part (see Appendix B):

$$e^{-iEt/\hbar} = \cos(-Et/\hbar) + i\sin(-Et/\hbar) = \cos(Et/\hbar) - i\sin(Et/\hbar) \tag{14.4-23}$$

where we have used the fact that the cosine is an even function and the sine is an odd function. For an even function, $f(-x) = f(x)$, and for an odd function, $f(-x) = -f(x)$. The real part and the imaginary parts oscillate with the same frequency, but out of phase. If the coordinate wave function is real, the real and imaginary parts of the complete wave function have stationary nodes in the same locations, since they have the same coordinate factor.

The Schrödinger Equation in Three Dimensions

For a single particle moving in three dimensions, the Hamiltonian operator is

$$\hat{H} = \frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \mathscr{V}(x, y, z) = -\frac{\hbar^2}{2m}\nabla^2 + \mathscr{V}(x, y, z) \tag{14.4-24}$$

where the potential energy $\mathcal{V}$ can depend on x, y, and z. The operator ∇^2 is the **Laplacian operator**, introduced in Eq. (11.2-13) and in Eq. (B-40) of Appendix B. In cartesian coordinates,

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \tag{14.4-25}$$

Since the Hamiltonian operator depends on x, y, and z, the coordinate wave function will depend on x, y, and z. To write the Schrödinger equation for a particular system, one must find an expression for the potential energy function that applies to that system. If it is convenient to express the potential energy in coordinates other than cartesian coordinates, the Laplacian operator can also be expressed in those coordinates in order to obtain a solution (see Appendix B).

The Schrödinger Equation for a Mutiparticle System

If the system consists of n point-mass particles moving in three dimensions, the potential energy can depend on $3n$ coordinates. The Hamiltonian operator for such a system is

$$\hat{H} = -\sum_{j=1}^{n} \frac{\hbar^2}{2m_j} \nabla_j^2 + \mathcal{V}(q) \tag{14.4-26}$$

where ∇_j^2 is the Laplacian operator for the coordinates of particle number j and where we use the abbreviation q to stand for the coordinates of all n particles. Since the Hamiltonian operator contains the coordinates of all of the particles, the solution to the Schrödinger equation must depend on all of these coordinates. Just as with the Schrödinger equation of a single particle, a solution to the time-independent Schrödinger equation for a system of many particles gives a solution to the time-dependent Schrödinger equation when multiplied by the time-dependent function of Eq. (14.4-21), but there can be other solutions of the time-dependent Schrödinger equation that are not of this form.

Exercise 14.19

Carry out the steps to show that equations analogous to Eqs. (14.4-19) and (14.4-20) hold for a system of n particles.

Eigenvalue Equations

The time-independent Schrödinger equation is one of 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 (the **eigenvalue**) multiplying the same function, which is called the **eigenfunction**. In the time-independent Schrödinger equation, the eigenvalue is E, the value of the energy, and is called the **energy eigenvalue**. The coordinate wave function is often called the **energy eigenfunction**.

There is generally a set of eigenfunctions to a given eigenvalue equation, with each eigenfunction corresponding to a specific eigenvalue. Two common cases occur: (1) the eigenvalue can take on any value within some range of values (a **continuous spectrum** of eigenvalues); (2) the eigenvalue can take on values only from a discrete set, with the values between the allowed values not permitted (a **discrete spectrum** of eigenvalues). The occurrence of a discrete spectrum of eigenvalues corresponds to quantization.

In addition to satisfying the Schrödinger equation, the wave function must satisfy other conditions. Since it represents a wave, we assume that it has the properties that are shared by all 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.

14.5

The Particle in a Box. The Free Particle

In this section we solve the time-independent Schrödinger equation for the two simplest cases. 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 structureless 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 $x = a$. Inside this interval (the box) there is no force on the particle. This model system could represent a particle sliding in a tight-fitting (but frictionless) tube with closed ends or a bead sliding on a frictionless wire between barriers. The principal chemical system represented by this model is an electron moving in a conjugated system of single and double bonds. The model only very crudely represents this system since the electron interacts with the other electrons and with nuclei, but we will discuss this application in Chapter 18. Since the 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 absolute confinement within the box we say that this potential energy outside the box is made to approach infinity.

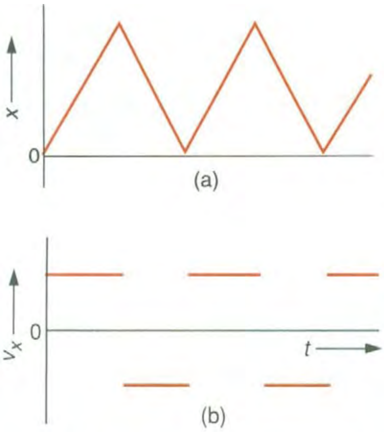

Figure 14.18. Mechanical Variables of a Particle in a Hard One-Dimensional Box. (a) **The position according to classical mechanics.** (b) **The velocity according to classical mechanics.** This diagram shows that the particle in a box moves back and forth at constant speed, according to classical mechanics.

Figure 14.18a shows the position of the particle as a function of time according to classical mechanics, and Figure 14.18b shows the velocity of the particle as a function of time. We will see that the quantum mechanics solution is qualitatively very different from this behavior. The time-independent Schrödinger equation for the system is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} + \mathcal{V}(x)\psi(x) = E\psi(x) \tag{14.5-1}$$

where $\psi(x)$ is the coordinate wave function (energy eigenfunction) and E is the energy eigenvalue. 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 will adjust the three solutions so that ψ is continuous at the boundaries between the regions.

In regions I and III the potential energy must approach an infinite value, so we write Eq. (14.5-1) as

$$\frac{d^2\psi}{dx^2} - \lim_{\mathcal{V}\to\infty} \frac{2m\mathcal{V}}{\hbar^2}\psi = -\frac{2mE}{\hbar^2}\psi \tag{14.5-2}$$

We assume that E is finite, so the right-hand side of this equation is finite. The left-hand side would be infinite unless ψ vanished, so the solution is

$$\psi^{(\mathrm{I})}(x) = \psi^{(\mathrm{III})}(x) = 0 \tag{14.5-3}$$

For region II

$$\frac{d^2\psi^{(\mathrm{II})}}{dx^2} = -\kappa^2\psi^{(\mathrm{II})} \tag{14.5-4}$$

where κ is given by

$$\kappa^2 = \frac{2mE}{\hbar^2} \tag{14.5-5}$$

Equation (14.5-4) is of the same form as Eq. (14.2-9). Its general solution is

$$\psi^{(\mathrm{II})}(x) = B\cos(\kappa x) + C\sin(\kappa x) \tag{14.5-6}$$

In order for ψ to be continuous at $x = 0$ and $x = a$, we must have the boundary conditions

$$\psi^{(\mathrm{II})}(0) = \psi^{(\mathrm{I})}(0) = 0; \qquad \psi^{(\mathrm{II})}(a) = \psi^{(\mathrm{III})}(a) = 0 \tag{14.5-7}$$

These conditions are similar to the boundary conditions for the vibrations of a string described in Section 14.2. In order for $\psi^{(\mathrm{II})}(0)$ to vanish, the constant B must vanish, because cos(0) equals unity while sin(0) equals zero. Thus

$$\psi^{(\mathrm{II})}(x) = C\sin(\kappa x) \tag{14.5-8}$$

The condition that $\psi^{(\mathrm{II})}(a)$ vanishes imposes a condition on κ, as in Eq. (14.2-14). The sine function vanishes when its argument is an integral multiple of π, so that

$$n\pi = \kappa a \qquad \text{or} \qquad \kappa = \frac{n\kappa}{a} \tag{14.5-9}$$

where n is a quantum number that can take on integral values. Specifying a value of n is equivalent to specifying which energy eigenfunction is "occupied" by the system. We can now write a formula for the set of energy eigenfunctions:

$$\psi_n(x) = C\sin\left(\frac{n\pi x}{a}\right) \tag{14.5-10}$$

where we now omit the superscript (II).

The energy eigenvalues are quantized, with values determined by the value of n:

$$E = E_n = \frac{\hbar^2\kappa^2}{2m} = \frac{\hbar^2 n^2\pi^2}{2ma^2} = \frac{h^2n^2}{8ma^2} \tag{14.5-11}$$

We disregard negative values of n, because replacing a value of n by its negative does not change the energy eigenvalue and is equivalent to changing the sign of C since the sine is an odd function. We also disregard $n = 0$ since $n = 0$ corresponds to $\psi = 0$. The value of C is unimportant at this stage since the Schrödinger equation is satisfied for any value of C and since the energy eigenvalue does not depend on C. We will later introduce a normalization procedure to assign convenient values to such constants.

There is a single energy eigenfunction for each energy eigenvalue. This is called the **nondegenerate** case. In the **degenerate** case there is more than one energy eigenfunc-

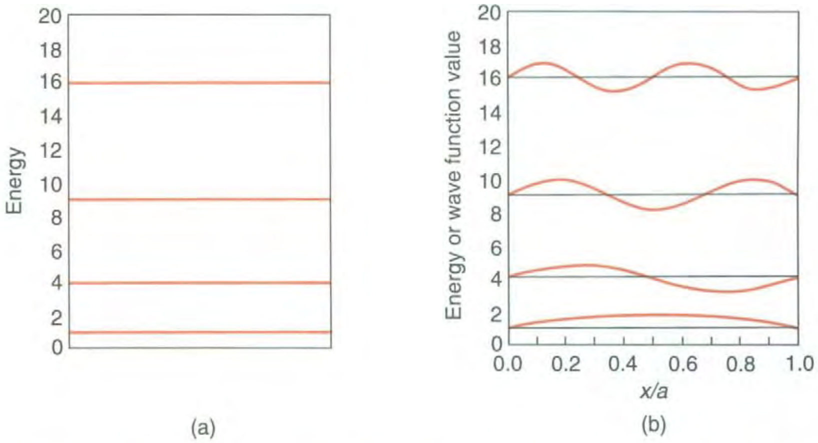

Figure 14.19. The Solutions to the Schrödinger Equation for a Particle in a One-Dimensional Box. (a) **The energy eigenvalues.** (b) **The energy eigenfunctions.** Compare the information about the motion of the particle in this figure with that in Figure 14.18.

tion corresponding to a given eigenvalue, and the number of eigenfunctions for a given eigenvalue is called its **degeneracy**. A single eigenfunction never corresponds to more than one eigenvalue. Figure 14.19a represents the energy eigenvalues by horizontal line segments at heights proportional to their energy values and Figure 14.19b shows the wave functions (energy eigenfunctions). Each wave function is plotted on a separate axis, placed at a height in the diagram corresponding to its energy eigenvalue. Equation (14.5-10) resembles Eq. (14.2-14) for the vibrating string and each wave function in Figure 14.19b resembles one of the standing waves in Figure 14.7.

The quantization of the energy eigenvalues comes not only from solving the Schrödinger equation but also from the boundary condition that the wave function must vanish at the ends of the box. Unlike the quantization by hypothesis of the old quantum theory, quantization has arisen from the mathematical analysis of the eigenvalue equation.

The energy in Eq. (14.5-11) is 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 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 classical mechanics, which allows a particle to be at rest with zero kinetic energy.

EXAMPLE 14.6

Find the energy of an electron in a box of length 1.000 nm for $n = 1$.

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 14.20

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 the clearest illustration of the fact that the Schrödinger equation is the wave equation for de Broglie waves. In the case of zero potential energy, the total energy is equal to the kinetic energy so that

$$E = \frac{1}{2}mv^2 = \frac{p^2}{2m} \tag{14.5-12}$$

where we use the definition of the momentum, $\mathbf{p} = m\mathbf{v}$. From Eq. (14.4-3) and Eq. (14.5-12),

$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mE}} \tag{14.5-13}$$

which is the same as

$$E = \frac{h^2}{2m\lambda^2} \tag{14.5-14}$$

The energy of a de Broglie wave is inversely proportional to the square of its wavelength. When the relationship between the wavelength and the length of the box is used, this becomes the same as the energy expression in Eq. (14.5-11).

Exercise 14.21

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. (14.5-11) is obtained by substituting the result of part (a) into Eq. (14.5-14).

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 the value of $\mathcal{V}_0$.

Exercise 14.22

a. 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

$$E_n = \mathcal{V}_0 + \frac{h^2n^2}{8ma^2}$$

but that the wave function is unchanged.

b. The result of part (a) is generally true. That is, adding a constant to the potential energy adds the same constant to the energy eigenvalues. Write the time-independent Schrödinger equation for a general system of n particles, Eq. (14.4-26), and show that this statement is correct.

If a particle in a box is electrically charged, it can absorb or emit photons. 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 14.23

Calculate the wavelength and frequency of the photon emitted if an electron in a one-dimensional box of length 10.0 Å (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.

Equation (14.4-22) can be used to obtain the time-dependent wave function for a particle in a one-dimensional box:

$$\begin{aligned}\Psi_n(x, t) &= C \sin\left(\frac{n\pi x}{a}\right) e^{-iE_n t/\hbar} \\ &= C \sin\left(\frac{n\pi x}{a}\right)(\cos(-iE_n t/\hbar) + i \sin(-iE_n t/\hbar)) \qquad (14.5\text{-}15)\end{aligned}$$

It is generally possible to choose a real energy eigenfunction for a particle confined in a finite region, but the time-dependent wave function is always complex. We will usually refer to the energy eigenfunction as the coordinate wave function and the time-dependent wave function as the complete wave function. At times when we do not need to discuss the complete wave function we will simply call the energy eigenfunction "the wave function."

Exercise 14.24

*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.

b. Calculate the difference between these frequencies.

c. Compare these frequencies and their difference with the photon frequency in Exercise 14.23. 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 which wave function and energy eigenvalue correspond to the state of the particle. We recognize two cases:

1. The wave function of the system is known to be an energy eigenfunction times the appropriate time-dependent factor as in Eq. (14.5-15). Chemists are usually interested in this case. 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 an energy eigenfunction times the appropriate time-dependent factor. Such a function must obey the time-dependent Schrödinger equation and the same boundary conditions as the energy eigenfunctions. It can be represented by a linear combination analogous to that of Eq. (14.2-23):

$$\Psi(x, t) = \sum_{n=1}^{\infty} A_n \psi_n(x) e^{-iE_n t/\hbar} \qquad (14.5\text{-}16)$$

where $A_1, A_2, \ldots$ are a set of time-independent constants. As in the classical case, this equation expresses the principle of superposition.

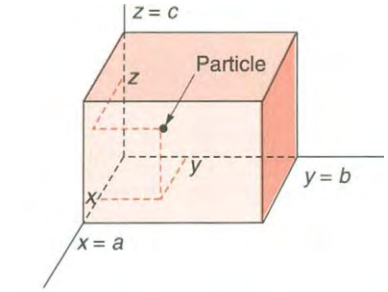

Figure 14.20. A Particle in a Hard Three-Dimensional Box. This system contains a single particle that moves freely so long as it remains in the box.

Exercise 14.25

Show that the function of Eq. (14.5-16) satisfies the time-dependent Schrödinger equation for the particle in a one-dimensional box.

The Particle in a Three-Dimensional Box

We now consider a model system consisting of a single point-mass particle confined in a three-dimensional rectangular box, which is placed so that its lower left rear corner is at the origin of coordinates and its walls are perpendicular to the coordinate axes, as depicted in Figure 14.20. 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. We will use this model system to represent the motion of an electron or of a gas molecule in a container.

The solution of the Schrödinger equation is carried out in Appendix F. The energy eigenfunction (coordinate wave function) is a product of three wave functions for particles in one-dimensional boxes

$$\psi_{n_x n_y n_z}(x, y, z) = C\sin\left(\frac{n_x \pi x}{a}\right)\sin\left(\frac{n_y \pi y}{b}\right)\sin\left(\frac{n_z \pi z}{c}\right) \qquad (14.5\text{-}17)$$

where C is a constant. The energy eigenvalue is the sum of three energy eigenvalues for particles in one-dimensional boxes:

$$E_{n_z n_y n_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \qquad (14.5\text{-}18)$$

There are three quantum numbers n_x, n_y, and n_z, which we will sometimes denote by the three values in parentheses, as for example (1,1,2), etc. A particular energy eigenfunction and its energy eigenvalue are specified by giving the values of the three quantum numbers.

If $a = b = c$ (a cubical box) the energy eigenvalue is

$$E_{n_z n_y n_z} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2) \qquad (14.5\text{-}19)$$

There can be several states that correspond to the same energy eigenvalue in this case. The two sets of quantum numbers (1,2,3) and (3,2,1) both correspond to the same energy although they correspond to different states. A set of states with equal energies is called an **energy level**, and the number of states making up the energy level is called the **degeneracy** of the energy level.

EXAMPLE 14.7

For an electron in a cubical box of side 1.00×10^{-9} m, find the energy and the degeneracy of the level in which the state corresponding to (1,2,3) occurs.

Solution

The energy eigenvalue is

$$E_{123} = \frac{14h^2}{8ma^2} = \frac{(14)(6.6261 \times 10^{-34}\,\mathrm{J\,s})^2}{(8)(14.109 \times 10^{-31}\,\mathrm{kg})(1.00 \times 10^{-9}\,\mathrm{m})^2}$$
$$= 8.43 \times 10^{-19}\,\mathrm{J}$$

There are six permutations of the three distinct numbers: (1,2,3), (2,3,1), (3,1,2), (3,2,1), (1,3,2) and (2,1,3). There are no other sets of three integers whose squares add up to 14, so the degeneracy is 6.

***Exercise 14.26**

For an electron in the cubical box of Example 14.7 find the energy eigenvalues and degeneracies of all energy levels of lower energy than that in Example 14.7.

The Free Particle in One Dimension

The free particle is an object on which no forces act. The potential energy of the particle is equal to a constant, which we set equal to zero. If a point-mass particle can move only parallel to the x axis, the time-independent Schrödinger equation is

$$-\frac{\hbar^2}{2m}\frac{d^2\psi}{dx^2} = E\psi \qquad (14.5\text{-}20)$$

Equation (14.5-20) is the same as Eq. (14.5-4) for the motion of a particle in a box, but the boundary conditions are different. The general solution to Eq. (14.5-20) is the same as that in Eq. (14.5-6). We write this solution (the energy eigenfunction) in a different way:

$$\psi(x) = De^{i\kappa x} + Fe^{-i\kappa x} \qquad (14.5\text{-}21)$$

where the constant κ is given by Eq. (14.5-5).

***Exercise 14.27**

Use the identity

$$e^{ix} = \cos(x) + i\sin(x) \qquad (14.5\text{-}22)$$

to find the relations between the constants B, C, D and F that cause Eq. (14.5-6) and Eq. (14.5-21) to represent the same function.

There are now no walls at which the wave function must vanish. We must still conform our solution to the assumptions that the wave function be continuous and finite. The finiteness condition requires that κ be real. We let

$$\kappa = a + ib$$

where a and b are real. The solution is now

$$\psi(x) = De^{iax}e^{-bx} + Fe^{-iax}e^{bx} \qquad (14.5\text{-}23)$$

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, b must vanish and κ must be real. The energy eigenvalues are given by Eq. (14.5-5):

$$E = \frac{\hbar^2\kappa^2}{2m} \tag{14.5-24}$$

There is no restriction on the values of the parameter κ except that it must be real, so E can take on any real nonnegative value. The energy is not quantized and there is no zero-point energy.

If F vanishes, the complete wave function is

$$\Psi(x, t) = De^{i\kappa x - iEt/\hbar} = De^{i(\kappa x - Et/\hbar)} \tag{14.5-25}$$

where E is given by Eq. (14.5-24). Separating the real and imaginary parts, we obtain

$$\Psi(x, t) = D\left[\cos\left(\kappa x - \frac{Et}{\hbar}\right) + i\sin\left(\frac{\kappa x - Et}{\hbar}\right)\right] \tag{14.5-26}$$

Comparison of this with Eq. (14.2-24) shows both the real and imaginary parts to be traveling waves moving to the right with a speed given by

$$c = \frac{\hbar\kappa}{2m} \tag{14.5-27}$$

A nonzero value of the constant F corresponds to a traveling wave moving to the left.

Exercise 14.28

Show that Eq. (14.5-27) is correct.

*Exercise 14.29

Show that the function

$$\Psi(x, t) = Fe^{-i\kappa x - iEt/\hbar} \tag{14.5-28}$$

represents a traveling wave moving to the left, and find its speed.

If D and F are equal, the two traveling waves can produce a standing wave:

$$\psi(x) = D(e^{i\kappa x} + e^{-i\kappa x}) = 2D\cos(\kappa x) \tag{14.5-29}$$

Exercise 14.30

Use Eq. (14.5-22) to verify Eq. (14.5-29).

The complete wave function corresponding to Eq. (14.5-29) is

$$\Psi(x, t) = 2D\cos(\kappa x)e^{-iEt/\hbar} \tag{14.5-30}$$

Exercise 14.31

Show that if $D = -F$, a different standing wave results. How does it compare with that of Eq. (14.5-30)?

If the constants D and F are both nonzero but have unequal magnitudes, the complete wave function becomes

$$\Psi(x, t) = De^{i(\kappa x - Et/\hbar)} + Fe^{-i(\kappa x + Et/\hbar)} \qquad (14.5\text{-}31)$$

which represents a combination of traveling waves with different amplitudes, one moving to the right and one moving to the left. 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 impossible, but it is allowed 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

From the Hamiltonian operator in Eq. (14.4-24), the time-independent Schrödinger equation for a free particle moving in three dimensions is

$$\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) = -\frac{2mE}{\hbar^2}\psi \qquad (14.5\text{-}32)$$

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. For the special case of a traveling wave moving in a definite direction with a definite energy (definite values of κ_x, κ_y, and κ_z) the energy eigenfunction is

$$\psi(x, y, z) = De^{i\kappa_x x}e^{i\kappa_y y}e^{i\kappa_z z} \qquad (14.5\text{-}33)$$

where

$$\kappa_x^2 = \frac{2mE_x}{\hbar^2}, \qquad \kappa_y^2 = \frac{2mE_y}{\hbar^2}, \qquad \kappa_z^2 = \frac{2mE_z}{\hbar^2} \qquad (14.5\text{-}34)$$

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 three components of the wave vector can take on any real values.

The energy eigenvalue is given by

$$E = E_x + E_y + E_z = \frac{\hbar^2}{2m}(\kappa_x^2 + \kappa_y^2 + \kappa_z^2) = \frac{\hbar^2\kappa^2}{2m} \qquad (14.5\text{-}35)$$

The energy is not quantized and there is no zero-point energy. Just as Eq. (14.5-31) represents a linear combination of waves moving in opposite directions, an energy eigenfunction for a three-dimensional free particle can consist of a linear combination of waves moving in various directions as long as the wave vectors have the same magnitude.

14.6 The Harmonic Oscillator

The time-independent Schrödinger equation of the harmonic oscillator is

$$\hat{H}\psi = -\frac{\hbar^2}{2m}\frac{d^2\psi}{dz^2} + \frac{1}{2}kz^2\psi = E\psi \tag{14.6-1}$$

where we continue to use the letter z for the coordinate as in Section 14.1. We define the constants

$$b = \frac{2mE}{\hbar^2}, \qquad a = \frac{\sqrt{km}}{\hbar} \tag{14.6-2}$$

so that the Schrödinger equation can be written

$$\frac{d^2\psi}{dz^2} + (b - a^2z^2)\psi = 0 \tag{14.6-3}$$

Charles Hermite, 1822–1901, was 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 of the form of a well-known equation known as the Hermite equation (see Appendix F). The solutions to the Hermite equation are of the form

$$\psi(z) = e^{-az^2/2}S(z) \tag{14.6-4}$$

where $S(z)$ is a power series

$$S(z) = c_0 + c_1z + c_2z^2 + c_3z^3 + \cdots = \sum_{n=0}^{\infty} c_nz^n \tag{14.6-5}$$

with constant coefficients $c_1, c_2, c_3, \ldots$ Hermite showed that the series must terminate in order to keep ψ from becoming infinite as $|z|$ becomes large. The series S becomes one of a set of polynomials known as **Hermite polynomials**. Appendix F contains some information about the solution. As is shown in Appendix F, the termination of the polynomials determines the energy eigenvalues, which are given by

$$E = \frac{h}{2\pi}\sqrt{\frac{k}{m}}\left(v + \frac{1}{2}\right) = h\nu\left(v + \frac{1}{2}\right) \tag{14.6-6}$$

where ν is the frequency of the oscillator predicted by classical mechanics, (see Eq. (14.1-10)) and where $v = 0, 1, 2, 3, \ldots$. The energy is quantized and there is a zero-point energy:

$$E_0 = \tfrac{1}{2}h\nu \quad \text{(zero-point energy)} \tag{14.6-7}$$

With the particle in a box the quantization was produced by the condition that the wave function must be continuous. With the harmonic oscillator system, the energy quantization is produced by the condition that the wave function must be finite.

Exercise 14.32

***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 this frequency compare with the classical frequency of the oscillator? How do you interpret this comparison?

For $v = 0$, the energy eigenfunction of the harmonic oscillator is

$$\psi_0 = S_0 e^{-az^2/2} = c_0 e^{-az^2/2} = \left(\frac{a}{\pi}\right)^{1/4} e^{-az^2/2} \tag{14.6-8}$$

where the choice for the value of c_0 will be discussed later. For $v = 1$, the energy eigenfunction is

$$\psi_1 = \left(\frac{4a^3}{\pi}\right)^{1/4} z e^{-ax^2/2} \tag{14.6-9}$$

and for $v = 2$, the wave function is

$$\psi_2 = \left(\frac{a}{4\pi}\right)^{1/4} (2az^2 - 1) e^{-az^2/2} \tag{14.6-10}$$

The factor $(2az^2 - 1)$ is proportional to the Hermite polynomial $H_2(\sqrt{a}\,z)$. Other energy eigenfunctions can be generated from formulas for the Hermite polynomials in Appendix F.

Exercise 14.33

Obtain a formula for ψ_3 for the harmonic oscillator. Do not evaluate the constant c_0.

Figure 14.21 shows the energy eigenfunctions for $v = 0$, $v = 1$, $v = 2$, and $v = 3$. Each wave function is plotted on a separate axis at a height representing the energy eigenvalue. The potential energy as a function of z is also plotted with the same energy scale. The classical turning point for any given energy is the point at which the potential energy is equal to the total energy, and the wave function is nonzero in the regions past the turning points. A comparison of these graphs with those for the particle in a one-dimensional box in Figure 14.19b shows that the general pattern of the nodes is the same, with more nodes corresponding to higher energy. In addition to the nodes at infinite $|z|$ 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.

We can now compare the classical and quantum-mechanical solutions for the harmonic oscillator. The classical solution gives the position and velocity of the oscillator as a function of time, as shown in Figure 14.2, and the state of the oscillator at any instant is specified by giving the value of the position and the velocity. The quantum-mechanical state is specified by stating which wave function corresponds to the state of the system. The wave function describes a de Broglie wave and, if the wave function corresponds to a standing wave, the de Broglie wave oscillates with a certain frequency but does not move. The de Broglie wave oscillates over all values of the coordinate, including values beyond the classical turning points. As we will show in the next chapter, this behavior corresponds to possible penetration of the particle into a classically forbidden region, which is called **tunneling**.

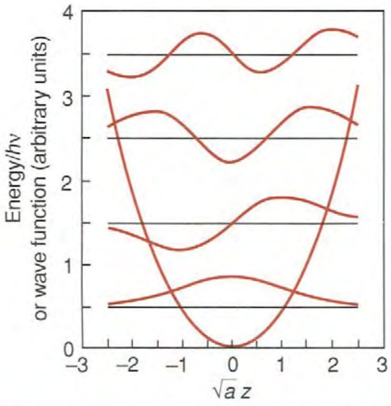

Figure 14.21. Harmonic Oscillator Wave Functions. This diagram shows the first four energy eigenfunctions for the harmonic oscillator, superimposed on a diagram of the energy eigenvalues.

EXAMPLE 14.8

Calculate the frequency of oscillation of the wave function corresponding to the $v = 0$ state of the oscillating hydrogen atom of Example 14.2.

Solution

From Eq. (14.4-21) the time-dependent factor of the wave function is

$$\zeta(t) = e^{-iE_0 t/\hbar} = e^{-ih\nu t/2\hbar} = e^{-\pi i\nu t}$$

Inspection of this equation shows that the frequency is $\nu/2$, where ν is the classical frequency of the oscillator, or $4.35 \times 10^{13}\ \mathrm{s}^{-1}$. It is interesting that this frequency is not the same as that of the classical oscillator, and is also not the same as that of the other wave functions.

*Exercise 14.34

a. Find a formula for the frequency of oscillation of the harmonic oscillator wave function for the $v = 1$ state.

b. Find a formula for the frequency of oscillation of the harmonic oscillator wave function for the $v = 2$ state.

c. Compare the frequencies from parts (a) and (b) and the frequency from Example 14.8 with the frequency of the photon in Exercise 14.32 and with the frequency of oscillation of the classical oscillator.

d. Compare the difference between the frequencies of the $v = 2$ state and the $v = 1$ state with the frequency of the photon.

EXAMPLE 14.9

Find the classical amplitude of oscillation for a hydrogen atom attached to a chemical bond as in Example 14.2 if the energy is equal to that of the $v = 0$ quantum state.

Solution

For a classical energy equal to the $v = 0$ quantum energy, the turning point is given by

$$z_t^2 = \frac{h\nu}{k} = \frac{h}{2\pi}\sqrt{\frac{1}{km}} = \frac{6.6261 \times 10^{-34}\ \mathrm{J\,s}}{\sqrt{(500\ \mathrm{N\,m^{-1}})(1.674 \times 10^{-27}\ \mathrm{kg})}}$$

$$= 1.15 \times 10^{-22}\ \mathrm{m}^2$$

$$z_t = 1.07 \times 10^{-11}\ \mathrm{m} = 0.107\ \text{Å}$$

*Exercise 14.35

Find the classical amplitude of oscillation 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 molecule vibrates like a harmonic oscillator with a mass equal to the reduced mass of the two nuclei (see Eq. (D-30) of Appendix D). The force constant is equal to $576\ \mathrm{N\,m^{-1}}$, and the reduced mass is equal to 8.369×10^{-28} kg (half the mass of a hydrogen atom).

Summary of the Chapter

The solution of the classical equation of motion for the harmonic oscillator provides formulas for the position and velocity of the mass as functions of time. 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.

The "old quantum theory" consists of theories with arbitrary assumptions of quantization, devised to explain phenomena that classical physics could not explain. This theory consists primarily of the black-body radiation theory of Planck, the photoelectric effect theory of Einstein, and the hydrogen atom theory of Bohr.

De Broglie sought a physical justification for Bohr's assumption of quantization, and hypothesized that all particles move with a wavelike character with a wavelength given by

$$\lambda = \frac{h}{mv}$$

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 these matter waves. The time-independent equation is an eigenvalue equation given by

$$\hat{H}\psi = E\psi$$

where E is the energy of the system, ψ is a wave function, and $\hat{H}$ is the Hamiltonian operator. The time-dependent Schrödinger equation is

$$\hat{H}\psi = i\hbar\frac{\partial\Psi}{\partial t}$$

By assuming that the wave function Ψ is a product of a coordinate factor ψ and a time factor ζ, 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 hard 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.

Problems for Section 14.1

14.36. The vibrational frequency of a $^{12}C^{16}O$ molecule is $6.5405 \times 10^{13}\ s^{-1}$. The atomic masses are: ^{12}C, 12.00000 amu; ^{16}O, 15.994915 amu.

a. Find the value of the force constant.
b. Find the vibrational frequency of a $^{13}C^{16}O$ molecule.
c. Find the vibrational frequency of a $^{12}C^{17}O$ molecule.

***14.37.** Assume that a $^{12}C^{16}O$ is adsorbed on a platinum surface in such a way that the carbon atom is held stationary. Find the vibrational frequency of the vibrating oxygen atom. See the previous problem for data.

14.38. The frequency of vibration of a $^{1}H^{35}Cl$ molecule is $8.966 \times 10^{13}\ s^{-1}$. What would the frequency be if the chlorine atom were infinitely massive?

Problems for Section 14.2

14.39. **a.** If a violin string has a fundamental frequency of $264\ s^{-1}$, find the frequency of each of the first three overtones.

b. If the speed of sound is $338\ m\ s^{-1}$, find the wavelength of the sound wave with frequency $264\ s^{-1}$.

14.40. **a.** In a closed organ pipe, the wavelength of the fundamental corresponds to twice the length of the pipe.

Find the length of the pipe for A above middle C, which has frequency equal to 440 s^{-1}. What do you think will happen to the pitch if the temperature increases?

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.

c. The overtones for the instruments of parts (a) and (b) have different patterns, since each overtone for an open pipe has a node at the closed end of the pipe and a maximum at the open end. Find the frequency of the first overtone for an organ pipe and for a clarinet for A above middle C.

14.41. Assume that the fundamental and the first overtone are simultaneously excited in a flexible string such that

$$z(y,t) = A_1 \sin\left(\frac{\pi y}{L}\right)\sin\left(\frac{\pi c t}{L}\right) + A_2 \sin\left(\frac{2\pi y}{L}\right)\sin\left(\frac{2\pi c t}{L}\right)$$

where

$$A_1 = 4A_2$$

Construct a graph representing the shape of the string at time $t = L/(4c)$ and at time $t = 3L/(4c)$. Comment on the differences in the two shapes.

14.42. Show that the relationship $\nu = c/\lambda$ for a traveling wave also holds for the standing wave in Eq. (14.2-31).

***14.43.** 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:

$$\text{Refractive index} = n = \frac{c_{\text{vacuum}}}{c_{\text{medium}}}$$

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.

Problems for Section 14.3

14.44. **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.

***14.45.** Interstellar space is filled with isotropic radiation that corresponds to black-body radiation with a temperature of 2.736 K. This fact substantiates the "big-bang" theory of cosmology. Find the wavelength of maximum spectral radiant emittance of black-body radiation at this temperature and draw a graph of the spectral radiant emittance curve for this temperature.

14.46. The work function of sodium metal is 2.28 eV, where $1\ \mathrm{eV} = 1.6022 \times 10^{-19}$ J. Find the frequency and wavelength of light capable of ejecting electrons from sodium metal with a speed of $4.00 \times 10^4\ \mathrm{m\,s^{-1}}$.

***14.47.** **a.** Calculate the speed of an electron in the $n = 4$ Bohr orbit and in the $n = 400$ Bohr orbit.

b. Express these speeds as fractions of the speed of light.

14.48. **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 $n = 1{,}000{,}000$.

***14.49.** 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 of all lines in the Balmer series that lie in the visible region.

14.50. Find the wavelengths of the first six lines in the hydrogen atom spectrum corresponding to transitions to $n = 1$. In what region of the electromagnetic spectrum do these lines lie?

***14.51.** A positronium atom is a hydrogenlike 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 Bohr radius for positronium.

b. Find the energy of the $n = 1$ state of positronium, and find the ratio of this energy to that of a hydrogen atom.

c. Find the radius of the circle in which each particle moves around the center of mass.

14.52. 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 $6.673 \times 10^{-11}\ \mathrm{m^3\,kg^{-1}\,s^{-2}}$ 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. Find the Bohr radius for such a hydrogen atom, 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.

Problems for Section 14.4

***14.53.** 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.

14.54. Thermal neutrons are neutrons with a distribution of speeds nearly like the equilibrium distribution for gas molecules. In Chapter 10 we found that the most probable speed of gas molecules of mass m is $\sqrt{2k_{\mathrm{B}}T/m}$. 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?

14.55. Find the de Broglie wavelength of a 1500 kg automobile moving at 65 miles per hour.

Problems for Section 14.5

14.56. 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 hard one-dimensional box of length a with quantum number n.

***14.57.** 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 is hard and 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 $n = 3$.

14.58. **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 and 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.

***14.59.** 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 14.5.

14.60. Consider a crude model representing a benzene molecule as a three-dimensional box with dimensions 3.5 Å by 3.5 Å by 1.25 Å. Include only the six π electrons, which are assumed to move in the entire box, and let them occupy the three lowest energy states. 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. If the height of the box in the z direction is 1.25 Å what can you say about n_z for this problem?

Problems for Section 14.6

14.61. **a.** Construct an accurate graph of the $v = 2$ wave function of a harmonic oscillator as a function of $\sqrt{a}\,z$.

b. Find the value of the wave function at the turning point.

14.62. Using the recursion relation, Eq. (F-12) in Appendix F, obtain the energy eigenfunctions ψ_3, ψ_4, and ψ_5 for the harmonic oscillator.

14.63. **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

$$\int_{-\infty}^{\infty} \psi_0(x)\psi_1(x)\,dx = 0$$

b. Work out the integral and show that ψ_0 and ψ_1 are orthogonal.

14.64. **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 in ψ_2^2.

c. Express the locations of the relative maxima from part (b) as fractions of the classical turning point for the energy corresponding to this energy eigenfunction.

d. Find the value of ψ_2^2 at each maximum.

14.65 In Appendix F it is shown that the coefficients in the series $S(z)$ of Eq. (14.6-5) obey a relation called a recursion relation

$$c_{n+2} = \frac{2an + a - b}{(n+2)(n+1)} c_n \qquad (n = 0, 1, 2, \ldots)$$

where a and b are the constants defined in Eq. (14.6-2).

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. (14.6-10).

c. Show that the formula in Eq. (F-6) produces coefficients in the same ratio for $H_2(\sqrt{a}\,z)$ as given in Eq. (14.6-10).

d. Generate the Hermite polynomial $H_4(\sqrt{a}\,z)$ from Eq. (F-6) and write the formula for ψ_4 for the harmonic oscillator. Do not include the constant in front, which will be discussed in Chapter 15.

14.66. 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.

***14.67.** The harmonic oscillator is used as a model for molecular vibrations, considering the nuclei to be masses connected by springlike chemical bonds. The molecule vibrates like a harmonic oscillator with mass equal to the reduced mass of the nuclei of the molecule (see Eq. (D-30) of Appendix D).

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.

14.68. A harmonic oscillator potential energy function is modified so that

$$\mathscr{V} = \begin{cases} kz^2/2 & \text{if } |z| < z' \\ \infty & \text{if } |z| > z' \end{cases}$$

where z' is some positive constant that is greater than the classical turning point for the energies that we will consider.

a. Say qualitatively how this will affect the classical solution.

b. Say 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.

General Problems

***14.69.** 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).

14.70. 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.

***14.71.** 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

$$F = -\frac{Gm_1m_2}{r^2}$$

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 332,958. The earth's orbit is slightly elliptical, but pretend that it is circular, with a radius of 1.4967×10^{11} m. Assume that the sun is stationary (as it would be if it were infinitely massive).

a. Find the value of the Bohr radius.

b. Find the value of the quantum number corresponding to the size of the earth's actual orbit.

c. Find the kinetic energy, the potential energy, and the total energy of the earth's orbital motion.

d. Find the ratio of the reduced mass of the earth–sun system to the mass of the earth. See. Eq. (D-27) for the definition of the reduced mass.

14.72. 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 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 of the theories of the old quantum theory.

f. The Schrödinger equation has been rigorously derived from first principles.

g. An eigenvalue equation can have solutions for arbitrary values of the eigenvalue.

h. Several different eigenvalues can correspond to the same eigenfunction.

i. Several different energy eigenfunctions can correspond to the same energy eigenvalue.

j. Light can be identified as a wave in a pervasive medium.

k. Light exhibits both wavelike and particlelike properties.

l. Electrons exhibit both wavelike and particlelike properties.

m. If the length of its box is made to approach infinity, a particle in a box behaves like a free particle.

n. 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.

15

The Principles of Quantum Mechanics. II. The Postulates of Quantum Mechanics

OBJECTIVES

After studying this chapter, the student should:

1. understand the use of postulates as the foundation of quantum mechanics;
2. be able to solve a variety of problems involving mathematical operators;
3. be able to construct a quantum-mechanical operator from the classical expression for the corresponding operator;
4. be able to calculate expectation values for mechanical variables and determine whether the variable has a unique value for the state in question;
5. understand the determination of the state of a system by a set of measurements.

PRINCIPAL FACTS AND IDEAS

1. Quantum mechanics is based on a set of postulates.
2. The first two postulates establish the role of the wave function in quantum mechanics.
3. The third postulate of quantum mechanics 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.

15.1

The First Two Postulates of Quantum Mechanics

Schrödinger did not derive his equation from other principles, and it is not based on experimental fact. We take the time-dependent Schrödinger equation as a **postulate**. A postulate is a fundamental assumption on which a theory is based, and the consequences of any postulates must be compared with experiment to validate the theory. Schrödinger, Heisenberg and others devised several postulates that form a consistent logical foundation for quantum mechanics. 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 14, without calling them postulates. They are:

Werner Karl Heisenberg, 1901–1976, was a German physicist who invented matrix mechanics, a form of quantum mechanics equivalent to the Schrödinger formulation, and who discovered the uncertainty principle, for which he received the 1932 Nobel prize in physics.

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.*

Postulate 2. *The wave function Ψ obeys the time-dependent Schrödinger equation*

$$\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t} \tag{15.1-1}$$

where $\hat{H}$ is the Hamiltonian operator.

Since the available information about the state is contained in the wave function, we can specify the state by specifying which wave function applies to the system at a given instant. There is a **one-to-one relationship** between the state of the system and its wave function. That is, to each state there corresponds one wave function, and to each wave function there corresponds one state. The terms "state" and "wave function" are often used interchangeably, and the wave function is sometimes referred to as the **state function**. Information about values of energy, momentum, etc., must be obtained from this wave function, instead of from values of coordinates and velocities as in classical mechanics. Specification of the state in quantum mechanics usually gives less information about the mechanical variables of the system than it does in classical mechanics, where specification of the state allows precise calculation of the values of all mechanical variables. In some cases we will be able to predict with certainty from a known wave function what result an error-free measurement of a mechanical variable will give. In other cases only statistical predictions can be made, even in the absence of experimental error. We will discuss this strange situation when we reach the fourth postulate.

There is no need to have a separate postulate for the time-independent Schrödinger equation. It can be derived from the time-dependent equation, as was shown in Chapter 14, by assuming that the wave function is a product of two factors,

$$\Psi(q, t) = \psi(q)\zeta(t) \tag{15.1-2}$$

where q stands for all of the coordinates of the particles in the system. With this assumption, the coordinate wave function ψ is an energy eigenfunction, and satisfies the time-independent Schrödinger equation. There are solutions to the time-dependent Schrödinger equation that are not of this form, but wave functions of the form of Eq. (15.1-2) are the most important wave functions in chemistry.

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[1] F. Mandl, *Quantum Mechanics*, Butterworths Scientific Publications, London, 1957, pp. 60ff.

[2] I. N. Levine, *Quantum Chemistry*, 4th ed., Prentice-Hall, Englewood Cliffs, N.J., 1991, pp. 173ff.

15.2 Mathematical Operators

The third postulate will assert that there is a mathematical operator that corresponds to each mechanical variable. A **mathematical operator** is a symbol standing for carrying out one or more mathematical operations. The Hamiltonian operator $\hat{H}$ in the Schrödinger equation is an important example of a quantum-mechanical operator. 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; $h(z)$ is a multiplication operator, standing for multiplication of a function by the function $h(z)$; and c is also a multiplication operator, standing for multiplication of the function by the constant c. We will usually denote an operator by putting a letter with a caret (^) over it.

The result of operating on a function with an operator is another function. If $f(x)$ is the function on which we operate and $g(x)$ is the resulting function, in most cases $g(x)$ is a different function from $f(x)$. Figure 15.1 shows an example of a function, $f(x) = \ln(x)$, and $g(x) = 1/x$, the result of operating on f with the derivative operator, d/dx.

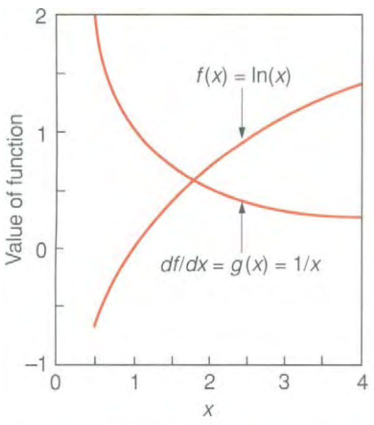

Figure 15.1. A Function and Its Derivative. This figure illustrates the fact that operating on a function generally yields a different function.

Operator Algebra

There is an **operator algebra** in which we symbolically operate on operators themselves without specifying the functions on which the operators operate. For example, an operator can be set equal to another operator in an **operator equation**. The operator that always produces the same function as the one on which it operates is called the **identity operator** and is denoted by $\hat{E}$. It is equivalent to multiplying by unity:

$$\hat{E}f(q) = f(q) \tag{15.2-2}$$

where q is an abbreviation for the independent variables of the function f. Equation (15.2-1) can be written as an operator equation:

$$\hat{E} = 1 \tag{15.2-2}$$

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, which is not written explicitly in the equation. It is not an operator equation if it must be applied to a certain function or set of functions in order to give an equality.

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:

$$\hat{C}f(q) = \hat{A}\hat{B}f(q) = \hat{A}(\hat{B}f(q)) = \hat{A}g(q) \tag{15.2-3}$$

where $g(q)$ is the function produced when $\hat{B}$ operates on $f(q)$. The operator written on the right operates first. That is, the operator closest to the function operates first. The first equality in Eq. (15.2-3) is equivalent to the operator equation:

$$\hat{C} = \hat{A}\hat{B} \tag{15.2-4}$$

Operator multiplication is **associative**, which means that

$$\hat{A}\hat{B}\hat{C} = (\hat{A}\hat{B})\hat{C} = \hat{A}(\hat{B}\hat{C}) \tag{15.2-5}$$

Operator multiplication is not necessarily **commutative**. It can happen that

$$\hat{A}\hat{B} \neq \hat{B}\hat{A} \quad \text{(in some cases)} \tag{15.2-6}$$

If $\hat{A}\hat{B} = \hat{B}\hat{A}$, the operators $\hat{A}$ and $\hat{B}$ are said to **commute**.

The **commutator** of two operators $\hat{A}$ and $\hat{B}$ is denoted by $[\hat{A}, \hat{B}]$ and is equal to the two-term operator

$$[\hat{A}, \hat{B}] = \hat{A}\hat{B} - \hat{B}\hat{A} \quad \text{(definition of commutator)} \tag{15.2-7}$$

If two operators commute, their commutator vanishes.

EXAMPLE 15.1

Find the commutator $\left[x, \frac{d}{dx}\right]$.

Solution

We let the commutator act an arbitrary 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,

$$\left[x, \frac{d}{dx}\right] = -\hat{E} = -1$$

***Exercise 15.1**

Find the commutator $\left[x^2, \frac{d}{dx}\right]$.

The following facts 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.
4. Operators that act on different variables commute with each other.
5. A derivative operator almost never commutes with a multiplication operator containing the same independent variable.

EXAMPLE 15.2

Find the operator $\hat{C} = (\hat{\mathscr{H}} + \hat{\mathscr{V}})^2$ if $\hat{\mathscr{H}}$ and $\hat{\mathscr{V}}$ are two operators that do not commute.

Solution

$$C = (\hat{\mathscr{H}} + \hat{\mathscr{V}})^2 = (\hat{\mathscr{H}} + \hat{\mathscr{V}})(\hat{\mathscr{H}} + \hat{\mathscr{V}}) = (\hat{\mathscr{H}}^2 + \hat{\mathscr{H}}\hat{\mathscr{V}} + \hat{\mathscr{V}}\hat{\mathscr{H}} + \hat{\mathscr{V}}^2)$$

Terms like $\hat{\mathscr{H}}\hat{\mathscr{V}}$ and $\hat{\mathscr{V}}\hat{\mathscr{H}}$ are different from each other if the two operators do not commute.

*Exercise 15.2

a. Find the operator $(\hat{\mathscr{H}}+\hat{\mathscr{V}})^3$ if $\hat{\mathscr{H}}$ and $\hat{\mathscr{V}}$ do not commute.
b. Find the operator $(\hat{A}+\hat{B})^3$ if $\hat{A}$ and $\hat{B}$ do commute.

The operators that are used in quantum mechanics have two important properties: they are linear and hermitian. We discuss these two properties before establishing the operators that correspond to specific mechanical variables.

Linear Operators

An operator $\hat{A}$ is **linear** if

$$\hat{A}[f(q)+g(q)]=\hat{A}f(q)+\hat{A}g(q)\quad \text{(linear operator)} \tag{15.2-8}$$

and if

$$\hat{A}[cf(q)]=c\hat{A}f(q)\quad \text{(linear operator)} \tag{15.2-9}$$

where c is an arbitrary constant and where f and g are arbitrary functions. That is, Eq. (15.2-8) and (15.2-9) must hold no matter what the functions f and g are, so long as the functions are well-behaved (for example, if $\hat{A}$ is a derivative operator, they must be differentiable).

Hermitian Operators

An operator $\hat{A}$ is **hermitian** if it obeys the relation

$$\int f^*\hat{A}g\,dq=\int(\hat{A}f)^*g\,dq=\int(\hat{A}^*f^*)g\,dq\quad \text{(hermitian operator)} \tag{15.2-10}$$

The functions f and g must obey boundary conditions such that the integral converges. All independent variables must be integrated over their entire ranges of values. For example, if q represents the cartesian coordinates of two particles that can move in three dimensions, the integral in this equation is a sixfold integral, and dq stands for $dx_1\,dy_1\,dz_1\,dx_2\,dy_2\,dz_2$. If the particles can move in all of space, the integration limits are $-\infty$ to ∞ for each cartesian coordinate. In Eq. (15.2-10), f^* denotes the complex conjugate of the function f and $\hat{A}^*$ denotes the complex conjugate of the operator $\hat{A}$. The complex conjugate of an operator is taken in the same way as is that of a complex number, by changing the sign of its imaginary part. A real quantity or a real operator is equal to its complex conjugate, and an imaginary quantity or an imaginary operator is the negative of its complex conjugate. Complex quantities are surveyed briefly in Appendix B.

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.
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.

The proofs for Properties 4 and 5 are in Appendix B.

EXAMPLE 15.3

Show

a. the operator d/dx is linear;
b. it is not hermitian.

Solution

a. Linearity:

$$\frac{d}{dx}(f+g) = \frac{df}{dx} + \frac{dg}{dx}$$

$$\frac{d(cf)}{dx} = c\frac{df}{dx}$$

b. Integrating by parts, we obtain

$$\int_{-\infty}^{\infty} f(x)^* \frac{dg}{dx}\,dx = f(x)^* g(x)\Big|_{-\infty}^{\infty} - \int_{-\infty}^{\infty} g(x)\frac{df^*}{dx}\,dx$$

If f and g obey the same boundary conditions as wave functions, they will vanish at the limits of integration, and 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.

Exercise 15.3

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.

---

*Exercise 15.4

Show that the two hermitian operators x and $i(d/dx)$ do not commute and find their commutator.

Two functions f and g are **orthogonal** to each other if

$$\int f^* g\,dq = \int g^* f\,dq = 0 \quad \begin{pmatrix}\text{definition of}\\ \text{orthogonality}\end{pmatrix} \tag{15.2-11}$$

where f^* is the complex conjugate of f and g^* is the complex conjugate of g. The two integrals in Eq. (15.2-11) are the complex conjugates of each other, so that if one vanishes, so does the other.

EXAMPLE 15.4

Show that the first two eigenfunctions of the Hamiltonian operator for the particle in a hard one-dimensional box are orthogonal to each other.

Solution

Since the wave function vanishes outside of the region $0 \leq x \leq a$, we can change the limits of the integral to 0 and a. In general, quantum-mechanical integrals are taken over all values of the coordinates. When we integrate wave functions between finite limits instead of between infinite limits, it is because for the particular system the wave functions vanish outside of the finite limits.

$$\int_{-\infty}^{\infty} \psi_1(x)\psi_2(x)\,dx = \frac{2}{a}\int_0^a \sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{2\pi x}{a}\right)dx = \frac{2}{\pi}\int_0^{\pi} \sin(y)\sin(2y)\,dy = 0$$

where we have looked the integral up in Appendix C. One can also make a graph of the integrand and argue that the positive and negative contributions to the integral cancel each other.

Exercise 15.5

Show that the first two energy eigenfunctions of the harmonic oscillator are orthogonal to each other.

Property 6, that two commuting hermitian operators can have a set of common eigenfunctions, means that a set of functions $f_{jk}(q)$ can be found such that

$$\hat{A}f_{jk}(q) = a_j f_{jk}(q) \tag{15.2-12a}$$

$$\hat{B}f_{jk}(q) = b_k f_{jk}(q) \tag{15.2-12b}$$

where $\hat{A}$ and $\hat{B}$ are two hermitian operators that commute and where a_j and b_k are eigenvalues. Two indices are needed to enumerate all of the functions in the set, because several functions can have the same eigenvalue for $\hat{A}$ but have different eigenvalues for $\hat{B}$. 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.

The completeness specified in Property 7 means we can accurately represent any wave function as a **linear combination** (sum of functions multiplied by constant coefficients) of all of the eigenfunctions of a hermitian operator if the function obeys the same boundary conditions as the eigenfunctions:

$$\psi = \sum_{j=1}^{\infty} c_j f_j \tag{15.2-13}$$

where $f_1, f_2, f_3, \ldots$ are the set of eigenfunctions of some hermitian operator $\hat{A}$, having eigenvalues $a_1, a_2, a_3, \ldots$. The wave function ψ is said to be **expanded** in terms of the set of functions $f_1, f_2, f_3, \ldots$. This set of functions $f_1, f_2, f_3, \ldots$ is called the **basis set**. Sometimes the notation $\{f\}$ or $\{f_j\}$ is used to represent the entire set of functions. The coefficients $c_1, c_2, c_3, \ldots$ are called the **expansion coefficients**, and must have values chosen to represent the specific function ψ. Equation (15.2-13) corresponds to the principle of superposition, already mentioned in Chapter 14 in connection with waves in a flexible string. The sine and cosine functions in a Fourier series are an example of a complete set of functions for representing periodic functions. Although a general proof of this property for eigenfunctions of hermitian operators is lacking, it is generally accepted.

It is possible to represent a time-dependent wave function in terms of time-independent basis functions if the expansion coefficients are time-dependent. For example, we choose the energy eigenfunctions of a system as our basis functions and write

$$\Psi = \sum_{j=1}^{\infty} c_j(t)\psi_j \tag{15.2-14}$$

where $\psi_1, \psi_2, \ldots$ are the energy eigenfunctions (which are time-independent). This function can satisfy the time-dependent Schrödinger equation if the set of expansion coefficients have the proper time dependence.

Exercise 15.6

Show that the function Ψ in Eq. (15.2-14) satisfies the time-dependent Schrödinger equation if

$$c_j(t) = c_j(0)e^{-iE_jt/\hbar} \tag{15.2-15}$$

The result of this exercise shows that the wave function of a system at a given instant can be any function of the proper coordinates that satisfies the boundary conditions required of a wave function (continuity and finiteness). It will then evolve according to the time dependence of the expansion coefficients given in Eq. (15.2-15).

15.3

Postulate 3. Mathematical Operators Corresponding to Mechanical Variables in Quantum Mechanics

This postulate asserts that every mechanical variable has its own hermitian operator.

> **Postulate 3.** *There is a hermitian mathematical operator in one-to-one correspondence with every mechanical variable.*

Finding the Operator to Correspond with a Particular Variable

We begin by asserting that the Hamiltonian operator is the mathematical operator that is in one-to-one correspondence with the energy of a system. This is plausible because the operator $\hat{H}$ occurs on one side of the time-independent Schrödinger equation and the eigenvalue E occurs on the other side of the equation. There is a **one-to-one correspondence** between $\hat{H}$ and E in this equation, which means that the variable E has a unique connection with the operator $\hat{H}$ and vice versa.

We next write the classical Hamiltonian (the classical expression for the energy), which is written as a function of momenta and coordinates (see Appendix D), and associate it with the Hamiltonian operator. For one particle moving in the direction of the x axis,

$$\frac{p_x^2}{2m} + \mathcal{V}(x) \leftrightarrow -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \mathcal{V}(x) \tag{15.3-1}$$

where p_x stands for the x component of the momentum, equal to mv_x. The symbol $\leftrightarrow$ means "is in one-to-one correspondence with." The potential energy function $\mathcal{V}(x)$ occurs on both sides of this equation in the same way, so we postulate that the operator for the potential energy is the operator for multiplication by the potential energy function.

$$\hat{\mathscr{V}} \leftrightarrow \mathscr{V}(x) \tag{15.3-2}$$

We extend this assumption, and postulate that *any function of coordinates corresponds to the operator for multiplication by that function.*

If the potential energy is canceled from the two sides of Eq. (15.3-1), the remaining terms indicate that the operator for the kinetic energy $\mathscr{K}$ is

$$\mathscr{K} \leftrightarrow \frac{1}{2m}\hat{p}_x^2 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \tag{15.3-3}$$

The operator for the square of the x component of the momentum is therefore

$$\hat{p}_x^2 = -\hbar^2 \frac{d^2}{dx^2} \tag{15.3-4}$$

The operator for the square of a momentum component must be the square of the operator for that momentum component. The square of an operator means operating twice with the operator. Therefore, the operator for p_x is

$$p_x \leftrightarrow \hat{p}_x = -i\hbar\frac{d}{dx} = \frac{\hbar}{i}\frac{d}{dx} \tag{15.3-5}$$

If more than one coordinate is involved, we replace the derivative in Eq. (15.3-5) by a partial derivative. Since any quantity has two square roots, the opposite sign could also have been taken. The sign in Eq. (15.3-5) gives the momentum the correct sign when a particle is moving in a known direction (see Problem 15.37).

We complete the third postulate by the additional assumption that the pattern of Eq. (15.3-5) holds for all cartesian momentum components and all functions of momentum components: *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 $\hbar/i$ times the derivative with respect to the corresponding coordinate.* If the use of a coordinate system other than cartesian coordinates is required in a particular problem, the expression for an operator is constructed in cartesian coordinates and then transformed to the other coordinate system. The operator must be hermitian, and it must be verified by comparison of its action with experimental fact.

We can now obtain the Hamiltonian operator for motion in three dimensions, Eq. (14.4-24). For one particle moving in three dimensions

$$\mathscr{K} = \frac{p_x^2 + p_y^2 + p_z^2}{2m} \tag{15.3-6a}$$

and

$$\hat{\mathscr{K}} = -\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) \tag{15.3-6b}$$

EXAMPLE 15.5

Construct the operator for the z component of the angular momentum of one particle about the origin of a cartesian coordinate system.

Solution

The angular momentum is defined in Appendix D as the vector product (cross product)

$$\mathbf{L} = \mathbf{r} \times \mathbf{p} \qquad (15.3\text{-}7)$$

The expression for the z component is

$$L_z = xp_y - yp_x \qquad (15.3\text{-}8)$$

The operator for this component is

$$\hat{L}_z = \frac{\hbar}{i}\left[x\frac{\partial}{\partial y} - y\frac{\partial}{\partial x}\right] \qquad (15.3\text{-}9)$$

The expressions for $\hat{L}_x$ and $\hat{L}_y$ can be obtained similarly.

*Exercise 15.7

a. Construct the operator for $\hat{L}_x$.
b. Construct the operator for $\hat{L}_y$.
c. Construct the operator for $\hat{L}_z^2$.

EXAMPLE 15.6

For motion in the x–y plane, transform the expression for $\hat{L}_z$ to plane polar coordinates.

Solution

The necessary relations are

$$\phi = \arctan(y/z), \qquad \rho^2 = (x^2 + y^2)$$

If f is an arbitrary 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,

$$\hat{L}_z f = \frac{\hbar}{i}\left(\frac{\partial f}{\partial \phi}\frac{x^2}{x^2 + y^2} - \frac{\partial f}{\partial \phi}\frac{-y^2}{x^2 + y^2}\right) = \frac{\hbar}{i}\frac{\partial f}{\partial \phi}$$

so that

$$\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial \phi} \qquad (15.3\text{-}10)$$

This operator equation also holds for spherical polar coordinates and for cylindrical polar coordinates in three dimensions.

Example 15.6 illustrates the procedure that must be used if an operator is needed in other than cartesian coordinates. The operator is first written in cartesian coordinates and then transformed to another coordinate system. The expression for the operator $\hat{L}_z$ in Eq. (15.3-10) will be important in our later discussions of atomic and molecular wave functions. We will also use the expression for $\hat{L}^2$ in spherical polar coordinates, which we present without derivation:

$$\hat{L}^2 = -\hbar^2\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\sin(\theta)\frac{\partial}{\partial\theta} + \frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}\right] \tag{15.3-11}$$

Equation (15.3-11) can also be written

$$\hat{L}^2 = -\hbar^2\left[\frac{\partial^2}{\partial^2\theta} + \cot(\theta)\frac{\partial}{\partial\theta} + \frac{1}{\sin^2(\theta)}\frac{\partial^2}{\partial\phi^2}\right] \tag{15.3-12}$$

EXAMPLE 15.7

Find the commutator $[\hat{x}, \hat{p}_x]$.

Solution

Operate on an arbitrary function $f(x)$:

$$[\hat{x}, \hat{p}_x]f = \frac{\hbar}{i}\left[x\frac{\partial f}{\partial x} - \frac{\partial(xf)}{\partial x}\right] = -\frac{\hbar}{i}f$$

so that

$$[\hat{x}, \hat{p}_x] = -\frac{\hbar}{i} = i\hbar \tag{15.3-13}$$

This example was solved by operating on an arbitrary function. The result does not depend on what this function is.

The commutation relations between operators are important. Some authors find the form of $\hat{p}_x$ by postulating that the commutation relation of Eq. (15.3-13) and its analogues must hold, instead of deducing the form of $\hat{p}_x$ by inspecting the Hamiltonian operator.

Exercise 15.8

***a.** Find the commutator $[\hat{p}_x, \hat{p}_y]$.
b. Show that $[\hat{L}_x, \hat{p}_y] = i\hbar\hat{p}_z$.

15.4 Postulate 4. Expectation Values

The first postulate of quantum mechanics asserts that the wave function of a system determines its state. Any information about the values of mechanical variables must therefore be obtained from the wave function. The fourth postulate provides the methods for obtaining this information:

> **Postulate 4: (a)** *If a mechanical variable A is measured without experimental error, the only possible measured values of a variable A are eigenvalues of the operator $\hat{A}$ that corresponds to A.*

(b) *The expectation value of the error-free measurement of a mechanical variable A can be calculated from the formula*

$$\langle A\rangle = \frac{\int \Psi^* \hat{A} \Psi \, dq}{\int \Psi^* \Psi \, dq} \tag{15.4-1}$$

where $\hat{A}$ is the operator corresponding to the variable A, and where $\Psi = \Psi(q, t)$ is the wave function corresponding to the state of the system immediately prior to the measurement.

As is the case with all quantum-mechanical integrations, the integrals in Eq. (15.4-1) extend over all values of all of the coordinates, which are abbreviated by q. The **expectation value** is defined to be 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 immediately prior to each measurement. It is therefore a statistical piece of information unless it can be shown that every measurement will give the same result.

If the wave function Ψ is a product of a coordinate wave function and a time-dependent factor as in Eq. (14.4-22), the expectation value can be calculated from the coordinate wave function. We substitute the product wave function into Eq. (15.4-1) and use the fact that the complex conjugate of any complex function can be obtained by changing the sign in front of every i symbol that occurs (see Appendix B):

$$(e^{iEt/\hbar})^* = e^{-iEt/\hbar}$$

Therefore,

$$\langle A\rangle = \frac{\int \psi^* e^{iEt/\hbar} \hat{A} \psi e^{-iEt/\hbar} \, dq}{\int \psi^* e^{iEt/\hbar} \psi e^{-iEt/\hbar} \, dq} \tag{15.4-2}$$

The two time-dependent factors in the denominator cancel. If the operator $\hat{A}$ is the operator for an ordinary mechanical variable, it does not depend on time. The time-dependent factor to its right can be factored through it, and cancels with the other time-dependent factor as in the denominator. Therefore,

$$\langle A\rangle = \frac{\int \psi^* \hat{A} \psi \, dq}{\int \psi^* \psi \, dq} \tag{15.4-3}$$

The expectation value in Eq. (15.4-3) is time-independent. This behavior occurs with any expectation value if the operator is independent of the time and if the wave function is the product of an energy eigenfunction and a time factor. A state corresponding to such a wave function is called a **stationary state**. For stationary states, coordinate wave functions can be used to calculate expectation values.

Normalization

There is a conventional way to simplify the formula for the expectation value. The denominator in Eq. (15.4-1) is the same whether we are calculating the expectation value of the angular momentum, the energy, or any other variable. We use the following fact: **If any wave function that satisfies the Schrödinger equation is multiplied by an arbitrary constant it will still satisfy the Schrödinger equation and will still give the same value for any expectation value.**

Exercise 15.9

a. Show that if a wave function Ψ satisfies the time-dependent Schrödinger equation

$$\hat{H}\Psi = i\hbar\frac{\partial\Psi}{\partial t}$$

then the function $C\Psi$ also satisfies it, where C is any constant.

b. Show that if a wave function ψ satisfies the time-independent Schrödinger equation

$$\hat{H}\psi = E\psi$$

then the function $C\psi$ also satisfies it, where C is any constant.

c. Show that the formula in Eq. (15.4-1) for the expectation value is unchanged if Ψ is replaced by $C\Psi$, where C is any constant.

If we choose a value of a constant multiplying a wave function such that

$$\int \Psi^*\Psi\,dq = 1 \quad \text{(definition of normalization)} \tag{15.4-4}$$

the wave function Ψ is then said to be **normalized**. If a normalized wave function is used in Eq. (15.4-1), the expectation value is unchanged and the denominator in the equation equals unity.

$$\langle A\rangle = \int \Psi^*\hat{A}\Psi\,dq \quad (\Psi \text{ is a normalized wave function}) \tag{15.4-5}$$

If the time-dependent wave function in Eq. (15.4-4) is the product of a coordinate factor and a time-dependent factor, the coordinate factor is normalized if the full wave function is normalized.

Exercise 15.10

a. Show that if

$$\Psi(q,t) = \psi(q)e^{-iEt/\hbar}$$

and if

$$\int \Psi^*\Psi\,dq = 1$$

then

$$\int \psi^*\psi\,dq = 1$$

b. Carry out the integration to show that the harmonic oscillator coordinate wave function in Eq. (14.6-8) is normalized.

The Use of Postulate 4 to Obtain Information about Variables

Part (a) of the fourth postulate allows us to determine the list of possible values for any variable by solving the eigenvalue equation for that variable. If there is a discrete spectrum of eigenvalues, the variable is quantized (can take on values from a discrete list). This part of the postulate is not related to a particular state. Part (b) of the postulate provides the means to extract all possible information about mechanical variables from knowledge of the state of the system, but sometimes provides only statistical information about the values of state variables. We distinguish between two different cases. For certain systems, certain states, and certain variables, it is possible to make a precise prediction of the outcome of a measurement from knowledge of the wave function. We will refer to this case as case 1. For some states and some variables, the outcomes of individual measurements will be distributed over various values (all of which must be eigenvalues of the operator). Only statistical predictions can be made. We will refer to this case as case 2.

Position Measurements

Position measurements provide an important example of case 2. Consider the position of 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, $\Psi(x, t)$, just before each measurement. The expectation value of x is

$$\langle x\rangle = \int \Psi(x, t)^* x \Psi(x, t)\, dx \tag{15.4-6}$$

where we assume that the wave function Ψ is normalized. We will not discuss the eigenfunctions of the position operator in detail, but all values of x can be eigenvalues and are thus possible outcomes of the position measurement. See Problem 15.33 for some information about these eigenfunctions and eigenvalues.

Since the multiplication operator x commutes with multiplication by Ψ^*, we can write

$$\langle x\rangle = \int \Psi(x, t)^* x \Psi(x, t)\, dx = \int x \Psi(x, t)^* \Psi(x, t)\, dx = \int x |\Psi(x, t)|^2\, dx \tag{15.4-7}$$

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. (15.4-3):

$$\langle x\rangle = \int x \psi(x, t)^* \psi(x, t)\, dx = \int x |\psi(x, t)|^2\, dx \tag{15.4-8}$$

EXAMPLE 15.8

Find the expectation value for the position of a particle in a one-dimensional hard box of length a if the coordinate wave function is the energy eigenfunction with $n = 1$.

Solution

The normalized particle-in-a-box energy eigenfunction is

$$\psi_n(x) = \sqrt{\frac{2}{a}} \sin\left(\frac{n\pi x}{a}\right) \tag{15.4-9}$$

Since this wave function is normalized and since we are dealing with a stationary state, the expectation value for $n = 1$ can be written as in Eq. (15.4-8):

$$\langle x\rangle = \frac{2}{a} \int_0^a \sin\left(\frac{\pi x}{a}\right) x \sin\left(\frac{\pi x}{a}\right) dx = \frac{2}{a} \int_0^a x \sin^2\left(\frac{\pi x}{a}\right) dx \tag{15.4-10}$$

Integrations like the one in this example are to be taken over all values of the coordinates. The wave function vanishes except in the region between $x = 0$ and $x = a$, so we omit the rest of the region of integration. We change variables and write

$$\langle x\rangle = \frac{2}{a}\left(\frac{a}{\pi}\right)^2 \int_0^{\pi} y\sin^2(y)\,dy = \frac{a}{2} \tag{15.4-11}$$

The predicted mean position of the particle is the middle of the box. This is a reasonable result, since the two halves of the box are like mirror images of each other.

Exercise 15.11

a. Show that the particle-in-a-box energy eigenfunction given in Eq. (15.4-9) is normalized.

b. Verify the value of the integral used in Example 15.8 without using a table.

***Exercise 15.12**

Find $\langle x\rangle$ for a particle in a hard one-dimensional box of length a for the $n = 2$ state.

Probability Densities

We have asserted that position measurements belong to case 2 for almost any kind of wave function. The mean of a set of many repeated measurements of the position of a particle is well defined, but individual members of the set can have different values. We now want to study the probabilities of different outcomes of the position measurement. In Chapter 10, we defined a probability density for a variable denoted by u:

$$\begin{pmatrix}\text{Probability that } u \text{ lies}\\ \text{between } u' \text{ and } u' + du\end{pmatrix} = f(u')\,du$$

The function $f(u)$ is a probability per unit length on the u axis. The mean value of u is given by

$$\langle u\rangle = \int uf(u)\,du \tag{15.4-12}$$

Comparison of Eq. (15.4-7) with Eq. (15.4-12) shows that the probability of finding the particle between x and $x + dx$ is equal to

$$(\text{Probability}) = |\Psi(x, t)|^2\,dx \tag{15.4-13}$$

or

$$(\text{Probability density}) = |\Psi(x, t)|^2 \tag{15.4-14}$$

This is an important result, which we will 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 a single cartesian coordinate, the probability density is a probability per unit length. At any location where the square of the wave function is nonzero, there is some probability of finding the particle. Where the wave function vanishes there is no probability of finding the particle. This corresponds to our earlier assertion that a wave function equal to zero corresponds to the absence of a particle.

For the motion of one 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. (15.4-13):

$$(\text{Probability}) = |\Psi(x, y, z, t)|^2 \, dx \, dy \, dz \tag{15.4-15}$$

The probability density in this case is a probability per unit volume in three dimensions.

$$(\text{Probability density}) = |\Psi(x, y, z, t)|^2 \tag{15.4-16}$$

To obtain the probability that a particle is to be found in a finite region, we integrate $|\Psi(x, y, z, t)|^2$ over the region of interest.

*Exercise 15.13

For a particle in a three-dimensional hard box, the eigenfunction of the Hamiltonian operator is given by Eq. (14.5-39). For the $n_x = 1$, $n_y = 1$, $n_z = 1$ state, find the probability that the particle is in a small rectangular region in 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. Avoid an integration by proceeding as though the wave function were constant in the region so that the probability is the product of the wave function squared times the volume of the region.

For the motion of two particles in three dimensions, the probability that the first particle is between x_1 and $x_1 + dx_1$ and between y_1 and $y_1 + dy_1$ and between z_1 and $z_1 + dz_1$ and that simultaneously the second particle is between x_2 and $x_2 + dx_2$ and between y_2 and $y_2 + dy_2$ and between z_2 and $z_2 + dz_2$ is

$$\begin{aligned}(\text{Probability}) &= |\Psi(x_1, y_1, z_1, x_2, y_2, z_2, t)|^2 \, dx_1 \, dy_1 \, dz_1 \, dx_2 \, dy_2 \, dz_2 \\ &= |\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 \, d^3\mathbf{r}_1 \, d^3\mathbf{r}_2 \end{aligned} \tag{15.4-17}$$

$$(\text{Probability density}) = |\Psi(\mathbf{r}_1, \mathbf{r}_2, t)|^2 \tag{15.4-18}$$

That is, $|\Psi|^2$ is a probability per unit six-dimensional volume. For a system with n particles the square of the magnitude of the wave function is a probability density in a space with $3n$ dimensions (a probability per unit $3n$-dimensional volume).

If a wave function is normalized, its probability density is also normalized. 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, which equals unity for a normalized wave function. For a stationary state, in which the wave function is a product of a coordinate wave function and time factor, the probability density is time-independent:

$$|\Psi(x, t)|^2 = \psi(x)^* e^{iEt/\hbar} \psi(x) e^{-iEt/\hbar} = \psi^*(x)\psi(x) = |\psi(x)|^2 \tag{15.4-19}$$

The analogue of Eq. (15.4-19) can be written for a wave function that depends on more than one coordinate.

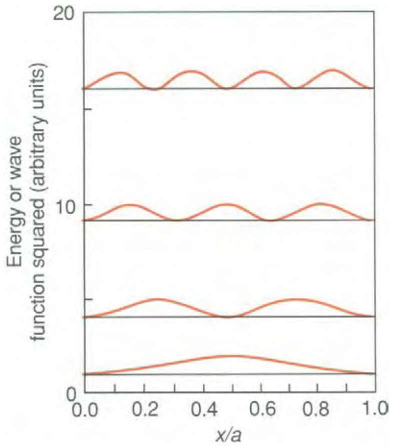

Figure 15.2. The Probability Density for Positions of a Particle in a One-Dimensional Hard Box. This diagram shows the squares of the energy eigenfunctions (probability densities) for the first four states of a particle in a one-dimensional hard box.

Figure 15.2 shows the probability density (square of the magnitude of the wave function) for four energy eigenfunctions of a particle in the box. These four graphs are placed at heights proportional to the energy eigenvalue corresponding to each 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 will be nonzero at only one point, as in Figure 15.3a. The classical

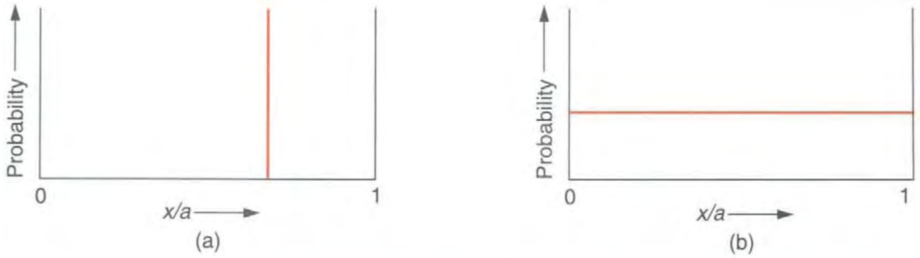

Figure 15.3. The Probability Density for Positions of a Particle in a One-Dimensional Hard Box according to Classical Mechanics. (a) **The instantaneous probability.** At a given time, there is no uncertainty about the position of the particle. (b) **The probability averaged over a long time.** The average probability density is uniform, with all parts of the box equally probable.

probability density averaged over a long time would be uniform, with all parts of the box being equally probable, as shown in Figure 15.3b.

The quantum-mechanical probability density for a stationary state of a particle in a box is time-independent, and is best compared with the time-average classical probability distribution. The probability is distributed over the entire box but is not uniform, and there are points at which the probability density vanishes. However, if a very large value of n is taken, these points become closer and closer together, as schematically shown in Figure 15.4, which is drawn for $n = 10$. For very large values of n, the probability density resembles that of the classical case, since the width of the oscillations in the curve become smaller than the experimental uncertainty of a real measurement. 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.

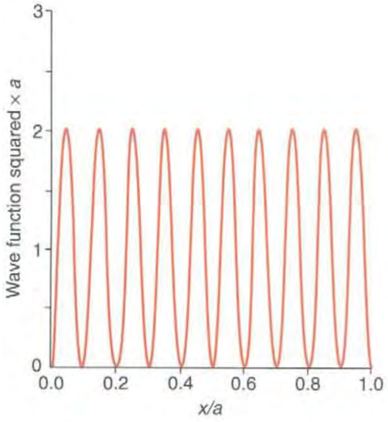

Figure 15.4. The Probability Density for Positions of a Particle in a One-Dimensional Hard Box for $n = 10$. This probability density resembles the time-averaged classical probability density more closely than does that of the lower-energy states.

EXAMPLE 15.9

For a particle in a one-dimensional box 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. The probability of finding the particle in the center region will be

$$(\text{Probability}) = 1 - 2(0.402249) = 0.195501$$

Near a node, the probability density is relatively small. 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.

*Exercise 15.14

From inspection of Figure 15.2, 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 an accurate calculation of the probability.

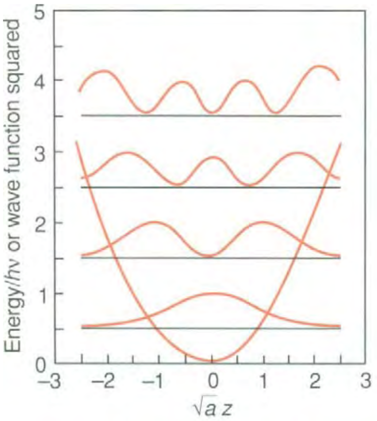

Figure 15.5. The Probability Density for the First Few Energy Eigenstates of the Harmonic Oscillator. Each wave function graph is placed at the height corresponding to its energy eigenvalue, and the potential energy is also plotted The point where the potential energy curve crosses the energy level line is the classical turning point.

Figure 15.5 shows the probability densities for the first few energy eigenfunctions of a harmonic oscillator. Each graph is placed at a height in the figure proportional 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 energy is all potential energy. The vertical axis is used for two different variables, as in Figure 15.2. The behavior of the harmonic oscillator probability density is qualitatively like that of the particle in a box, and the numbers of nodes follows the same pattern. However, for the harmonic oscillator the probability density does not vanish outside of the classically permitted region, but extends beyond the classical turning points. 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.

Distinguishing Case 1 from Case 2

A common measure of the "spread" of a probability distribution is the **standard deviation**, which we have already defined in Eq. (10.2-38). The standard deviation for the measurement of a variable A is denoted by σ_A and defined by

$$\sigma_A = (\langle A^2\rangle - \langle A\rangle^2)^{1/2} \quad \text{(definition)} \tag{15.4-20}$$

The square of the standard deviation is called the **variance**.

Exercise 15.15

Show that application of the definition of the standard deviation in Eq. (15.4-20) to the gaussian probability distribution in Eq. (10.2-37) gives the same standard deviation as specified in that equation.

Calculation of the standard deviation provides a general way to distinguish case 1 from case 2. In case 1, all outcomes for repetition of a measurement will be equal, so that the standard deviation will equal zero. In case 2, the outcomes will be distributed statistically and the standard deviation will be nonzero.

EXAMPLE 15.10

Find the standard deviation for the position of a particle in a hard one-dimensional box of length a for the $n = 1$ state.

Solution

$$\begin{aligned}\langle x^2\rangle &= \frac{2}{a}\int_0^a \sin\left(\frac{\pi x}{a}\right)x^2\sin\left(\frac{\pi x}{a}\right)dx\\ &= \frac{2}{a}\left(\frac{a}{\pi}\right)^3\int_0^\pi y^2\sin(y)\,dy = a^2\left[\frac{1}{3}-\frac{1}{2\pi^2}\right] = 0.282673a^2\end{aligned}$$

From Example 15.8 we have $\langle x\rangle = a/2$, so that

$$\sigma_x = [0.282673a^2 - (a/2)^2]^{1/2} = 0.180756a$$

The fact that the standard deviation is nonzero shows that for this system and this wave function, case 2 applies to the position of the particle, as can be deduced from inspection of the probability distribution.

EXAMPLE 15.11

Calculate the probability that a particle in a one-dimensional hard 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:

$$(\text{Probability}) = \frac{2}{a}\int_{0.319244a}^{0.6807566a} \sin^2\left(\frac{\pi x}{a}\right) dx = \frac{2}{\pi}\int_{1.00293}^{2.13866} \sin^2(y)\, dy$$

$$= \frac{2}{\pi}\left[\frac{y}{2} - \frac{\sin(2y)}{4}\right]\Bigg|_{1.00293}^{2.13866} = 0.65017$$

This value is reasonably close to 0.683, which is the probability for a gaussian distribution that the variable will lie within one standard deviation of the mean. For most probability distributions, approximately two-thirds of a statistical population lie within one standard deviation of the mean.

*Exercise 15.16

a. Calculate the probability that a particle in a one-dimensional hard box will be found within one standard deviation of its mean position for the $n = 2$ state. Comment on the comparison with the fact that with a gaussian distribution the probability would be 0.683.

b. Calculate the probability that a particle in a one-dimensional hard box will be found within one standard deviation of its mean position for the $n = 3$ state.

Uncertainty in the Measurement of a Variable

If case 2 applies, we will use the standard deviation, which we can evaluate from Eq. (15.4-20), as a measure of the width of the probability distribution, or of the **uncertainty** of the measurements of the variable. In general, a single measurement will have roughly a two-thirds probability of lying within one standard deviation of the expectation value.

EXAMPLE 15.12

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

$$z_t^2 = \frac{h\nu}{k} = \frac{h}{k}\frac{1}{2\pi}\sqrt{\frac{k}{m}} = \frac{\hbar}{\sqrt{km}} = \frac{1}{a}$$

$$|z_t| = \sqrt{\frac{1}{a}}$$

The probability that the harmonic oscillator is in the classically permitted region is

$$(\text{Probability}) = \left(\frac{a}{\pi}\right)^{1/2}\int_{-\sqrt{1/a}}^{\sqrt{1/a}} e^{-az^2}\, dz = 2\left(\frac{a}{\pi}\right)^{1/2}\int_{0}^{\sqrt{1/a}} e^{-az^2}\, dz$$

where we have used the fact that since the integrand is an even function, the integral over half of the interval is equal to half of the integral over the entire interval. This integral is related to the error function, which was introduced in Chapter 10 and for which tables of values are available.[3] The error function is defined by

$$\operatorname{erf}(x) = \frac{2}{\sqrt{\pi}}\int_0^x e^{-y^2}\,dy \quad \text{(definition)} \tag{15.4-21}$$

If we make the substitution $y = \sqrt{a}\,z$, we have, from the table of values of the error function in Appendix C:

$$\text{(Probability)} = \frac{2}{\sqrt{\pi}}\int_0^1 e^{-y^2}\,dy = \operatorname{erf}(1) = 0.8427$$

The probability that the oscillating particle is farther away from its equilibrium position than the classical turning point is thus $1.0000 - 0.8427 = 0.1573$, or 15.73% (7.86% being past each end of the classically permitted region). This probability is represented by the two shaded areas in Figure 15.6, which shows the probability density superimposed on a graph of the potential energy function.

*Exercise 15.17

Calculate the value of the following ratio for the harmonic oscillator:

$$\text{Ratio} = \frac{|\psi_0(z_t)|^2}{|\psi_0(0)|^2}$$

Explain in words what this ratio represents.

We have used the position of a particle as an example of a mechanical variable. We must consider other variables, such as the momentum, the energy, and the angular momentum.

EXAMPLE 15.13

For a particle in a one-dimensional box, find $\langle p_x\rangle$, $\langle p_x^2\rangle$ and σ_{p_x} for the $n = 1$ state.

Solution

$$\langle p_x\rangle = \frac{2}{\pi}\int_0^a \sin\left(\frac{\pi x}{a}\right)\frac{\hbar}{i}\frac{d}{dx}\sin\left(\frac{\pi x}{a}\right)dx = \frac{2\hbar}{\pi i}\int_0^a \sin\left(\frac{\pi x}{a}\right)\cos\left(\frac{\pi x}{a}\right)dx = 0$$

$$\langle p_x^2\rangle = \frac{2}{a}\int_0^a \sin\left(\frac{\pi x}{a}\right)(-\hbar^2)\frac{d^2}{dx^2}\sin\left(\frac{\pi x}{a}\right)dx = \frac{2}{a}\hbar^2\left(\frac{\pi}{a}\right)^2\int_0^a \sin\left(\frac{\pi x}{a}\right)\sin\left(\frac{\pi x}{a}\right)dx$$

$$= \frac{2}{a}\hbar^2\left(\frac{\pi}{a}\right)^2\frac{a}{2} = \frac{\hbar^2\pi^2}{a^2}$$

$$\sigma_{p_x} = [\langle p_x^2\rangle - \langle p_x\rangle^2]^{1/2} = \langle p_x^2\rangle^{1/2} = \frac{\hbar\pi}{a} = \frac{h}{2a}$$

---

[3] M. Abramowitz and I. A. Stegun, eds. *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables*, U.S. Government Printing Office, Washington, D.C., 1964. See Appendix 8 for a table of values.

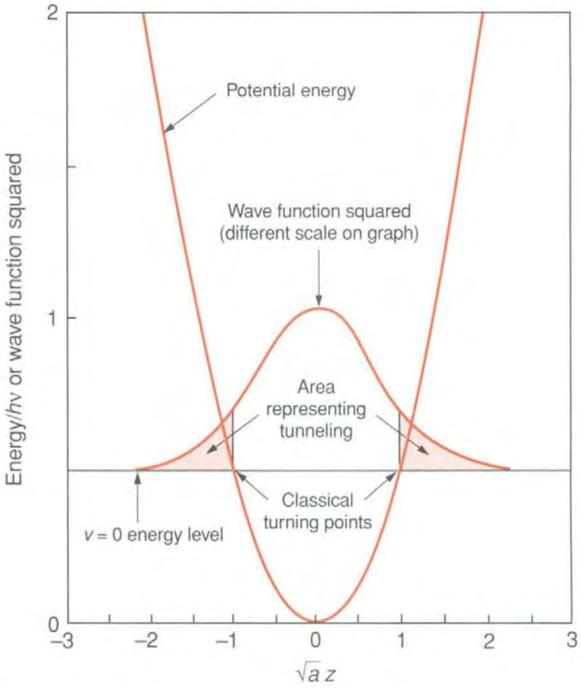

Figure 15.6. The Probability Density of a Harmonic Oscillator in Its Ground State, Showing Tunneling. The shaded areas represent the probability that the oscillator will be in classically forbidden regions.

Exercise 15.18

Show that the uncertainty in the energy of a particle in a box is equal to zero if it is known that the particle is in the $n = 1$ state or any other state corresponding to an energy eigenfunction.

The nonzero value of the standard deviation shows that for this system and this state, case 2 applies to the momentum, while the zero value for the standard deviation of the energy in Exercise 15.18 shows that the energy belongs to case 1 for this system and this state.

Heisenberg's Uncertainty Principle

We use σ_x and σ_{p_x} as measures of the uncertainty in predictions of position and momentum. Their product is a measure of the combined uncertainty of the two variables, and is called an **uncertainty product**. From Examples 15.10 and 15.13, the value of the uncertainty product of x and p_x for the $n = 1$ state of the particle in a one-dimensional hard box is

$$\sigma_x\sigma_{p_x} = (0.180756a)\frac{\hbar\pi}{a} = 0.56786\hbar = 0.09038h \qquad (15.4\text{-}22)$$

Table 15.1 gives some values of σ_x and p_{p_x} for a particle in a box. The coordinate x and the momentum component p_x are **conjugate variables** in the sense of Eq. (D-19) of Appendix D. The **Heisenberg uncertainty principle** is a general statement of the combined uncertainties of two conjugate variables: *The product of the uncertainties of*

Table 15.1. Values of the Uncertainty Product for a Particle in a One-Dimensional Box

n	σ_x	σ_{p_x}	$\sigma_x \sigma_{p_x}$
1	$0.18076a$	$h/2a$	$0.09038h = 0.56786\hbar$
2	$0.26258a$	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 π 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}	∞	∞

two conjugate variables is equal to or larger than $h/4\pi$, 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

$$\boxed{\Delta x \, \Delta p_x \geq \frac{h}{4\pi} = \frac{\hbar}{2}} \tag{15.4-23}$$

Equation (15.4-23) corresponds to the use of the standard deviation as the measure of uncertainty. There are other measures of the uncertainty of a statistical prediction besides the standard deviation. 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 probability the right-hand side of Eq. (15.4-23) would be replaced by a larger value. The actual value of the uncertainty product depends on the nature of 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 $h/(4\pi)$.

Coordinates and momenta are not the only variables that have nonzero uncertainty products. The commutator of the operators of two conjugate variables is nonzero, as we have already seen for the commutator $[x, p_x]$. Any two variables whose operators do not commute must have a nonzero uncertainty product. There is a general relation

$$\Delta A \, \Delta B \geq \left| \frac{1}{2} \int \psi^* [\hat{A}, \hat{B}] \psi \, dq \right| \tag{15.4-24}$$

where $[\hat{A}, \hat{B}]$ is the commutator of $\hat{A}$ and $\hat{B}$.[4] From the commutator of two angular momentum components, we can see that two components of the angular momentum

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[4] Levine (*Quantum Chemistry*, 4th ed, Prentice-Hall, Engelwood Cliffs, N.J., 1991 pp. 82, 188) assigns the proof as a homework problem. A lot of hints are included, but it is a fairly long proof.

obey an uncertainty relation, at least for states for which the eigenvalue of the third component is not equal to zero. See Problem 15.36.

Exercise 15.19

Use Eqs. (15.4-24) and (15.3-13) to obtain the uncertainty relation for x and p_x.

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 case 2 applies to at least one of a conjugate pair of variables, and if case 1 applies to one of the variables, the other variable has an infinite uncertainty.

EXAMPLE 15.14

Find $\langle p_x \rangle$ and σ_{p_x} for a free particle in a state corresponding to the wave function of Eq. (14.5-25).

Solution

We cancel the time-dependent factors to obtain

$$\langle p_x \rangle = \frac{\dfrac{\hbar}{i} D^*D \displaystyle\int e^{-i\kappa x}\frac{d}{dx}e^{i\kappa x}\,dx}{D^*D\displaystyle\int e^{-i\kappa x}e^{i\kappa x}\,dx} = \hbar\kappa\frac{D^*D\displaystyle\int e^{-i\kappa x}e^{i\kappa x}\,dx}{D^*D\displaystyle\int e^{-i\kappa x}e^{i\kappa x}\,dx} = \hbar\kappa\frac{D^*D\displaystyle\int dx}{D^*D\displaystyle\int dx}$$

We have not written the limits on the integrals, which are $-\infty$ and ∞. We specify that the limits are $-L$ and L, with the intention of taking the limit that $L \to \infty$. We cancel the integrals in the last quotient of integrals prior to taking the limit, and obtain

$$\langle p_x \rangle = \hbar\kappa$$

To calculate σ_{p_x}, we require $\langle p_x^2 \rangle$, which is given by a similar quotient of integrals except that the second derivative is taken:

$$\langle p_x^2 \rangle = \hbar^2\kappa^2$$

The square of the standard deviation is

$$\sigma_{p_x}^2 = \langle p_x^2 \rangle - \langle p_x \rangle^2 = \hbar^2\kappa^2 - \hbar^2\kappa^2 = 0$$

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.

Exercise 15.20

Write the integral to calculate σ_x for the free particle of Example 15.14 and argue that its value is 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. (15.3-5). 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 15.14. If we combine this coordinate wave function with the appropriate time factor, $\exp(-iEt/\hbar)$, we obtain the time-dependent wave function

$$\Psi = D\exp^{i(\kappa x - Et/\hbar)}$$

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 15.21

Show that taking the opposite sign for the momentum operator leads to a negative value of $\langle p_x \rangle$.

The Time–Energy Uncertainty Relation

Like position and momentum, energy and time also obey an uncertainty relation:

$$\Delta E\, \Delta t \geq \frac{h}{4\pi} \tag{15.4-25}$$

The time–energy uncertainty relation is different from that of position and momentum, since 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. Although the time-dependent Schrödinger equation has the Hamiltonian operator on one side and the time derivative operator on the other, this does not imply that $i\hbar\, \partial/\partial t$ can be used as an operator for the energy, although such an operator relationship would lead to a commutator that would establish Eq. (15.4-25).[5] The Hamiltonian operator is the operator corresponding to the energy, and a single variable cannot correspond to two different operators.

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 state as given by Eq. (15.4-25). This is a different interpretation from the interpretation of the uncertainties in position and momentum, which can be expressed as standard deviations. Even if the state being considered corresponds to an energy eigenfunction, which has a zero value of σ_E, the fact that it is known to be in this state for only a finite length of time imposes an uncertainty on the energy, which we understand to be an actual uncertainty in the value of the energy eigenvalue. It is as though when a system makes a transition into a new state, the energy of the system gradually settles toward the fixed value corresponding to having been in the state forever. This uncertainty 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." It is important only if a system is observed very shortly after it makes a transition to a given state.

EXAMPLE 15.15

The lowest energy eigenvalue for a hydrogen atom is −13.6 eV. Calculate the uncertainty in this energy if the atom has been in the state corresponding to this energy for 1.0 nanosecond.

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[5] Y. Aharanov and D. Bohm, *Phys. Rev.*, **122**, 1649 (1961).

Solution

$$\Delta E \geq \frac{\hbar}{2}\frac{1}{\Delta t} = \frac{6.6261 \times 10^{-34}\,\mathrm{J\,s}}{4\pi}\frac{1}{1.0 \times 10^{-9}\,\mathrm{s}} = 5.3 \times 10^{-26}\,\mathrm{J}$$
$$= 3.3 \times 10^{-7}\,\mathrm{eV}$$

This uncertainty is smaller than the energy eigenvalue by a factor of 2.4×10^{-8}.

*Exercise 15.22

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.

We have stated that case 1 applies when the state of the system just prior to a measurement corresponds to an eigenfunction of the operator for the variable. The time–energy uncertainty principle means that it must be known that the system has been in this state for an infinite length of time for case 1 to apply with absolute accuracy.

EXAMPLE 15.16

For a particle in a one-dimensional hard box, find $\langle E\rangle$ and σ_E for the state corresponding to the $n = 1$ energy eigenfunction.

Solution

$$\sigma_E = [\langle E^2\rangle - \langle E\rangle^2]^{1/2} \tag{15.4-26}$$

Using the normalized wave function,

$$\langle E\rangle = \int \psi_1^*\hat{H}\psi\,dx = \int \psi_1^* E_1\psi_1\,dx = E\int \psi_1^*\psi_1\,dx = E_1 = \frac{h^2}{8ma^2}$$

since the wave function is an eigenfunction of $\hat{H}$. Also

$$\langle E^2\rangle = \int \psi_1^*\hat{H}^2\psi_1\,dx = \int \psi_1^* E_1^2\psi_1\,dx = E_1^2\int \psi_1^*\psi_1\,dx = E_1^2$$

where we have used the fact that $\hat{H}^2$ means operation twice with $\hat{H}$. The standard deviation vanishes:

$$\sigma_E = (E_1^2 - E_1^2)^{1/2} = 0$$

However, it must be known that the system has been in this state for an infinite length of time for this result to apply exactly.

The result of Example 15.16 illustrates the important general fact: *If the wave function is an eigenfunction of the operator corresponding to the variable being measured, the outcome of an error-free measurement is completely predictable (the measurement belongs to case 1).* The only value that will occur is the eigenvalue corresponding to the given eigenfunction.

Exercise 15.23

a. For a general system whose wave function ψ_j is an eigenfunction of the operator $\hat{A}$ with eigenvalue a_j, show that $\langle A\rangle = a_j$ and that the standard deviation, σ_A, vanishes.

***b.** For a one-dimensional harmonic oscillator, find $\langle E\rangle$ and σ_E for the state corresponding to the $v = 1$ energy eigenfunction.

Although we have discussed energy eigenfunctions to the exclusion of other kinds of wave functions, there is no requirement that the wave function actually corresponding to the state of a system be an energy eigenfunction.

EXAMPLE 15.17

For a one-dimensional harmonic oscillator, find $\langle E\rangle$ and σ_E if the state just prior to the measurements 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. (14.6-8) and (14.6-9).

Solution

Since ψ is normalized, we can omit the denominator in the formula for the expectation value:

$$\begin{aligned}\langle E\rangle &= \frac{1}{2}\int_{-\infty}^{\infty}(\psi_0^* + \psi_1^*)\hat{H}(\psi_0 + \psi_1)\,dx = \frac{1}{2}\int_{-\infty}^{\infty}(\psi_0^* + \psi_1^*)(E_0\psi_0 + E_1\psi_1)\,dx \\ &= \frac{1}{2}\left[E_0\int_{-\infty}^{\infty}\psi_0^*\psi_0\,dx + E_1\int_{-\infty}^{\infty}\psi_0^*\psi_1\,dx + E_0\int_{-\infty}^{\infty}\psi_0^*\psi_0\,dx + E_1\int_{-\infty}^{\infty}\psi_1^*\psi_1\,dx\right] \\ &= \frac{1}{2}(E_0 + 0 + 0 + E_1) = \frac{1}{2}(E_0 + E_1) = h\nu\end{aligned}$$

We have used the normalization of the energy eigenfunctions, the fact that the two energy eigenfunctions are orthogonal to each other, and the expression for the energy eigenvalues.

$$\begin{aligned}\langle E^2\rangle &= \frac{1}{2}\int_{-\infty}^{\infty}(\psi_0^* + \psi_1^*)\hat{H}^2(\psi_0 + \psi_1)\,dx \\ &= \frac{1}{2}\int_{-\infty}^{\infty}(\psi_0^* + \psi_1^*)(E_0^2\psi_0 + E_1^2\psi_1)\,dx = \frac{1}{2}(E_0^2 + E_1^2) = \frac{5}{4}(h\nu)^2\end{aligned}$$

We have omitted some steps. We now have

$$\sigma_E = [\langle E^2\rangle - \langle E\rangle^2]^{1/2} = \left[\frac{5}{4}(h\nu)^2 - (h\nu)^2\right]^{1/2} = \frac{h\nu}{2}$$

For the state corresponding to this wave function, case 2 applies to the energy.

*Exercise 15.24

For a particle in a one-dimensional hard 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.

We now obtain a general formula for the expectation value of $\hat{A}$ when the wave function is expressed as a linear combination of basis functions as in Eq. (15.2-13). If the set of functions $f_1, f_2, f_3, \ldots,$ are eigenfunctions of a hermitian operator $\hat{A}$ they form a complete set and we can write

$$\psi = \sum_{k=1}^{\infty} c_k f_k^* \qquad (15.4\text{-}27)$$

If a complete set consists of normalized functions that are orthogonal to each other, we call it a **complete orthonormal set**. We substitute the expansion of Eq. (15.4-27) into the expression for the expectation value, Eq. (15.4-1), assuming that ψ is normalized:

$$\langle A \rangle = \int \psi^* \hat{A} \psi \, dq = \sum_{j=1}^{\infty} \sum_{k=1}^{\infty} c_j^* c_k a_k \int f_j^* f_k \, dq \tag{15.4-28}$$

We have used the eigenfunction property, have factored the constants out of the integrals, and have exchanged the order of integrating and summing. In order for it to be possible to exchange the order of summing and integrating, the sums and integrals must be uniformly convergent

Since the functions $f_1, f_2, \ldots$ are an orthonormal set, those integrals in which $j \neq k$ will vanish, and the integrals with $j = k$ will equal unity. We write

$$\int f_j^* f_k \, dq = \delta_{jk} = \begin{cases} 1 & \text{if } j = k \\ 0 & \text{if } j \neq k \end{cases} \tag{15.4-29}$$

This equation defines the quantity δ_{jk}, which equals unity when its two indices are equal 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, and the sum over k collapses to a single term and the double sum collapses to a single sum.

$$\langle A \rangle = \sum_{j=1}^{\infty} \sum_{k=1}^{\infty} c_j^* c_k a_k \delta_{jk} = \sum_{j=1}^{\infty} c_j^* c_j a_j = \sum_{j=1}^{\infty} |c_j|^2 a_j \tag{15.4-30}$$

Comparison of Eq. (15.4-30) with Eq. (1.5-4) shows that $\langle A \rangle$ is given in the same way as a mean value is given from individual values and their probabilities. We have already asserted in Postulate 4 that individual measurements of A can give as a result only one or another of the eigenvalues of the operator $\hat{A}$, and we now assert that the probability that the eigenvalue a_j will occur is

$$p_j = |c_j|^2 \tag{15.4-31}$$

***Exercise 15.25**

Find the probability of each of the eigenvalues in Exercise 15.24.

15.5 Postulate 5. The Determination of the State of a System

The fifth and final postulate gives the rule for determining the mechanical state of a quantum-mechanical system:

> **Postulate 5.** *Immediately after an error-free measurement of the mechanical variable A in which the outcome was the eigenvalue a_j, the state of the system corresponds to a wave function that is an eigenfunction of $\hat{A}$ with eigenvalue equal to a_j.*

This postulate says nothing about the state of the system prior to the measurement, because the act of measurement can change the state of the system. If the energy of a particle in a box is measured and the result equals E_2, then the system is definitely in the state corresponding to the energy eigenfunction ψ_2 immediately after the measurement. It could have been in any state prior to the measurement so long as the wave function for that state if represented as a linear combination of energy eigenfunctions included a term for ψ_2.

The measurement of a variable belonging to case 2 is more complicated. Consider the determination of the position of a particle by allowing it to scatter electromagnetic radiation, much as an airplane reflects radar waves. When a macroscopic object such as an airplane reflects an electromagnetic wave, the effect on the object is negligible. When an object of small mass such as an electron scatters light, the effect is not negligible. If the position of an electron is to be determined to an accuracy of 0.1 nm, radiation with a wavelength of no more than 0.1 nm is needed.

EXAMPLE 15.18

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. Compare the energy of a photon of wavelength 0.10 nm with the lowest kinetic energy of an electron in a one-dimensional box of length 1.0 nm.

Solution

$$E(\text{photon}) = h\nu = \frac{hc}{\lambda} = \frac{(6.6261 \times 10^{-34}\,\text{J s})(3.00 \times 10^{8}\,\text{m s}^{-1})}{1.00 \times 10^{-10}\,\text{m}}$$

$$= 1.99 \times 10^{-15}\,\text{J}$$

From the result of Example 14.6,

$$E(\text{electron}) = 6.0 \times 10^{-20}\,\text{J}$$

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.

There is another argument. Assume that a particle in a box of length a is in a state corresponding to one of the energy eigenfunctions. The square of the wave function is the probability density for finding the particle, and this quantity is nonzero over the entire box except for the locations of nodes in the wave function. However, a single position measurement will give a single well-defined outcome, such as the location of a flash of light at a screen. An immediate repetition of the measurement would have to give a position very near the first position, since there would be no time for the particle to move appreciably. The wave function immediately after the first measurement must be a function that is nonzero only in the immediate vicinity of the measured position, since the square of the magnitude of the wave function is the probability density for finding the particle. The act of measurement must have changed the wave function. Figure 15.7a shows a possible wave function just before the measurement of position. Figure 15.7b shows the wave function schematically immediately after the position measurement. Figure 15.7c shows the wave function after a fairly short time has elapsed. The wave function has begun to evolve back into a delocalized wave function. We could follow this evolution by solving the time-dependent Schrödinger equation.

The fifth postulate asserts that the wave function immediately after the measurement of an observable A is an eigenfunction of $\hat{A}$ with eigenvalue a_i equal to the outcome of the measurement. If the eigenvalue is nondegenerate, the act of measurement has put the system into a known state. If several eigenfunctions of $\hat{A}$ have the same eigenvalue, the act of measurement has not put the system into a known state. Let g_i be the number

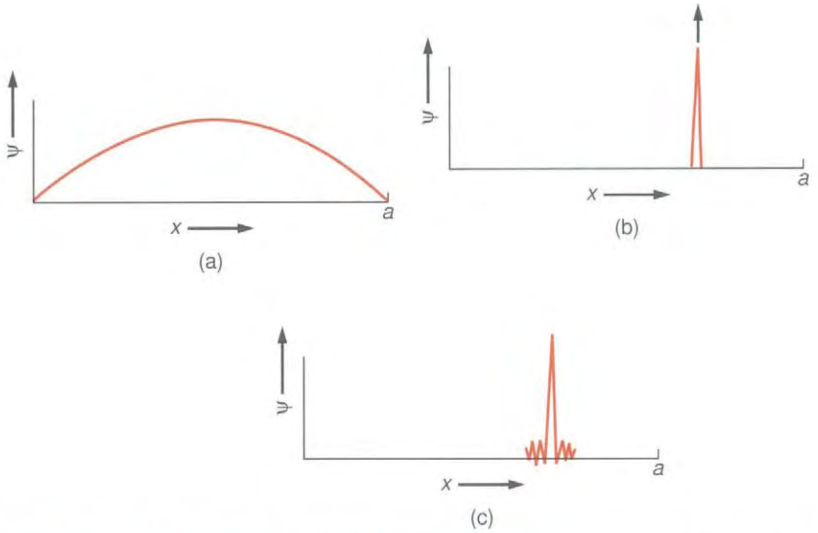

Figure 15.7. The Wave Function of a Particle in a Box. (a) **Before a position measurement (schematic).** The probability density is nonzero over the entire box (except for the endpoints). (b) **Immediately after the position measurement (schematic).** In a very short time, the particle cannot have moved far from the position given by the measurement, and the probability density must be a sharply peaked function. (c) **Shortly after a position measurement (schematic).** After a short time, the probability density can be nonzero over a larger region.

of different eigenfunctions whose eigenvalues equal a_i. If these are numbered from 1 to g, the wave function immediately after the measurement is

$$\psi(\text{after}) = \sum_{j=1}^{g_i} c_j(\text{after}) f_j \tag{15.5-1}$$

where $f_1, f_2, \ldots,$ are the eigenfunctions whose eigenvalues equal 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. However, if there are other variables whose operators commute with $\hat{A}$, measurement of enough of these variables can put the system into a known state. We say that such a set of variables form a **complete set of commuting observables**. For example, a complete set of commuting observables for the electron in a hydrogen atom has four variables. We will discuss this in the next chapter.

Information about the State Prior to a Measurement

A single measurement gives us information about the state after the measurement. Some information about the original wave function of a quantum-mechanical system can be obtained by repeated measurements if we have a procedure to put the system back into the original state before each measurement.

Consider the nondegenerate case, that each eigenfunction of the operator $\hat{A}$ corresponding to a variable A has a distinct eigenvalue. Since the set of eigenfunctions is assumed to be a complete set, the wave function prior to the measurement can be represented as a linear combination of eigenfunctions of $\hat{A}$, as in Eq. (15.2-13):

$$\psi(\text{prior}) = \sum_{j=1}^{\infty} c_j(\text{prior}) f_j \tag{15.5-2}$$

We now make a set of many measurements of A, ensuring somehow that the system is in the same state prior to each measurement. (If this cannot be done, we cannot determine anything about the state prior to the measurements.) Each outcome will be an eigenvalue of $\hat{A}$, and we can determine the fraction of measurements corresponding to each eigenvalue. Let the fraction that results in the value a_j be equal to p_j. By Eq. (15.4-31),

$$|c_j(\text{prior})| = \sqrt{p_j} \tag{15.5-3}$$

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 more than one eigenvalue has a nonzero probability, we can determine the magnitudes of the $c_j(\text{prior})$ coefficients. 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 measurement unless case 1 applies.

Summary of the Chapter

In this chapter we have presented 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 Schrödinger equation, which governs the wave functions.

The third postulate was that there is a hermitian mathematical operator in one-to-one correspondence to each mechanical variable for a given system. The recipe for writing the operator for a given variable is: (1) write the classical expression for the variable in terms of cartesian coordinates and momentum component, (2) replace each momentum component by the relation

$$p_{x_j} \leftrightarrow \frac{\hbar}{i}\frac{\partial}{\partial x}$$

and its analogues.

The fourth postulate provides the means for predicting values of mechanical variables from operators and the wave function of the system. The first part of the postulate is that the only possible outcomes of a measurement of a variable are the eigenvalues of the operator corresponding to that variable, and the second part is that the expectation value of the variable A is given by

$$\langle A \rangle = \frac{\int \Psi^* \hat{A} \Psi \, dq}{\int \Psi^* \Psi \, dq}$$

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 $\hat{A}$, the only possible outcome of the measurement is the eigenvalue corresponding to that eigenfunction. In this case, a measurement is completely predictable, similar to the case in classical mechanics. If the wave function is not an eigenfunction of $\hat{A}$, the standard deviation gives a measure of the spread of the distribution of results.

The fifth postulate states that in a measurement of A, if the result is a_j, one of the eigenvalues of $\hat{A}$, 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.

PROBLEMS

Problems for Section 15.2

15.26. 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. $\sin(\ldots)$

***15.27.** Determine whether each of the following operators is linear and whether it is hermitian.

a. $\ln(\ldots)$

b. $\dfrac{c}{x} + i\dfrac{d}{dx}$, where c is a constant and $i = \sqrt{-1}$.

c. $ix\dfrac{d}{dx}$, where $i = \sqrt{-1}$.

15.28. Find an expression for the commutator $\left[x, \dfrac{d^2}{dx^2}\right]$.

***15.29.** Find a simplified expression for the operator $\left[\dfrac{1}{x} + \dfrac{d}{dx}\right]^2$

15.30. A **function of an operator** is defined through the Taylor series representing the function. For example, the exponential of an operator is defined as the series

$$e^{\hat{A}} = 1 + \hat{A} + \frac{1}{2!}\hat{A}^2 + \frac{1}{3!}\hat{A}^3 + \cdots$$

where the operator products are defined in the usual way, as successive operations of the operator.

a. Write the formula for the result when $e^{\hat{A}}$ operates on an eigenfunction of $\hat{A}$.

b. Write the expression for the first three terms of $e^{(\hat{A}+\hat{B})}$, where $\hat{A}$ and $\hat{B}$ are two operators that do not necessarily commute.

15.31. a. Find the expression for $\sin(\hat{A})$.

b. Find the expression for $\cos(\hat{A})$.

c. Find the expression for $\ln(\hat{A})$.

c. Write the expression for the first two terms of $\sin(\hat{A} + \hat{B})$, where $\hat{A}$ and $\hat{B}$ are two operators that do not necessarily commute.

15.32. Find the complex conjugate of each of the following. Do it once by replacing i by $-i$, and once by separating the real and imaginary parts. In each case $z = x + iy$, where x and y are real.

a. $\sinh(z)$

b. $\cos(z)$

c. $\tan(z)$

Problems for Section 15.3

15.33. The eigenfunctions of coordinate operators are **Dirac delta functions**, defined such that $\delta(x - a) \to \infty$ if $x = a$ and $\delta(x - a) = 0$ if $x \neq a$, and such that

$$\int_b^c \delta(x - a)\, dx = 1$$

if $b < a < c$.

a. Show that $\delta(x - a)$ is an eigenfunction of x.

***b.** What is the eigenvalue of $\delta(x - a)$?

15.34. a. Show that the operator x is linear and hermitian.

b. Show that the operator for multiplication by a function, $h(x)$, is linear and hermitian.

***15.35. a.** Find the eigenfunctions and eigenvalues of $\hat{p}_x = -i\hbar(\partial/\partial x)$.

b. Are the energy eigenfunctions for a particle in a hard 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.

15.36. **a.** Show that $[\hat{L}_x, \hat{L}_y] = i\hbar\hat{L}_z$.

b. Argue from the result of part (a) that $[\hat{L}_z, \hat{L}_x] = i\hbar\hat{L}_y$ and that $[\hat{L}_y, \hat{L}_z] = i\hbar\hat{L}_x$.

Problems for Section 15.4

15.37. 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

$$\Psi = e^{i\kappa x}e^{-iEt/\hbar}$$

15.38. **a.** Find the eigenfunctions $\Phi(\phi)$ of the operator for the z component of the angular momentum, $\hat{L}_z = -i\hbar(\partial/\partial\phi)$.

b. Since $\phi = 0$ and $\phi = 2\pi$ refer to the same location, the boundary condition

$$\Phi(0) = \Phi(2\pi)$$

is imposed. Find the eigenvalues of $\hat{L}_z$.

15.39. **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.

15.40. 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 $\langle\mathscr{K}\rangle + \langle\mathscr{V}\rangle = E$. Do you think that this will also be true for the other energy eigenfunctions? Check it out for $v = 1$.

*15.41. **a.** Calculate $\langle p_x^2\rangle$ for each of the first three energy eigenfunctions for the particle in a one-dimensional hard 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 for a particle in a one-dimensional hard box.

c. Find the limit of the expression of part (b) as $n \to \infty$.

15.42. **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. The identity in Problem 10.29 can be used.

*15.43. 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.

15.44. **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 $n \to \infty$.

*15.45. **a.** Calculate the uncertainty product $\sigma_x\sigma_{p_x}$ for a harmonic oscillator for 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.

15.46. **a.** Find the commutator $[\hat{x}, \hat{L}_z]$.

b. Using Eq. (15.4-24), find an uncertainty relation for $\hat{x}$ and $\hat{L}_z$ for a particular state, the lowest-energy state of a particle in a cubical box of size a by a by a.

Problems for Section 15.5

*15.47. **a.** Find $\langle E\rangle$for the coordinate wave function

$$\psi(x) = \sqrt{\tfrac{1}{3}}\psi_0 + \sqrt{\tfrac{1}{3}}\psi_1 + \sqrt{\tfrac{1}{3}}\psi_2$$

where ψ_0, ψ_1, and ψ_2 are the three lowest-energy harmonic oscillator energy eigenfunctions.

b. Find σ_E for the wave function in part (a).

c. Say 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.

15.48. **a.** A measurement of the energy of a particle in a three-dimensional cubical box gives a value $14h^2/(8ma^2)$. Say 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?

•15.49. The energy of a particle in a one-dimensional hard 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?

General Problems

15.50. **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).

15.51. **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 $\sigma_x\sigma_{p_x}$ for a particle in a one-dimensional box of length a corresponding to a general energy eigenfunction ψ_n.

e. For the baseball in Problem 14.59, find the value of the uncertainty σ_x.

f. For the baseball in Problem 14.59, find the value of the uncertainty σ_{p_x}.

g. For the baseball in Problem 14.59, find the value of the uncertainty product $\sigma_x\sigma_{p_x}$.

15.52. Label each statement as either true or false. If a statement is true only under certain circumstances, label it as false.

a. Every wave function satisfies the time-independent Schrödinger equation.

b. Every 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.

16

The Electronic States of Atoms. I. The Hydrogen Atom and the Simple Orbital Approximation for Multielectron Atoms

OBJECTIVES

After studying this chapter, a student should:

1. understand the central-force problem, including the angular momentum properties of a central-force system;
2. be able to solve problems related to the angular momentum of a single particle;
3. understand the solution of the Schrödinger equation for the hydrogen atom and be able to solve problems related to it;
4. be familiar with the principal properties of the hydrogenlike orbitals and be able to solve problems related to them;
5. understand the possible states for multielectron atoms and be able to assign term symbols for different electron configurations of multielectron atoms.

PRINCIPAL FACTS AND IDEAS

1. The Schrödinger equation for the hydrogen atom is an example of the "central-force problem," in which the potential energy depends only on the distance between the two particles that make up the system.
2. In the central-force problem, the angular momentum of the system can have definite values if the system is in a state corresponding to an energy eigenfunction.
3. The Schrödinger equation for the hydrogen atom can be solved exactly, giving electronic wave functions called orbitals.
4. Electrons have intrinsic (spin) angular momentum in addition to the angular momentum of orbital motion. Spin orbitals describe both space and spin behavior.
5. Each electron in a multielectron atom occupies a hydrogenlike spin orbital if the simple orbital approximation is applied.
6. The wave function for a multielectron atom must be antisymmetric. That is, the wave function changes sign if the coordinates of two electrons are exchanged.
7. In an orbital wave function, every electron must occupy a different spin orbital (the Pauli exclusion principle).
8. The total orbital angular momentum and the total spin angular momentum correspond to the same pattern as other angular momenta, and are used to characterize the energy levels of multielectron atoms.

16.1 The Hydrogen Atom and the Central Force System. Angular Momentum

A hydrogen atom consists of a single electron with charge $-e$ and a nucleus containing a single proton with charge e, as depicted in Figure 16.1. The Hamiltonian operator for this system contains the potential energy function that corresponds to Coulomb's law

$$\mathcal{V}(r) = -\frac{e^2}{4\pi\varepsilon_0 r} \tag{16.1-1}$$

where ε_0 is the permittivity of the vacuum and where r is the distance between the particles. The hydrogen atom is a member of a class of systems called **central-force systems**, which consist of two particles separated by a distance r with a potential energy function $\mathcal{V}$ that depends only on r. The Schrödinger equation will be expressed in spherical polar coordinates, and the variables can be separated in this coordinate system. The solution for the θ and ϕ factors is the same for any central-force system. The results of this part will give us all of the information that can be obtained about the angular momentum of the hydrogen atom or any other central-force system. We will then proceed to the solution for the r factor, which is specific to the hydrogen atom.

To construct the Hamiltonian operator for any system we write the classical Hamiltonian function in cartesian coordinates and then make the replacements analogous to Eq. (15.3-5) to form the Hamiltonian operator. The cartesian coordinates of the nucleus are denoted by x_n, y_n, and z_n, and the cartesian coordinates of the electron are denoted by x_e, y_e, and z_e. However, the variables cannot be separated with these coordinates. We transform to relative coordinates and center-of-mass coordinates. The **relative coordinates**: x, y and z are

$$x = x_e - x_\mathrm{n} \tag{16.1-2a}$$

$$y = y_e - y_\mathrm{n} \tag{16.1-2b}$$

$$z = z_e - z_\mathrm{n} \tag{16.1-2c}$$

The potential energy depends on the distance between the particles, which is

$$r = (x^2 + y^2 + z^2)^{1/2} \tag{16.1-3}$$

The coordinates of the center of mass are

$$X = \frac{m_e x_e + m_\mathrm{n} x_\mathrm{n}}{M} \tag{16.1-4a}$$

$$Y = \frac{m_e y_e + m_\mathrm{n} y_\mathrm{n}}{M} \tag{16.1-4b}$$

$$Z = \frac{m_e z_e + m_\mathrm{n} z_\mathrm{n}}{M} \tag{16.1-4c}$$

where the sum of the masses is denoted by M:

$$M = m_e + m_\mathrm{n} \tag{16.1-5}$$

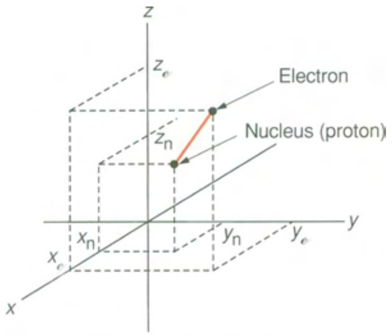

Figure 16.1. The System Consisting of a Nucleus and an Electron. This figure shows the cartesian coordinates of both particles, with a line segment drawn between the particles.

The classical Hamiltonian contains the kinetic energy in terms of momentum components. The kinetic energy in terms of the velocity of the center of mass and the relative velocity is given in Eq. (D-26) of Appendix D:

$$\mathscr{K} = \frac{M}{2}(V_x^2 + V_y^2 + V_z^2) + \frac{\mu}{2}(v_x^2 + v_y^2 + v_z^2) \tag{16.1-6}$$

where **V** and **v** are the velocity of the center of mass and the relative velocity, respectively. The **reduced mass** is denoted by μ:

$$\mu = \frac{m_{\mathrm{n}} m_e}{m_{\mathrm{n}} + m_e} \tag{16.1-7}$$

The momenta conjugate to the center-of-mass coordinates X, Y, and Z are

$$P_x = MV_x, \qquad P_y = MV_y, \qquad P_z = MV_z \tag{16.1-8a}$$

The momenta conjugate to the relative coordinates x, y, and z are

$$p_x = \mu v_x, \qquad p_y = \mu y_y, \qquad p_z = \mu v_z \tag{16.1-8b}$$

The classical Hamiltonian function is

$$H_{\mathrm{cl}} = \frac{1}{M}(P_x^2 + P_y^2 + P_z^2) + \frac{1}{\mu}(p_x^2 + p_y^2 + p_z^2) + \mathscr{V}(r) \tag{16.1-9}$$

The Hamiltonian operator is obtained by the usual replacements for cartesian momentum components as in Eq. (15.3-5):

$$\begin{aligned}\hat{H} &= -\frac{\hbar^2}{2M}\left(\frac{\partial^2}{\partial X^2} + \frac{\partial^2}{\partial Y^2} + \frac{\partial^2}{\partial Z^2}\right) - \frac{\hbar^2}{2\mu}\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2}\right) + \mathscr{V}(r)\\ &= -\frac{\hbar^2}{2M}\nabla_{\mathrm{c}}^2 - \frac{\hbar^2}{2\mu}\nabla_{\mathrm{r}}^2 + \mathscr{V}(r)\end{aligned} \tag{16.1-10}$$

where ∇^2 is the Laplacian operator defined in Eq. (14.4-25) and Eq. (B-40).

The first term in the Hamiltonian operator is the **center-of-mass Hamiltonian**:

$$\hat{H}_{\mathrm{c}} = -\frac{\hbar^2}{2M}\nabla_{\mathrm{c}}^2 \tag{16.1-11}$$

and the other two terms are the **relative Hamiltonian**.

$$\hat{H}_{\mathrm{r}} = -\frac{\hbar^2}{2\mu}\nabla_{\mathrm{r}}^2 + \mathscr{V}(r) \tag{16.1-12}$$

The time-dependent Schrödinger equation is

$$(\hat{H}_{\mathrm{c}} + \hat{H}_{\mathrm{r}})\Psi = E\Psi \tag{16.1-13}$$

This equation can be solved by the separation of variables. We assume the trial function

$$\Psi = \psi_{\mathrm{c}}(X, Y, Z)\psi(x, y, z) \tag{16.1-14}$$

In previous chapters Ψ has represented a time-dependent wave function. We will use both Ψ and ψ for coordinate wave functions in the next several chapters, usually using Ψ for wave functions of more than one particle.

By separation of variables, Eq. (16.1-14) leads to the two equations

$$\hat{H}_{\mathrm{c}}\psi_{\mathrm{c}} = E_{\mathrm{c}}\psi_{\mathrm{c}} \tag{16.1-15}$$

$$\hat{H}\psi = E_{\mathrm{r}}\psi \tag{16.1-16}$$

with the energy eigenvalue E,

$$E = E_c + E_r \tag{16.1-17}$$

Exercise 16.1

Carry out the steps to obtain Eq. (16.1-15)–(16.1-17).

Equation (16.1-15) for the center of mass is the same as the Schrödinger equation for a free particle. We can transcribe the energy eigenfunctions and energy eigenvalues from Chapter 14 with replacement of the symbol for the mass by M. We will return to the motion of the center of mass in Chapter 19 and will then also consider the possibility that the atom or molecule is contained in a box.

Solution of the Relative Schrödinger Equation

Equation (16.1-16) is the Schrödinger equation for the relative motion. It is mathematically equivalent to the problem of the motion of a particle of mass μ moving at distance r from a fixed origin under the effect of the potential energy $\mathcal{V}(r)$ (see Appendix D). Figure 16.2 depicts this equivalence. The vector from the nucleus, (labeled n) to the electron (labeled e) in Figure 16.2a is equal to the vector from a fixed origin to the fictitious particle of mass μ in Figure 16.2b. If one of the particles is much heavier than the other, as is the case in the hydrogen atom, the reduced mass is nearly equal to the mass of the lighter object, the center of mass is much closer to the heavier particle than to the other, and the motion is nearly the same as though the heavier particle were stationary with the lighter particle moving around it.

***Exercise 16.2**

The mass of the electron is 9.10939×10^{-31} kg and the mass of the proton is 1.672623×10^{-27} kg.

a. Calculate the ratio of the reduced mass of the hydrogen atom to the mass of the electron.

b. For a hydrogen atom with the electron at a distance 1.000×10^{-10} m from the nucleus, find

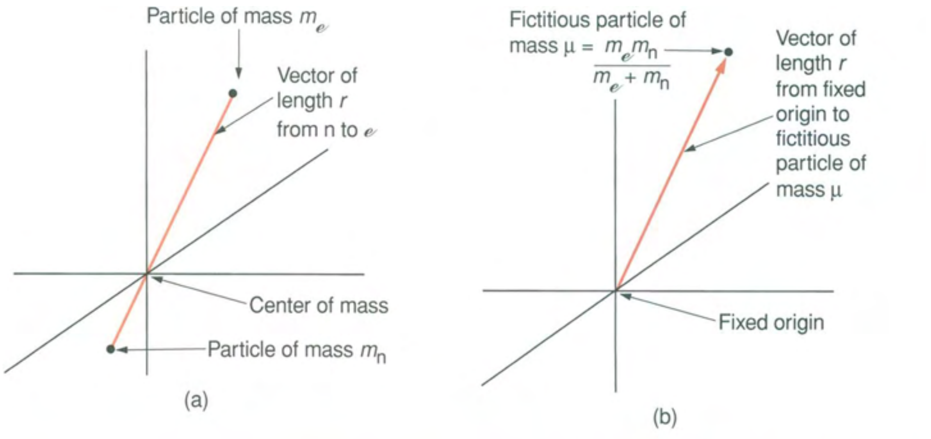

Figure 16.2. Figure to Illustrate the Equivalence between the Motion of a Particle of Mass μ around a Fixed Center and the Relative Motion of Two Particles (a) **The actual two-particle system.** (b) **The fictitious particle of mass μ.** The two vectors move in exactly the same way.

the distance from the center of mass to the nucleus and to the electron. Hint: Assume that the particles are temporarily on the x axis.

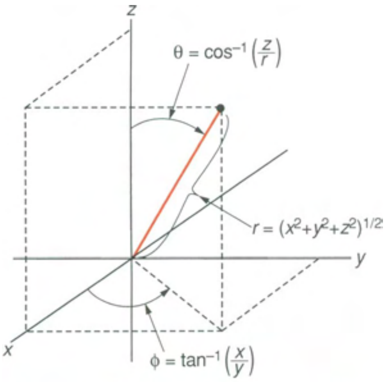

Figure 16.3. Spherical Polar Coordinates. These coordinates are used to simplify the solution of the Schrödinger equation.

We now transform the relative Schrödinger equation to spherical polar coordinates, in which r is one of the coordinates. These coordinates are shown in Figure 16.3. The expression for the Laplacian operator in spherical polar coordinates in Eq. (B-42) of Appendix B gives the relative Schrödinger equation:

$$\begin{aligned}\hat{H}_{\mathrm{r}}\psi &= -\frac{\hbar^2}{2\mu r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial\psi}{\partial\theta}\right)+\frac{1}{\sin^2(\theta)}\frac{\partial^2\psi}{\partial\phi^2}\right]+\mathcal{V}(r)\psi\\ &= E_{\mathrm{r}}\psi \qquad (16.1\text{-}18)\end{aligned}$$

Comparison of this equation with Eq. (15.3-11) shows that the operator for the square of the angular momentum is contained in the Hamiltonian operator:

$$-\frac{\hbar^2}{2\mu r^2}\frac{\partial}{\partial r}\left(r^2\frac{\partial\psi}{\partial r}\right)+\frac{1}{2\mu r^2}\hat{L}^2\psi+\mathcal{V}(r)\psi=E_{\mathrm{r}}\psi \qquad (16.1\text{-}19)$$

This equation can be solved by another separation of variables. We assume the trial solution

$$\psi(r,\theta,\phi)=R(r)Y(\theta,\phi) \qquad (16.1\text{-}20)$$

The separation of variables is a little more difficult in this case than in previous cases since the coordinates do not occur only in separate terms in the Hamiltonian operator. We have to do it in two steps.

Since the operator $\hat{L}^2$ does not contain r, substitution of the trial solution into Eq. (16.1-19) gives

$$-\frac{\hbar^2}{2\mu}\left[Y\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+R\hat{L}^2Y\right]+(\mathcal{V}-E_{\mathrm{r}})RY=0 \qquad (16.1\text{-}21)$$

We multiply this equation by $2\mu r^2/\hbar^2$ and divide by RY. This separates r from the other variables, giving

$$-\frac{1}{R}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right)+\frac{2\mu r^2}{\hbar^2}(\mathcal{V}-E_{\mathrm{r}})+\frac{1}{\hbar^2}\frac{1}{Y}\hat{L}^2Y=0 \qquad (16.1\text{-}22)$$

The Angular Factors in the Wave Function

The final term on the left-hand side of Eq. (16.1-22) contains no r and the other terms contain no θ or ϕ. 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

$$\hat{L}^2Y=\hbar^2KY \qquad (16.1\text{-}23)$$

which we can solve for the angular factor Y, which is also the eigenfunction of $\hat{L}^2$. The factor R in the eigenfunction will be different for different potential energy functions, but the factor Y will be the same for every potential energy function $\mathcal{V}$ that depends only on r.

Equation (16.1-23) can be written

$$-\hbar^2\left[\frac{1}{\sin(\theta)}\frac{\partial}{\partial\theta}\left(\sin(\theta)\frac{\partial Y}{\partial\theta}\right)+\frac{1}{\sin^2(\theta)}\frac{\partial^2Y}{\partial\phi^2}\right]=\hbar^2KY \qquad (16.1\text{-}24)$$

To carry out a second separation for the variables θ and ϕ, we assume the trial solution

$$Y = \Theta(\theta)\Phi(\phi) \tag{16.1-25}$$

Substitution into Eq. (16.1-24) followed by division by $\Theta(\theta)\Phi(\phi)$ and multiplication by $\sin^2(\theta)$ gives

$$\frac{\sin(\theta)}{\Theta}\frac{d}{d\theta}\left(\sin(\theta)\frac{d\Theta}{d\theta}\right) + \frac{1}{\Phi}\frac{d^2\Phi}{d\phi^2} = -K\sin^2(\theta) \tag{16.1-26}$$

The last term on the left-hand side of this equation depends only on ϕ, so it must be a constant function of ϕ, which we call $-m^2$. If this choice for the constant is made, m will turn out to be a real integer. Multiplication by Φ gives the equation

$$\frac{d^2\Phi}{d\phi^2} = -m^2\Phi \tag{16.1-27}$$

Except for the symbols used, Eq. (16.1-27) is exactly the same as several equations already encountered, and its general solution can be written as in Eq. (14.5-21):

$$\Phi = Ae^{im\phi} + Be^{-im\phi} \tag{16.1-28}$$

where A and B are constants. The version of the general solution with sine and cosine functions could also have been used.

A wave function must be continuous. The variable ϕ ranges from 0 to 2π radians. Since $\phi = 0$ and $\phi = 2\pi$ refer to the same location for given values of r and θ,

$$\Phi(0) = \Phi(2\pi) \tag{16.1-29}$$

This condition is satisfied only if m is real and equal to an integer.

Exercise 16.3

Use the identity

$$e^{im\phi} = \cos(m\phi) + i\,\sin(m\phi)$$

to show that m is real and equal to an integer.

There are two standard forms of the function in Eq. (16.1-28). For the first form, we choose the values so that Φ is an eigenfunction of $\hat{L}_z$, given by Eq. (15.3-10):

$$\hat{L}_z = \frac{\hbar}{i}\frac{\partial}{\partial\phi} \tag{16.1-30}$$

We operate on Φ with $\hat{L}_z$:

$$\hat{L}_z\Phi = \frac{\hbar}{i}\left(imAe^{im\phi} - imBe^{-im\phi}\right) \tag{16.1-31}$$

We have an eigenfunction of $\hat{L}_z$ with eigenvalue $\hbar m$ if B is chosen to equal zero, or an eigenfunction of $\hat{L}_z$ with eigenvalue $-\hbar m$ if A is chosen to equal zero. It can be shown that $\hat{L}^2$ and $\hat{L}_z$ commute with each other and with $\hat{H}_r$, so that these three operators can have a set of common eigenfunctions. It is sometimes useful to have wave functions that are eigenfunctions of $\hat{L}_z$.

Exercise 16.4

Show that $\hat{H}_r$, $\hat{L}^2$, and $\hat{L}_z$ all commute.

With $B = 0$, the normalized Φ function is

$$\Phi = \Phi_m = \frac{1}{\sqrt{2\pi}} e^{im\phi} \tag{16.1-32}$$

where we label the members of the set of functions with the quantum number m.

For the second standard form the constants A and B are chosen so that Φ is a real function. If A and B are equal,

$$\Phi = \Phi_{mx} = A\left(e^{im\phi} + e^{-im\phi}\right) = 2A\cos(m\phi)$$

In normalized form,

$$\Phi_{mx} = \frac{1}{\sqrt{\pi}} \cos(m\phi) \qquad (m \neq 0) \tag{16.1-33}$$

If $B = -A$, then

$$\Phi = \Phi_{my} = A\left(e^{im\phi} - e^{-im\phi}\right) = 2iA\sin(m\phi)$$

In normalized form,

$$\Phi_{my} = \frac{1}{\sqrt{\pi}} \sin(m\phi) \qquad (m \neq 0) \tag{16.1-34}$$

where the values of A and B are chosen for normalization. The complex Φ functions are eigenfunctions of the $\hat{L}_z$ operator. The real functions are not eigenfunctions of the $\hat{L}_z$ operator if $m \neq 0$, but sometimes it is convenient to have real wave functions.

Exercise 16.5

Show that Φ_{mx} and Φ_{my} are not eigenfunctions of $\hat{L}_z$ for $m \neq 0$.

After replacement of the constant term by $-m^2$ and multiplication by Θ, Eq. (16.1-26) becomes an equation that can be solved for the Θ function:

$$\sin(\theta)\frac{d}{d\theta}\left(\sin(\theta)\frac{d\Theta}{d\theta}\right) - m^2\Theta + K\sin^2(\theta)\Theta = 0 \tag{16.1-35}$$

This equation can be transformed into the **associated Legendre equation** by a change of variables:

$$y = \cos(\theta), \qquad P(y) = \Theta(\theta) \tag{16.1-36}$$

The equation is named for Adrien-Marie Legendre, 1752–1833, a famous French mathematician.

The associated Legendre equation and its solutions are given in Appendix F. The solutions are called **associated Legendre functions**, and are derivatives of polynomials known as **Legendre polynomials**.

For a solution to exist that obeys the relevant boundary conditions, the constant K must be equal to $l(l+1)$ where l is an integer at least as large as $|m|$. There is one solution for each set of values of the two quantum numbers l and m:

$$\Theta(\theta) = \Theta_{lm}(\theta) \tag{16.1-37}$$

The solutions are the same for a given value of m and its negative:

$$\Theta_{lm}(\theta) = \Theta_{l,-m}(\theta) \tag{16.1-38}$$

where we insert a comma to avoid confusing two subscripts having values l and $-m$ with a single subscript having a value equal to $(l - m)$.

The Y functions are called **spherical harmonic functions**. Each one is a product of a $\Theta_{lm}(\theta)$ function and a $\Phi_m(\phi)$ function having the same value of m as the Θ function:

$$Y = Y_{lm}(\theta, \phi) = \Theta_{lm}(\theta)\Phi_m(\phi)$$

Table 16.1 gives the normalized spherical harmonic functions for $l = 0$, $l = 1$, and $l = 2$. Additional functions can be derived from formulas in Appendix F.

Table 16.1. Spherical harmonic functions $\psi_{lm}(\theta, \phi) = \Theta_{lm}(\theta)\Phi_m(\phi)$

Complex Φ functions, eigenfunctions of $\hat{L}_z$

$$\Phi_m(\phi) = \frac{1}{\sqrt{2\pi}} e^{im\phi}$$

Real Φ functions, not necessarily eigenfunctions of $\hat{L}_z$

$$\Phi_{mx}(\phi) = \frac{1}{\sqrt{\pi}} \cos(m\phi)$$

$$\Phi_{my}(\phi) = \frac{1}{\sqrt{\pi}} \sin(m\phi)$$

Θ functions

$$\Theta_{00}(\theta) = \frac{\sqrt{2}}{2}$$

$$\Theta_{10}(\theta) = \frac{\sqrt{6}}{2} \cos(\theta)$$

$$\Theta_{11}(\theta) = \Theta_{1,-1}(\theta) = \frac{\sqrt{3}}{2} \sin(\theta)$$

$$\Theta_{20}(\theta) = \frac{\sqrt{10}}{4} (3\cos^2(\theta) - 1)$$

$$\Theta_{21}(\theta) = \Theta_{2,-1}(\theta) = \frac{\sqrt{15}}{2} \sin(\theta)\cos(\theta)$$

$$\Theta_{22}(\theta) = \Theta_{2,-2}(\theta) = \frac{\sqrt{15}}{4} \sin^2(\theta)$$

Additional Θ functions can be obtained from Appendix F.

Angular Momentum Values

The spherical harmonic functions, $Y_{lm}(\theta, \phi)$, are eigenfunctions of the operator for the square of the angular momentum with eigenvalue $\hbar^2 K$, as in Eq. (16.1-23). The fact that K must equal $l(l + 1)$ where l is a nonnegative integer gives us the eigenvalues of the square of the angular momentum:

$$\hat{L}^2 Y_{lm} = \hat{L}^2 \Theta_{lm}\Phi_m = \hbar^2 l(l+1)\Theta_{lm}\Phi_m \qquad (l = 0, 1, 2, \ldots) \tag{16.1-39}$$

The square of the angular momentum takes on the values

$$L^2 = 0, \quad 2\hbar^2, \quad 6\hbar^2, \quad 12\hbar^2, \quad 20\hbar^2, \quad \ldots \tag{16.1-40}$$

so that the magnitude of the angular momentum takes on the values

$$L = |\mathbf{L}| = 0, \quad \sqrt{2}\hbar, \quad \sqrt{6}\hbar, \quad \sqrt{12}\hbar, \quad \sqrt{20}\hbar, \ldots \tag{16.1-41}$$

Compare these mathematically generated values with the assumed values $\hbar$, $2\hbar$, $3\hbar, \ldots$, in the Bohr theory of the hydrogen atom. Not only is the origin of the quantization different, but the values are different from those of the Bohr theory. The Bohr theory gave the correct value of the energy of the hydrogen atom, but not of the angular momentum.

The function Φ_m in Eq. (16.1-32) is an eigenfunction of $\hat{L}_z$ with eigenvalue $\hbar m$, so that Y_{lm} is also an eigenfunction:

$$\hat{L}_z Y_{lm} = \Theta_{lm}\hat{L}_z\Phi_m = \Theta_{lm}\hbar m\Phi_m \qquad (m = 0, \pm 1, \ldots, \pm l) \tag{16.1-42}$$

The possible values of L_z are

$$L_z = m\hbar = 0, \quad \pm\hbar, \quad \pm 2\hbar, \quad \pm 3\hbar, \quad \ldots \pm l\hbar \tag{16.1-43}$$

The magnitude of the angular momentum and the z component can simultaneously have predictable values. In order to specify completely the direction of the angular momentum vector, values of L_x and L_y would have to be specified as well as L_z. However, $\hat{L}_x$, $\hat{L}_y$, and $\hat{L}_z$ do not commute with each other, so all three of these operators cannot have a full set of common eigenfunctions. Only one component of the angular momentum can have a predictable value for the full set of states, and the exact direction of the angular momentum vector cannot be determined.

Exercise 16.6

a. Use Eq. (15.4-24) and the expression for the commutator $[\hat{L}_x, \hat{L}_y]$ in Problem 15.36 to obtain an uncertainty relation for L_x and L_y. As the wave function in the integral, use the spherical harmonic function Y_{21}.

b. Repeat part (a) using the spherical harmonic function Y_{00}. Comment on your result.

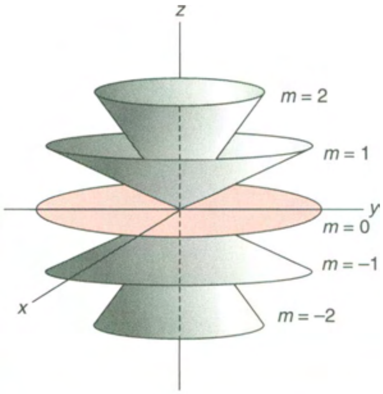

Figure 16.4. Cones of Possible Angular Momentum Directions for $l = 2$. These cones are similar to the cones of precession of a gyroscope, and represent possible directions for the angular momentum vector. The z component is arbitrarily chosen as the one component that can have a definite value.

Figure 16.4 depicts 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 $-2\hbar$. The angular momentum vector can point anywhere on the five cones drawn in the figure. If the wave function is known to correspond to particular values of l and m, then it is known which cone applies, but the direction on that cone is not known. For any values of l, there are $2l + 1$ cones, one for each possible value of m. Notice the similarity between each cone on Figure 16.4 and the cone of directions around which a gyroscope axis precesses, as shown in Figure D-3 of Appendix D.

There is nothing unique about the z direction. One could choose $\hat{L}_x$ or $\hat{L}_y$ as a member of a set of commuting observables instead of $\hat{L}_z$. In that event, the Φ functions would be different, and would correspond to cones in Figure 16.4 that would be oriented around either the x axis or the y axis. We choose L_z since its operator is simpler in spherical polar coordinates than those of the other components.

***Exercise 16.7**

Transform the expression for $\Theta_{11}\Phi_{1x}$ to cartesian coordinates. Show that this function is an eigenfunction of the operator $\hat{L}_x$ and find its eigenvalue.

16.2 The Wave Functions of the Hydrogen Atom

In Section 16.1, we wrote the energy eigenfunction for any central-force system as

$$\Psi(r, \theta, \phi) = R(r)Y_{lm}(\theta, \phi) = R(r)\Theta_{lm}(\theta)\Phi_m(\phi) \tag{16.2-1}$$

The spherical harmonic functions $Y_{lm}(\theta, \phi) = \Theta_{lm}(\theta)\Phi_m(\phi)$ are the same functions for any central-force problem. The R function (the **radial factor**) is different for each choice of the potential energy function $\mathcal{V}(r)$. We replace $\hat{L}^2 Y$ by $\hbar^2 l(l+1)Y$ in Eq. (16.1-22), according to Eq. (16.1-39) and multiply the resulting equation by R to obtain the differential equation for R:

$$-\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + \frac{2\mu r^2}{\hbar^2}(\mathcal{V} - E)R + l(l+1)R = 0 \tag{16.2-2}$$

where we now omit the subscript r from the symbol for the relative energy. For the hydrogen atom, $\mathcal{V}(r)$ is given by the expression in Eq. (16.1-1). Expanding the derivative term into two terms gives

$$-r^2\frac{d^2R}{dr^2} - 2r\frac{dR}{dr} - \frac{2\mu r^2}{\hbar^2}\left(E + \frac{e^2}{4\pi\varepsilon_0 r}\right)R + l(l+1)R = 0 \tag{16.2-3}$$

We make the following substitutions:

$$\alpha^2 = -\frac{2\mu E}{\hbar^2}, \qquad \beta = \frac{\mu e^2}{4\pi\varepsilon_0\alpha\hbar^2}, \qquad \rho = 2\alpha r \tag{16.2-4}$$

This equation is named for Edmund Laguerre, 1834–1866, a famous French mathematician who solved the equation.

The resulting equation is divided by ρ^2, giving an equation that is known as the **associated Laguerre equation**:

$$\frac{d^2R}{d\rho^2} + \frac{2}{\rho}\frac{dR}{d\rho} - \frac{R}{4} + \frac{\beta R}{\rho} - l(l+1)\frac{R}{\rho^2} = 0 \tag{16.2-5}$$

where we use the letter R for the function of ρ that is equal to $R(r)$.

Exercise 16.8

Carry out the manipulations to obtain Eq. (16.2-5) from Eq. (16.2-3).

The solution is written as

$$R(\rho) = G(\rho)e^{-\rho/2} \tag{16.2-6}$$

where $G(\rho)$ is a power series

$$G(\rho) = \sum_{j=0}^{\infty} a_j\rho^j \tag{16.2-7}$$

with constant coefficients $a_1, a_2, a_3, \ldots$. The solution of the equation, which we will not discuss, is reduced to the problem of determining these coefficients.

The Hydrogen Atom Energy Levels

As with the series in the harmonic oscillator solution, the series in Eq. (16.2-7) must terminate after a finite number of terms in order to keep the wave function from becoming infinite for large values of ρ, violating our boundary conditions.[1] The termination requires that the parameter β in Eq. (16.2-4) is equal to an integer n, which must be at least as large as $l + 1$. The minimum value of n is unity, and this value occurs only for $l = 0$. Solving the second equality in Eq. (16.2-4) for α, we obtain

$$\alpha = \frac{\mu e^2}{4\pi\varepsilon_0 \hbar^2 n} \tag{16.2-8}$$

From the first relation in Eq. (16.2-4) , the energy is quantized, with a value determined by the quantum number n:

$$E = E_n = -\frac{\hbar^2\alpha^2}{2\mu} = -\frac{\mu e^4}{2(4\pi\varepsilon_0 \hbar n)^2} \qquad (n = 1, 2, 3, \ldots) \tag{16.2-9}$$

The energy expression in Eq. (16.2-9) is identical with that of the Bohr theory. As in the case of the particle in a box and the harmonic oscillator, the energy is quantized by the nature of the Schrödinger equation and its boundary conditions, and not by arbitrary assumption as in the Bohr theory. These negative values of the energy eigenvalue E correspond to **bound states**, in which the system does not have sufficient relative energy for the electron to escape from the nucleus. There are also non-bound states called **scattering states** in which the energy is positive and in which the electron moves toward the nucleus, passes it, and continues on its way. We will not discuss these states, which do not have quantized energy values.[2]

Exercise 16.9

Substitute the values of the constants into Eq. (16.2-9) to show that the energy of relative motion of a hydrogen atom can take on the values

$$E = E_n = -\frac{2.1787 \times 10^{-18}\,\mathrm{J}}{n^2} = -\frac{13.60\,\mathrm{eV}}{n^2} \tag{16.2-10}$$

where 1 eV (electronvolt) is the energy required to move one electron through an electric potential difference of 1 volt, equal to 1.6022×10^{-19} J.

The parameter a is the same as the radius of the smallest orbit in the Bohr theory of the hydrogen atom in Eq. (14.3-14):

$$a = \frac{\hbar^2 4\pi\varepsilon_0}{\mu^2} = 5.2947 \times 10^{-11}\,\mathrm{m} = 52.947\,\mathrm{pm} = 0.52947\,\text{Å} \tag{16.2-11}$$

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[1] Frank L. Pilar, *Elementary Quantum Chemistry*, McGraw-Hill, New York, 1968, pp. 151ff.

[2] H. A. Bethe and E. E. Salpeter, *Quantum Mechanics of One- and Two-Electron Systems*, Plenum, New York, 1977, pp. 21ff, pp. 32ff.

where Å represents the angstrom unit, 10^{-10} m. When we express the energy in terms of this parameter, we get

$$E = E_n = -\frac{\hbar^2\alpha^2}{2\mu} = -\frac{e^2}{2(4\pi\varepsilon_0)an^2} \tag{16.2-12}$$

Exercise 16.10

Verify Eqs. (16.2-11) and (16.2-12).

In the (fictitious) limit that the nucleus is infinitely heavy compared to the electron, the electron moves about the stationary nucleus, and the reduced mass becomes

$$\lim_{m_n\to\infty} \mu = \lim_{m_n\to\infty}\left(\frac{m_e m_n}{m_e + m_n}\right) = m_e \tag{16.2-13}$$

where m_e is the mass of the electron. Equation (16.2-11) becomes

$$\lim_{m_n\to\infty} a = a_0 = \frac{\hbar^2 4\pi\varepsilon_0}{m_e e^2} = 5.29198 \times 10^{-11}\,\mathrm{m} \tag{16.2-14}$$

For ordinary purposes, the distinction between relative motion of the nucleus and electron about their center of mass and electronic motion about a stationary nucleus is numerically unimportant, because the nucleus is so much more massive than the electron. We usually refer to the relative motion as electronic motion.

***Exercise 16.11**

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 quantum numbers obey can be restated:

$$n = 1, 2, 3, \ldots \tag{16.2-15a}$$

$$l = 0, 1, 2, \ldots, n-1 \tag{16.2-15b}$$

$$m = 0, \pm 1, \pm 2, \ldots, \pm l \tag{16.2-15c}$$

The quantum number n is called the **principal quantum number**. The quantum number l has been called the **azimuthal quantum number**, but could also be called the **angular momentum quantum number**. The quantum number m has been called the **magnetic quantum number**, but could also be called the **angular momentum projection quantum number**. Since the energy eigenvalue depends only on the value of the principal quantum number, the energy levels are degenerate except for the $n = 1$ level.

EXAMPLE 16.1

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

$$g_n = \sum_{l=0}^{n-1}(2l+1) = 2n\frac{0+n-1}{2} + n = n^2 \qquad (16.2\text{-}16)$$

where we have used the fact that the sum of a set of successive integers is the mean of the first and the last times the number of members of the set (a fact that Gauss reportedly discovered when he was seven years old).

Figure 16.5 shows the energy level diagram for the first few bound-state electronic energy levels of a hydrogen atom. Each state is represented by a horizontal line segment at the appropriate height for its energy level. There is also a continuous spectrum of unbound states of positive energy. The characteristic pattern for the degeneracies of the bound states is that increasing the value of n by unity makes one more value of l available while increasing the value of l by unity makes two more values of m available.

The Radial Factor of the Hydrogen Atom Wave Functions

The polynomial G in Eq. (16.2-6) is expressed as a function of ρ, which is proportional to r. From Eqs. (16.2-4), (16.2-8) and (16.2-11),

$$\rho = 2\alpha r = \frac{2r}{na} \qquad (16.2\text{-}17)$$

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. There is a different R factor for each set of values of the quantum numbers n and l. Table 16.2 gives the R functions for $n = 1$, 2, and 3, and others can be written from the formulas for associated Laguerre functions given in Appendix F.

The energy eigenfunctions of relative motion in the hydrogen atom are called **orbitals**. Each orbital is obtained by multiplying a radial factor R_{nl} by a spherical harmonic function Y_{lm}, which must have the same value of l as the radial factor. The Y_{lm} factor consists of a $\Theta_{lm}(\theta)$ factor and a $\Phi_m(\phi)$ factor with the same value of m:

$$\Psi_{nlm} = R_{nl}Y_{lm} = R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\phi)$$

To each one of these eigenfunctions there corresponds a stationary state of the electron, with predictable values of the energy and the square of the angular momentum. If the complex Φ functions are used, there is also a predictable value of the z component of the angular momentum. The energy, the square of the angular momentum, and the z component of the angular momentum are a complete set of commuting observables for the electronic motion of the hydrogen atom. That is, if each of these variables is measured, the system will afterwards be in a state corresponding to a known wave function.

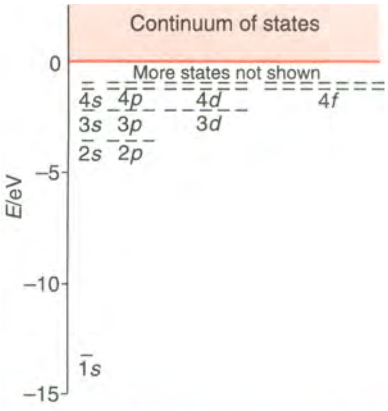

Figure 16.5. Energy Levels of the Hydrogen Atom. The bound-state energy levels are quantized.

Table 16.2. Radial Factors for Hydrogenlike Energy Eigenfunctions

$$R_{10}(r) = R_{1s}(r) = \left(\frac{Z}{a}\right)^{3/2} 2e^{-Zr/a}$$

$$R_{20}(r) = R_{2s}(r) = \frac{1}{2\sqrt{2}}\left(\frac{Z}{a}\right)^{3/2}\left(2 - \frac{Zr}{a}\right)e^{-Zr/2a}$$

$$R_{21}(r) = R_{2p}(r) = \frac{1}{2\sqrt{6}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)e^{-Zr/2a}$$

$$R_{30}(r) = R_{3s}(r) = \frac{1}{9\sqrt{3}}\left(\frac{Z}{a}\right)^{3/2}\left[6 - \frac{4Zr}{a} + \left(\frac{2Zr}{3a}\right)^2\right]e^{-Zr/3a}$$

$$R_{31}(r) = R_{3p}(r) = \frac{2}{27\sqrt{6}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{4Zr}{a} - \frac{2Z^2r^2}{3a^2}\right)e^{-Zr/3a}$$

$$R_{32}(r) = R_{3d}(r) = \frac{1}{9\sqrt{30}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{2Zr}{3a}\right)^2 e^{-Zr/3a}$$

Additional functions can be obtained from Appendix F.

The electronic energy levels of the hydrogen atom are called **shells**, because the expectation value of the distance of the electron from the nucleus is approximately the same for all states with the same value of n and is larger for larger values of n. The shells are labeled with the value of n, the principal quantum number. There is also an older notation in which the first shell is called the K shell, the second shell is called the L shell, etc. 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 in a shell 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. As further subshells appear, they are given the letters g, h, i, etc. (alphabetical after f). The letters s, p, d, and f came from the 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.

***Exercise 16.12**

Give the value of each of the three quantum numbers for each state of the fourth shell.

The Hydrogenlike Atom

A He^+ ion or a Li^{2+} ion has a single electron, and must be similar to a hydrogen atom. We define a **hydrogenlike atom** to have one electron and a number Z of protons in its nucleus. The only change that we need to make in our discussion of the hydrogen atom is to replace the potential energy function in Eq. (16.1-1) by

$$\mathscr{V}(r) = -\frac{Ze^2}{4\pi\varepsilon_0 r} \tag{16.2-18}$$

The energy eigenvalue of Eq. (16.2-12) is replaced by

$$E = E_n = -\frac{\hbar^2\alpha^2}{2\mu} = -\frac{Z^2e^2}{2(4\pi\varepsilon_0)an^2} = -(13.60\,\mathrm{eV})\frac{Z^2}{n^2} \tag{16.2-19}$$

and the variable ρ becomes

$$\rho = 2\alpha r = \frac{2Zr}{na} \tag{16.2-20}$$

Since ρ is proportional to Z, the effective radius of a shell is inversely proportional to Z. The first shell for a He^+ ion is closer to the nucleus than the first shell of a hydrogen atom, and so on. The orbital energy is directly proportional to Z^2 so that E_1 is larger in magnitude (more negative) for a He^+ ion than for a hydrogen atom, and so on.

Table 16.1 contains formulas for the first few spherical harmonic functions, and Table 16.2 contains formulas for the first few radial factors of the hydrogenlike atoms. Table 16.3 contains formulas for the real energy eigenfunctions for the first three shells (using Φ_{mx} and Φ_{my} instead of Φ_m and Φ_{-m}). The real Φ functions will often be more useful in describing chemical bonding, and the complex Φ functions will be more useful in discussing angular momentum values.

Instead of giving the value of the subscript l, we can give the letter of the subshell. The 210 function can be called the $2p0$ function and the 211 function can be called the $2p1$ function, etc. The $2p0$ function is also called the $2p_z$ function. The $2p$ function with Φ_{mx} is called the $2p_x$ function, and the $2p$ function with Φ_{mx} is called the $2p_y$ function. The labels on the real $3d$ functions can be seen in Table 16.3. The formulas in these tables can be applied to the hydrogen atom by letting $Z = 1$, to the He^+ ion by letting $Z = 2$, etc. Other wave functions can be constructed from formulas in Appendix F.

EXAMPLE 16.2

Write the formula for Ψ_{211}.

Solution

From Eq. (16.1-32),

$$\Phi_1 = \frac{1}{\sqrt{2\pi}}e^{i\phi}$$

From Table 16.1,

$$\Theta_{11} = \sqrt{\frac{3}{4}}\sin(\theta)$$

From Table 16.2,

$$R_{21}(\rho) = \left(\frac{Z}{a}\right)^{3/2}\frac{1}{2\sqrt{6}}\rho e^{-\rho/2}$$

The energy eigenfunction is

$$\psi_{211} = \left(\frac{Z}{a}\right)^{3/2}\frac{1}{8\sqrt{\pi}}\rho e^{-\rho/2}\sin(\theta)\,e^{i\phi} = \left(\frac{Z}{a}\right)^{3/2}\frac{1}{8\sqrt{\pi}}\frac{Zr}{a}e^{-Zr/2a}\sin(\theta)\,e^{i\phi}$$

It is important to have a grasp of the qualitative properties of the hydrogenlike orbitals. Figure 16.6 shows graphs of the R functions for the first three shells. The number of nodes in the R function increases by unity if n is increased by unity for fixed

Table 16.3. Real Hydrogenlike Energy Eigenfunctions

$$\psi_{10} = \psi_{1s} = \frac{1}{\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$$

$$\psi_{20} = \psi_{2s} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(2 - \frac{Zr}{a}\right)e^{-Zr/2a}$$

$$\psi_{21x} = \psi_{2p_x} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)e^{-Zr/2a}\sin(\theta)\cos(\phi)$$

$$\psi_{21y} = \psi_{2p_y} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)e^{-Zr/2a}\sin(\theta)\sin(\phi)$$

$$\psi_{210} = \psi_{2p_z} = \frac{1}{4\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)e^{-Zr/2a}\cos(\theta)$$

$$\psi_{300} = \psi_{3s} = \frac{1}{18\sqrt{3\pi}}\left(\frac{Z}{a}\right)^{3/2}\left[6 - \frac{4Zr}{a} + \left(\frac{2Zr}{3a}\right)^2\right]e^{-Zr/3a}$$

$$\psi_{310} = \psi_{3p_z} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{6Zr}{a} - \frac{Z^2r^2}{a^2}\right)e^{-Zr/3a}\cos(\theta)$$

$$\psi_{31x} = \psi_{3p_x} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{6Zr}{a} - \frac{Z^2r^2}{a^2}\right)e^{-Zr/3a}\sin(\theta)\cos(\phi)$$

$$\psi_{31y} = \psi_{3p_y} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{6Zr}{a} - \frac{Z^2r^2}{a^2}\right)e^{-Zr/3a}\sin(\theta)\sin(\phi)$$

$$\psi_{320} = \psi_{3d_{z^2}} = \frac{1}{81\sqrt{6\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)^2 e^{-Zr/3a}[3\cos^2(\theta) - 1]$$

$$\psi_{3d_{xz}} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)^2 e^{-Zr/3a}\sin(\theta)\cos(\theta)\cos(\phi)$$

$$\psi_{3d_{yz}} = \frac{\sqrt{2}}{81\sqrt{\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)^2 e^{-Zr/3a}\sin(\theta)\cos(\theta)\sin(\phi)$$

$$\psi_{3d_{x^2-y^2}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)^2 e^{-Zr/3a}\sin^2(\theta)\cos(2\phi)$$

$$\psi_{3d_{xy}} = \frac{1}{81\sqrt{2\pi}}\left(\frac{Z}{a}\right)^{3/2}\left(\frac{Zr}{a}\right)^2 e^{-Zr/3a}\sin^2(\theta)\sin(2\phi)$$

l, and decreases by unity if l is increased by unity for fixed n. The Θ_{00} function and the Φ_0 function for the s subshells are equal to constants. The orbitals in the s subshells depend only on r and are called **spherically symmetric** functions. The other Θ and Φ functions are more complicated, especially in the case of the complex Φ functions, which have a real and an imaginary part. Figure 16.7 shows graphs of several of these functions. The three spherical harmonic functions that occur in the $2p$ subshell are exactly the same as the three spherical harmonic functions that occur in the $3p$ subshell or any other p subshell, and those of the $3d$ subshell are the same as those of any other d subshell, and so on.

It is not possible to draw a graph representing a function of three independent variables, and it is also difficult to visualize the qualitative properties of the orbital by looking at three separate graphs for the R, Θ, and Φ functions. Therefore, we introduce the **orbital region**, which is the region in space where the magnitude of the orbital

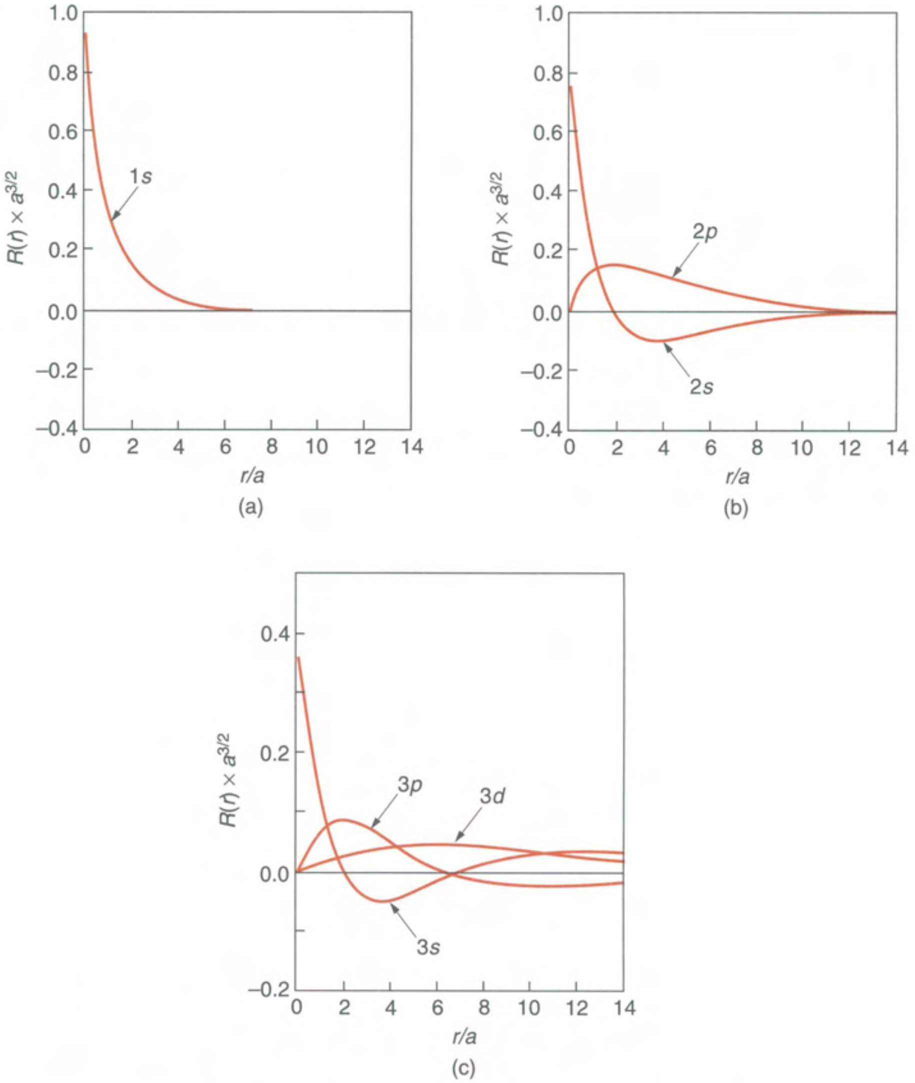

Figure 16.6. Radial Factors for Hydrogenlike Energy Eigenfunctions. (a) $n = 1$. (b) $n = 2$. (c) $n = 3$. The pattern of numbers of nodal surfaces is important. As n is increased with l fixed, the number of spherical nodal surfaces increases. As l is increased with n fixed, the number of sperhical nodal surfaces decreases.

function is larger than some specified small value. Since the square of the orbital function is the probability density, the orbital region is the region inside which the electron is likely to be found. A common policy chooses a constant magnitude of the orbital at the boundary of the orbital regions such that 90% of the total probability of finding the electron is inside the orbital region. Pictures of orbital regions are seen in almost all elementary chemistry and organic chemistry textbooks, but sometimes the distinction between the orbital and the orbital region is not made clear. The orbital is a one-electron wave function, while the orbital region is a three-dimensional region in space inside of which the orbital is larger in magnitude than some small value. Figure 16.8 shows several orbital regions. The sign of the orbital function is indicated for the

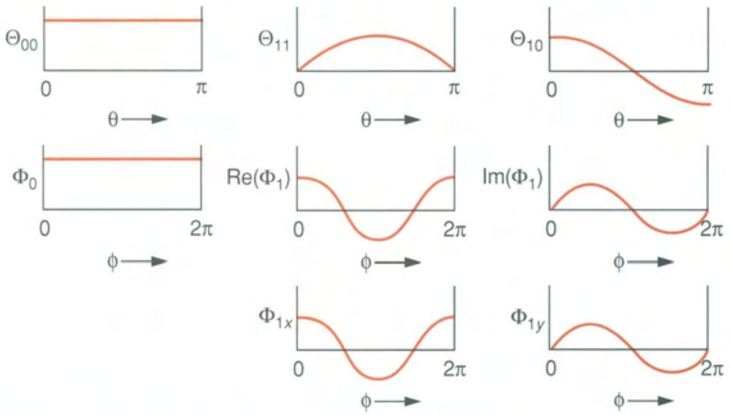

Figure 16.7. Some Factors of Spherical Harmonic Functions. These are the factors by which the radial functions must be multiplied to give the energy eigenfunctions.

real orbitals. Notice the differences between the orbital regions for the complex $2p$ and the real $2p$ orbitals. For the complex orbitals, we take the magnitude of the complex exponential $e^{im\phi}$ or $e^{-im\phi}$, which is a constant, while for the real orbitals we have either $\sin(m\phi)$ or $\cos(m\phi)$. The compactness of the orbital regions of the real p functions often makes them more useful than the complex p orbitals in discussing chemical bonding.

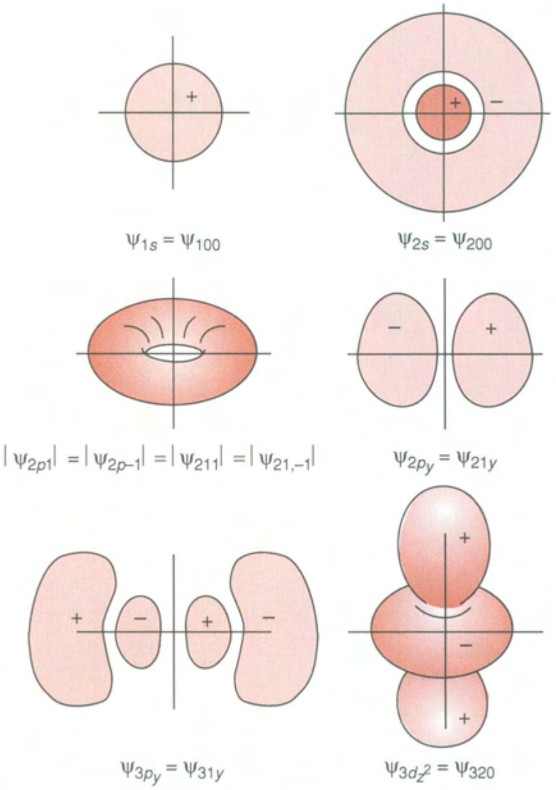

Figure 16.8. Some Orbital Regions for Hydrogenlike Orbitals. The orbital region is the region in space inside which the orbital function differs significantly from zero.

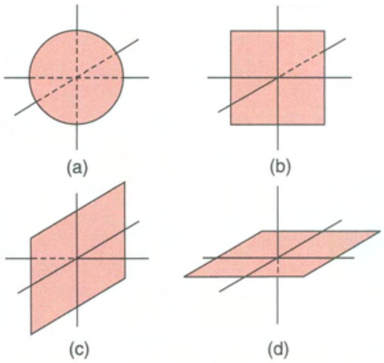

Figure 16.9. The Nodal Planes of the Real Energy Eigenfunctions of the Second Shell. (a) **The nodal sphere of the 2*s* wave function.** (b) **The nodal plane of the $2p_x$ wave function.** (c) **The nodal plane of the $2p_y$ wave function.** (d) **The nodal plane of the $2p_z$ wave function.** Each of these surfaces represents the points in space where the wave function vanishes.

The orbital regions can be approximately constructed from the pattern of the nodal surfaces in the R, Θ, and Φ functions. The orbital region cannot include any nodal surface, so any nodal surface divides the orbital region into two separate subregions, which are sometimes called "lobes". If there is a node in the R factor, the nodal surface is a sphere. If there is a node in the Φ factor the nodal surface is a cone, or a plane if the node occurs at $\theta = \pi/2$ (90°). If there is a node in a real Φ factor the nodal surface is a half-plane with edge at the z axis, which is always paired with another half-plane to make a nodal plane containing the z axis. The nodes in the real part of a complex Φ function are just like those of a real Φ function, and the nodes in the imaginary part of a complex Φ function are just like those of a different real Φ function. The number of nodal surfaces is always equal to $n - 1$ if the spherical nodal surface at $r \to \infty$ is excluded (and we will consistently exclude it). The 1*s* orbital has no nodal surfaces. Each of the orbitals in the second shell has one nodal surface, and each of the orbitals in the third shell has two nodal surfaces, and so on.

EXAMPLE 16.3

Describe the nodal surfaces for the real orbitals of the second shell.

Solution

We disregard the spherical nodal surface at $r \to \infty$ that occurs with each orbital. In each of the orbitals of the second shell there is one node. For the 2*s* function there is one node in the R function, producing a single spherical nodal surface. The $2p_z$ function has a node in the Θ function at $\theta = \pi/2$, producing a nodal plane in the x–y plane. The $2p_x$ function has nodes in the Φ function at $\phi = \pi/2$ and at $3\pi/2$, producing a nodal plane in the y–z plane. The $2p_y$ orbital has a nodal plane in the x–z plane. Figure 16.9 depicts the nodal surfaces in the real orbitals of the second shell.

Exercise 16.13

Describe the nodal surfaces for the real orbitals of the 3*d* subshell.

In general, a wave function with more nodes corresponds to a higher energy. This fact correlates with the fact that the de Broglie wavelength has a smaller value if there are more nodes. By Eq. (14.4-3), the de Broglie wavelength is inversely proportional to the speed, and thus has a smaller value when the kinetic energy is larger. 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. The energy was proportional to the square of n. With the harmonic oscillator, the number of nodes was equal to v, the quantum number, and the energy was proportional to $v + \frac{1}{2}$. In the real hydrogenlike orbitals, the number of nodal surfaces is equal to $n - 1$, where n is the principal quantum number, and the energy is also higher for larger values of n.

Normalization of the Hydrogenlike Orbitals

For motion of one particle in three dimensions, normalization in cartesian coordinates means

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \psi(x,y,z)^*\psi(x,y,z)\,dx\,dy\,dz = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} |\psi(x,y,z)|^2\,d^3\mathbf{r} = 1 \tag{16.2-21}$$

In spherical polar coordinates,

$$\int_0^\infty \int_0^\pi \int_0^{2\pi} |\psi(r,\theta,\phi)|^2 r^2 \sin(\theta)\, d\phi\, d\theta\, dr = \int_0^\infty \int_0^\pi \int_0^{2\pi} |\psi(r,\theta,\phi)|^2\, d^3\mathbf{r} = 1 \quad (16.2\text{-}22)$$

We abbreviate the volume element in any coordinate system by $d^3\mathbf{r}$ or by dq. The factor $r^2 \sin(\theta)$, which is called a **Jacobian**, is required to complete the element of volume in spherical polar coordinates.

$$d^3\mathbf{r} = r^2 \sin(\theta)\, d\phi\, d\theta\, dr \quad \text{(spherical polar coordinates)} \qquad (16.2\text{-}23)$$

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 $r\,d\theta$, and an infinitesimal arc length in the ϕ direction is $r \sin(\theta)\, d\phi$. Since the lengths are infinitesimal, there is no distinction between arc lengths and linear lengths. The element of volume is the product of these mutually perpendicular infinitesimal lengths, giving Eq. (16.2-23).

The normalization integral for the hydrogen orbitals can be factored in spherical polar coordinates:

$$\int_0^\infty R^*Rr^2\, dr \int_0^\pi \Theta^*\Theta \sin(\theta)\, d\theta \int_0^{2\pi} \Phi^*\Phi\, d\phi = 1 \qquad (16.2\text{-}24)$$

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. (16.2-24) simplify the calculation of many expectation values.

EXAMPLE 16.4

Calculate the expectation values $\langle 1/r\rangle$ and $\langle \mathcal{V}\rangle$, where $\mathcal{V}$ is the potential energy, for a hydrogenlike atom in the 1*s* state.

Solution

Since the wave function is normalized, we can omit the denominator in the formula for the expectation value shown in Eq. (15.4-1). We can factor the integral:

$$\left\langle \frac{1}{r} \right\rangle = \int_0^\infty R_{10}^* \frac{1}{r} R_{10} r^2\, dr \int_0^\pi \Theta_{00}^*\Theta_{00} \sin(\theta)\, d\theta \int_0^{2\pi} \Phi_0^*\Phi_0\, d\phi \qquad (16.2\text{-}25)$$

By our separate normalizations, the second and third integrals both equal unity, so that

$$\begin{aligned} \left\langle \frac{1}{r} \right\rangle &= \int_0^\infty R_{10}{}^* \frac{1}{r} R_{10} r^2\, dr = 4\left(\frac{Z}{a}\right)^3 \int_0^\infty e^{-2Zr/a} r\, dr \\ &= 4\left(\frac{Z}{a}\right)^3 \left(\frac{a}{2Z}\right)^2 (1) = \frac{Z}{a} \end{aligned} \qquad (16.2\text{-}26)$$

where we looked up the integral in Appendix C.

$$\langle \mathcal{V} \rangle = -\frac{Ze^2}{4\pi\varepsilon_0} \left\langle \frac{1}{r} \right\rangle = -\frac{Z^2e^2}{4\pi\varepsilon_0 a} \qquad (16.2\text{-}27)$$

Since the θ and the ϕ integrals in Eq. (16.2-25) both equal unity, we can omit them and use only the function R in calculating the expectation value of any function of r. The expectation value $\langle 1/r\rangle$ is proportional to Z, in agreement with the statement that the effective radius of a shell is inversely proportional to Z.

***Exercise 16.14**

Substitute the values of the constants into Eqs. (16.2-26) and (16.2-27) to obtain numerical values for $\langle 1/r \rangle$ and $\langle \mathcal{V} \rangle$ for a hydrogen atom.

As shown in Eq. (16.2-27) the expectation value of the potential energy of a hydrogenlike atom equals twice the total energy of Eq. (16.2-12). Therefore, the expectation value of 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.[3]

The Radial Distribution Function

The **radial distribution function,** f_r, is defined as the probability per unit value of r for finding the electron at a distance r from the nucleus. That is,

$$f_r\,dr = \begin{pmatrix} \text{Probability that the particle} \\ \text{lies at a distance from the} \\ \text{nucleus between } r \text{ and } r + dr \end{pmatrix} \tag{16.2-28}$$

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 in Figure 16.10a. The total probability of finding the electron in this shell is obtained by integrating over θ and ϕ:

$$f_r\,dr = \left(\int_0^{\pi}\int_0^{2\pi} |\psi(r, \theta, \phi)|^2 r^2 \sin(\theta)\phi\, d\theta\right)dr \tag{16.2-29}$$

where r is not integrated. The integral can be factored, and the θ and ϕ integrals give factors of unity:

$$f_r\,dr = R^*R\left(\int_0^{\pi} |\Theta|^2 \sin(\theta)\,d\theta \int_0^{2\pi} |\Phi|^2\,d\phi\right)r^2\,dr = R^*Rr^2\,dr \tag{16.2-30}$$

The expectation value of a quantity depending only on r can be computed using the radial distribution function. For example,

$$\left\langle \frac{1}{r} \right\rangle = \int_0^{\infty} \frac{1}{r} R^*Rr^2\,dr = \int_0^{\infty} \frac{1}{r} f_r\,dr \tag{16.2-31}$$

Figure 16.10b shows graphs of the radial distribution function for several energy eigenfunctions. 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. Since the radial distribution function is proportional to r^2, each one vanishes at the nucleus, and since it is proportional to an exponential function, each one approaches zero for large values of r. Therefore, each radial distribution function goes through one or more relative maxima. The s orbitals are nonzero at the nucleus (the origin) but even their radial distribution functions vanish at the nucleus.

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[3] Ira N. Levine, *Quantum Chemistry*, 4th ed., Prentice-Hall Englewood Cliffs, N.J., 1991, pp. 434ff.

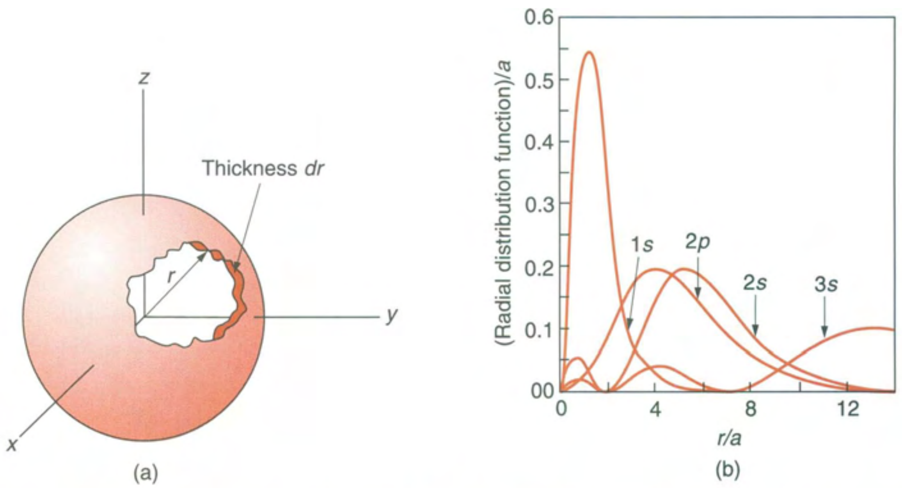

Figure 16.10. The Probability Distribution for Electron–Nucleus Distances. (a) **A spherical shell of radius *r*, and thickness *dr*.** This shell is centered on the origin, and contains the points that are at distances from the origin between r and $r + dr$. (b) **Radial distribution functions for hydrogenlike orbitals.** The radial distribution function is the probability density for finding the particle at a certain distance from the origin, irrespective of direction. It is somewhat analogous to the probability density for molecular speeds, although that probability density is a density in velocity space instead of coordinate space.

*Exercise 16.15

- **a.** Calculate the expectation value $\langle r \rangle$ for a hydrogenlike atom in the 1*s* state. Why is this not equal to $\langle 1/r \rangle^{-1}$?
- **b.** Calculate $\langle r^2 \rangle$ for a hydrogenlike atom in the 1*s* state. Why is this not equal to $\langle r \rangle^2$?
- **c.** Find the most probable value of r for a hydrogenlike atom in the 1*s* state. Why is this not equal to $\langle r \rangle$?

The Time-Dependent Wave Function of the Hydrogen Atom

We can now write the time-dependent wave function, using the three-dimensional analogue of Eq. (14.4-22):

$$\Psi_{nlm}(r, \theta, \phi, t) = \psi_{nlm}(r, \theta, \phi)e^{-iE_n t/\hbar} \tag{16.2-32}$$

This represents a stationary state. The probability density for finding the electron is time-independent. The expectation value of any time-independent variable is time-independent, and can be calculated with the coordinate wave function.

Exercise 16.16

Show that the expectation value $\langle 1/r \rangle$ is exactly the same as in Example 16.4 when the time-dependent wave function Ψ_{100} is used instead of the coordinate wave function ψ_{100}.

The Intrinsic Angular Momentum of the Electron. "Spin"

It is found experimentally that in addition to the angular momentum included in the solution to the Schrödinger equation, electrons have an additional angular momentum. To obtain adequate agreement with experiment, this feature must be added to the Schrödinger theory. The angular momentum included in the Schrödinger theory is now called the **orbital angular momentum** and the additional angular momentum is called the **intrinsic angular momentum** or the **spin angular momentum**. The Schrödinger theory is nonrelativistic and cannot be correct when particles have speeds near the speed of light. There is a version of quantum mechanics that is compatible with special relativity, based on the Dirac equation rather than the Schrödinger equation. The intrinsic angular momentum occurs naturally in this theory.

EXAMPLE 16.5

Calculate the expectation value of the square of the speed of the electron in a hydrogen atom in the 1*s* state, and from this calculate the root-mean-square speed. Compare this speed with the speed of light.

Solution

We can obtain this quantity from the expectation value of the kinetic energy:

$$\begin{aligned}\langle \mathscr{K} \rangle &= E_1 - \langle \mathscr{V} \rangle = -2.18 \times 10^{-18}\,\mathrm{J} + \frac{e^2}{4\pi\varepsilon_0}\left\langle \frac{1}{r} \right\rangle \\ &= -2.18 \times 10^{-18}\,\mathrm{J} + 2(2.18 \times 10^{-18}\,\mathrm{J}) = 2.18 \times 10^{-18}\,\mathrm{J} \\ \langle v^2 \rangle &= \frac{2\langle \mathscr{K} \rangle}{m} = \frac{2(2.18 \times 10^{-18}\,\mathrm{kg\,m^2\,s^{-2}})}{9.11 \times 10^{-31}\,\mathrm{kg}} = 4.69 \times 10^{12}\,\mathrm{m^2\,s^{-2}} \\ v_{\mathrm{rms}} &= \langle v^2 \rangle^{1/2} = 2.16 \times 10^6\,\mathrm{m\,s^{-1}}\end{aligned}$$

which is smaller than the speed of light by a factor of roughly 100. Although relativistic corrections are not important for the hydrogen atom, they are important for atoms beyond the middle of the periodic table.

The z component of the intrinsic angular momentum takes on one of only two possible values, $\hbar/2$ and $-\hbar/2$. We denote the intrinsic angular momentum by **S** and write

$$S_z = \pm\frac{\hbar}{2} \tag{16.2-33}$$

We assign a new quantum number, m_s, for the z component of the intrinsic angular momentum, with the values

$$m_s = \pm\frac{1}{2} \tag{16.2-34}$$

The total angular momentum of an electron is the vector sum of the orbital and intrinsic angular momenta. The total angular momentum is denoted by **J** and its z component is denoted by J_z. It has values

$$J_z = m\hbar + m_s\hbar \tag{16.2-35}$$

where m is the same quantum number as before.

The pattern of values of m_s is analogous to that of Eq. (16.1-43) for the orbital angular momentum if we assign a quantum number s for the square of the intrinsic angular momentum with a fixed value of $\frac{1}{2}$. If we allow half-integral values for quantum numbers, all angular momentum quantum numbers follow this pattern. The square of the intrinsic angular momentum has the fixed value

$$s^2 = \hbar^2 \frac{1}{2}\left(\frac{1}{2}+1\right) \tag{16.2-36}$$

following the same pattern as Eq. (16.1-40).

There are three principal differences between the orbital angular momentum and the intrinsic angular momentum. First, the orbital angular momentum occurred naturally in the nonrelativistic Schrödinger theory, while the intrinsic angular momentum is arbitrarily added to the theory in order to make it agree with experiment and with this aspect of relativistic quantum mechanics. Second, the intrinsic angular momentum has only one possible magnitude while the orbital angular momentum has variable (but quantized) magnitude. Third, this single magnitude corresponds to a quantum number that is a half-integer instead of an integer. Figure 16.11 shows the two cones of possible directions of the intrinsic angular momentum.

EXAMPLE 16.6

Find the angle between the z axis and the intrinsic angular momentum for $m_s = +\frac{1}{2}$.

Solution

$$\theta = \arccos\left(\frac{\hbar/2}{\hbar\sqrt{(1/2)(3/2)}}\right) = \arccos\left(\frac{1/2}{\sqrt{3/4}}\right)$$

$$= \arccos(0.57735) = 54.7356\ldots \text{ degrees} = 0.9553166\ldots \text{ radians}$$

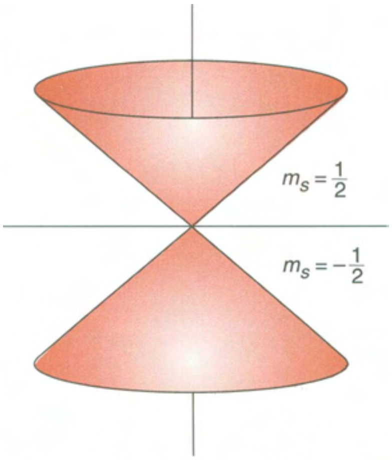

Figure 16.11. Cones of Spin Angular Momentum Directions for One Electron. Compare this diagram with that of Figure 16.5. The z component of an orbital angular momentum can take on various values, depending on the value of l. The z component of the spin angular momentum can take on only one of two possible values.

It is natural to seek a classical interpretation for the intrinsic angular momentum. Although we have previously treated the electron as a mass point, and although it is not known what its 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 **spin angular momentum**. The assumed motion is analogous to the rotation of the earth on its axis as it revolves about the sun. We will use this spin interpretation, although we could proceed if we wished without any mental picture of spinning motion, and there is no guarantee that it is physically accurate. We now have twice as many possible states of electronic motion in a hydrogenlike atom as we did before, since for every set of values of the quantum numbers n, l, and m, there are two possible values of m_s. We will call the state for $m_s = +\frac{1}{2}$ the "spin up" state and the state for $m_s = -\frac{1}{2}$ "spin down" state, corresponding to the direction of the intrinsic angular momentum vector.

There are two different ways to include spin in our notation. The first is to attach another subscript to the orbital symbol, replacing nlm by $nlmm_s$. There is no need to include the value of s since it is fixed. The orbital is now called a **spin orbital**. The second way is to multiply the original orbital by a **spin function** that is called α for $m_s = +\frac{1}{2}$ and β for $m = -\frac{1}{2}$. The original orbital is now called a **space orbital** and the product is called a spin orbital. The spin function is thought of as being a function of some spin coordinates that are not explicitly represented. The two ways of writing a spin orbital are equivalent:

$$\psi_{nlm,1/2} = \psi_{nlm}\alpha, \qquad \psi_{nlm,-1/2} = \psi_{nlm}\beta \tag{16.2-37}$$

We define operators for the spin angular momentum that are analogous to the orbital angular momentum operators. We do not write any explicit mathematical forms for them, but assign their properties by definition. The spin functions α and β are defined to be eigenfunctions of $\hat{S}^2$, the operator for the square of the spin angular momentum:

$$\hat{S}^2\alpha = \hbar^2(1/2)(3/2)\alpha \tag{16.2-38}$$

$$\hat{S}^2\beta = \hbar^2(1/2)(3/2)\beta \tag{16.2-39}$$

They are also defined to be eigenfunctions of $\hat{S}_z$, the operator for the z component of the spin angular momentum:

$$\hat{S}_z\alpha = +\frac{\hbar}{2}\alpha \tag{16.2-40}$$

$$\hat{S}_z\beta = -\frac{\hbar}{2}\beta \tag{16.2-41}$$

The spin functions are defined to be normalized and to be orthogonal to each other.

Addition of the intrinsic angular momentum modifies the Schrödinger theory of the electron so that it agrees adequately with experiment for many purposes. Further modifications can be made to include additional aspects of relativistic quantum mechanics such as small 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, although it is numerically important in heavy atoms.[4]

16.3

The Helium Atom in the "Zero-Order" Orbital Approximation

The hydrogenlike atom is the only atom for which the Schrödinger equation can be solved without approximation. This does not invalidate the Schrödinger quantum theory for other atoms, since approximate treatments of other atoms have been carried out that give accurate agreement with experimental energy values. It does mean that the only way to proceed with other atoms is with approximations.

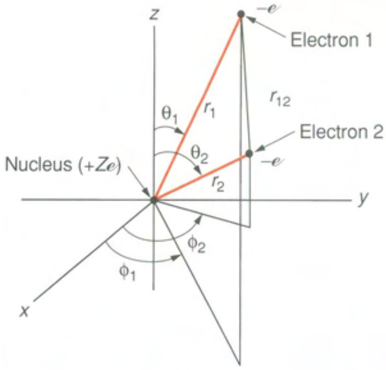

Figure 16.12. The Helium Atom System. The occurrence of two electrons makes it impossible to obtain an exact solution to the Schrödinger equation for this system.

The Hamiltonian of a Heliumlike Atom

The helium atom contains two electrons and a nucleus containing two protons. We define a "heliumlike" atom with Z protons in the nucleus, so that $Z = 2$ represents the He atom, $Z = 3$ represents the Li^+ ion, etc. The system is shown in Figure 16.12. The three-body problem cannot be solved exactly, either in classical or in quantum

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[4] Pilar, *op. cit.*, pp. 301ff (Note 1); K. Balasubramanian, *J. Phys. Chem.*, **93**, 6585 (1989).

mechanics, so we assume that the helium nucleus is stationary. This is a good approximation, as with the hydrogenlike atom. With a stationary nucleus, the classical Hamiltonian function is

$$H_{\mathrm{cl}} = \frac{1}{2m}p_1^2 + \frac{1}{2m}p_2^2 + \frac{1}{4\pi\varepsilon_0}\left(-\frac{Ze^2}{r_2} - \frac{Ze^2}{r_1} + \frac{e^2}{r_{12}}\right) \tag{16.3-1}$$

where $\mathbf{p}_1$ is the vector momentum of electron 1, $\mathbf{p}_2$ is the vector momentum of electron 2, m is the electron mass, and the distances are as labeled in Figure 16.12. The Hamiltonian operator is

$$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2) + \frac{1}{4\pi\varepsilon_0}\left(-\frac{Ze^2}{r_2} - \frac{Ze^2}{r_1} + \frac{e^2}{r_{12}}\right) \tag{16.3-2}$$

where ∇_1^2 and ∇_2^2 are the Laplacian operators for electrons 1 and 2.

The "Zero-Order" Orbital Approximation

The Hamiltonian operator of Eq. (16.3-2) gives a time-independent Schrödinger equation that has not been solved exactly. We begin with the **zero-order approximation**, which is obtained by neglecting the repulsion of the electrons for each other. It is not a good approximation, but it is a starting point for better approximations. The approximate Hamiltonian operator is now

$$\hat{H}^{(0)} = -\frac{\hbar^2}{2m}\nabla_1^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_1} - \frac{\hbar^2}{2m}\nabla_2^2 - \frac{Ze^2}{4\pi\varepsilon_0 r_2} \tag{16.3-3}$$

where we add a superscript (0) to distinguish the approximate "zero-order" Hamiltonian from the correct Hamiltonian. It is a sum of hydrogenlike Hamiltonian operators:

$$\hat{H}^{(0)} = \hat{H}_{\mathrm{HL}}(1) + \hat{H}_{\mathrm{HL}}(2) \tag{16.3-4}$$

where the subscript HL stands for "hydrogenlike," and where we abbreviate the coordinates of a particle by writing only the particle index. The approximate time-independent Schrödinger equation is

$$\hat{H}^{(0)}\Psi^{(0)}(1,2) = \left[\hat{H}_{\mathrm{HL}}(1) + \hat{H}_{\mathrm{HL}}(2)\right]\Psi^{(0)}(1,2) = E^{(0)}\Psi^{(0)}(1,2) \tag{16.3-5}$$

where we attach a superscript (0) to the zero-order wave function and eigenvalue. Equation (16.3-5) can be solved by separation of variables, using the trial solution:

$$\Psi^{(0)}(1,2) = \psi_1(r_1, \theta_1, \phi_1)\psi_2(r_2, \theta_2, \phi_2) = \psi_1(1)\psi_2(2) \tag{16.3-6}$$

where ψ_1 and ψ_2 are two orbitals (functions of the coordinates of one electron). In the second version of the orbitals, each particle's coordinates are represented only by their subscript. A multielectron wave function that is a product of orbitals is called an **orbital wave function**.

We substitute the trial solution into Eq. (16.3-5) and use the fact that $\psi_1(1)$ is treated as a constant when $\hat{H}_{\mathrm{HL}}(2)$ operates and $\psi_2(2)$ is treated as a constant when $\hat{H}_{\mathrm{HL}}(1)$ operates. The result is

$$\psi_2(2)\hat{H}_{\mathrm{HL}}(1)\psi_1(1) + \psi_1(1)\hat{H}_{\mathrm{HL}}(2)\psi_2(2) = E^{(0)}\psi_1(1)\psi_2(2) \tag{16.3-7}$$

Division of this equation by $\psi_1(1)\psi_2(2)$ completes the separation of variables:

$$\frac{1}{\psi_1(1)}\hat{H}_{\text{HL}}(1)\psi_1(1) + \frac{1}{\psi_2(2)}\hat{H}_{\text{HL}}(2)\psi_2(2) = E^{(0)} \tag{16.3-8}$$

Each of the terms on the left-hand-side of the equation contains only a set of variables not occurring in the other term, and the right-hand side is a constant. The first term must be equal to a constant, which we call E_1, and the second term must be equal to a constant, E_2, such that

$$E_1 + E_2 = E^{(0)} \tag{16.3-9}$$

We now have two differential equations:

$$\hat{H}_{\text{HL}}(1)\psi_1(1) = E_1\psi_1(1) \tag{16.3-10}$$

$$\hat{H}_{\text{HL}}(2)\psi_2(2) = E_2\psi_2(2) \tag{16.3-11}$$

Equations (16.3-10) and (16.3-11) are two hydrogenlike Schrödinger equations. Therefore, E_1 and E_2 are hydrogenlike energies (orbital energies). The total electronic energy in the zero-order approximation is

$$E^{(0)}_{n_1 n_2} = E_{n_1}(\text{HL}) + E_{n_2}(\text{HL}) = -(13.60\,\text{eV})(Z^2)\left[\frac{1}{n_1^2} + \frac{1}{n_2^2}\right] \tag{16.3-12}$$

where n_1 and n_2 are two values of the principal quantum number for a hydrogenlike atom. The orbitals $\psi_1(1)$ and $\psi_2(2)$ are hydrogenlike orbitals:

$$\Psi^{(0)}(1,2) = \psi_1(1)\psi_2(2) = \psi_{n_1 l_1 m_1 m_{s1}}(1)\psi_{n_2 l_2 m_2 m_{s2}}(2) \tag{16.3-13}$$

The values of a given quantum number for the two orbitals are not necessarily equal, so we add a subscript on each subscript to distinguish them from each other. The notation with separate spin functions can also be used.

Probability Densities for Two Particles

For a system of two particles whose wave function is $\Psi(1,2)$, the probability of finding particle 1 in the volume element $d^3\mathbf{r}_1$ and finding particle 2 in the volume element $d^3\mathbf{r}_2$ is given by

$$(\text{Probability}) = \Psi^*(1,2)\Psi(1,2)\,d^3\mathbf{r}_1\,d^3\mathbf{r}_2 = |\Psi(1,2)|^2\,d^3\mathbf{r}_1\,d^3\mathbf{r}_2 \tag{16.3-14}$$

The square of the magnitude of the wave function is a probability density in a six-dimensional space. For the orbital wave function of Eq. (16.3-13), the probability density for two particles is the product of two one-particle probability densities:

$$|\Psi(1,2)|^2 = |\psi_1(1)|^2|\psi_2(2)|^2 \tag{16.3-15}$$

Since we have neglected the interaction between the electrons, it is reasonable that the probability densities of the two particles are independent of each other. If this probability density is normalized,

$$\int |\Psi(1,2)|^2\,d^3\mathbf{r}_1\,d^3\mathbf{r}_2 = 1 \tag{16.3-16}$$

We consider the inclusion of spin functions later.

The Indistinguishability of Identical Particles

Although we have obtained a function that satisfies our approximate Schrödinger equation and the appropriate boundary conditions, it must be further modified to obtain agreement with experiment. It must conform to the condition: *Identical particles are inherently indistinguishable from each other.* This condition does not occur in classical mechanics and is an additional hypothesis that must be tested by comparing its consequences with experimental fact. It is plausible because of the uncertainty principle, which makes exact trajectories impossible to specify, so that if two identical particles approach each other closely it might not be possible to tell which is which after the encounter. Figure 16.13 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.

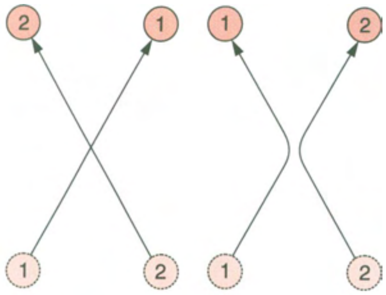

Figure 16.13. Two Encounters of Classical Particles. Since classical mechanics includes exact trajectories, we can "track" each particle exactly.

We must not build anything into our theory 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 would give an illusory means of distinguishing the particles. The probability density in Eq. (16.3-14) must remain unchanged if the locations of the two electrons are interchanged:

$$\Psi(1,2)^{*}\Psi(1,2)=\Psi(2,1)^{*}\Psi(2,1) \tag{16.3-17}$$

That is, the probability density $\Psi^{*}\Psi$ must be **symmetric** with respect to interchange of the two particles' locations. The probability density of two particles does not have to be symmetric if the particles are not identical. For example, the probability density for a hydrogen atom does not have to be symmetry with respect to interchange of the proton and the electron.

With real functions there are only two ways to satisfy Eq. (16.3-17). Either the wave function must be **symmetric** with respect to interchange of the particles:

$$\Psi(1,2)=\Psi(2,1) \qquad \text{(symmetric wave function)} \tag{16.3-18}$$

or the wave function must be **antisymmetric** with respect to interchange of the particles (change sign if the locations of the particles are switched):

$$\Psi(1,2)=-\Psi(2,1) \qquad \text{(antisymmetric wave function)} \tag{16.3-19}$$

Although our wave functions are not required to be real, they are also not required to be complex. We consider only these two possibilities.

Particles that obey Eq. (16.3-18) are called **bosons**, and particles that obey Eq. (16.3-19) are called **fermions**. Electrons are found experimentally to be fermions, so that our approximate two-electron wave function must be modified to obey Eq. (16.3-19). Protons and neutrons are also fermions. Photons are bosons. Atoms or molecules containing an even number of fermions are bosons, and molecules containing an odd number of fermions are fermions. The requirement that a two-electron wave function be antisymmetric is a requirement of the same sort as the requirement that a wave function be continuous, single-valued, and finite. These conditions, in addition to solution of the Schrödinger equation, must be applied to find an acceptable wave function.

The simplest way to obtain an antisymmetric two-electron orbital wave function is to add a second term that is the negative of the first term with the orbital labels interchanged, giving

$$\Psi(1,2)=C\left[\psi_1(1)\psi_2(2)-\psi_2(1)\psi_1(2)\right] \tag{16.3-20}$$

We say that we have **antisymmetrized** the wave function. With this wave function it is not possible to say which electron occupies which orbital, because the labels are in one order in the first term of the antisymmetric wave function and in the other order in the second term.

Exercise 16.17

By explicit manipulation, show that the function of Eq. (16.3-20) obeys Eq. (16.3-19).

The Pauli Exclusion Principle

There is an important fact about fermions that we can see in Eq. (16.3-20). If the orbitals ψ_1 and ψ_2 are the same function, the two-particle wave function is the difference of two identical terms and vanishes. A vanishing wave function cannot represent any state of the system. Therefore, a given spin orbital cannot occur more than once in any term of a two-electron wave function. We will later construct orbital wave functions for more than two electrons. When antisymmetrized, these will consist of a sum of terms with different signs. Each term will be a product of spin orbitals, one for each electron. The **Pauli exclusion principle** is a generalization of our observations for two electrons: *In an orbital wave function, the same spin orbital cannot occur more than once in each term.* A spin orbital that occurs in an orbital wave function is said to be "occupied" by an electron. Another statement of the Pauli exclusion principle is: *In an orbital wave function, no two electrons can occupy the same spin orbital.*

The Pauli exclusion principle is named for Wolfgang Pauli, 1900–1958, who received the 1945 Nobel Prize in physics for his contributions to quantum mechanics.

The probability density for the antisymmetrized wave function of Eq. (16.3-20) is

$$\Psi(1,2)^*\Psi(1,2) = |C|^2[|\psi_1(1)|^2|\psi_2(2)|^2 + |\psi_2(1)|^2|\psi_1(2)|^2 \\ - \psi_1(1)^*\psi_2(1)\psi_2(2)^*\psi_1(2) - \psi_2(1)^*\psi_1(1)\psi_1(2)^*\psi_2(2)] \quad (16.3\text{-}21)$$

where C is a normalizing constant. Each term in Eq. (16.3-21) gives an integral that factors into a product of two one-particle integrals. Each of the first two terms gives unity if the orbitals are normalized. Each of the last two terms gives zero if the orbitals are orthogonal to each other. To normalize the wave function,

$$1 = |C|^2[1+1] = 2|C|^2$$

or if C is taken to be real and positive,

$$C = \sqrt{\frac{1}{2}} \quad (16.3\text{-}22)$$

The probability of finding particle 1 in the volume element $d^3\mathbf{r}_1$ irrespective of the location of particle 2 is given by integrating the probability density in Eq. (16.3-14) over all positions of particle 2:

$$\begin{pmatrix}\text{Probability of finding}\\ \text{particle 1 in } d^3\mathbf{r}_1\end{pmatrix} = \left[\int \Psi(1,2)^*\Psi(1,2)\,d^3\mathbf{r}_2\right]d^3\mathbf{r}_1 \quad (16.3\text{-}23)$$

If the two-electron wave function is a one-term orbital wave function such as that of Eq. (16.3-6), the orbital function for electron 1 factors out of the integral:

$$\begin{pmatrix}\text{Probability of finding}\\ \text{particle 1 in } d^3\mathbf{r}_1\end{pmatrix} = \psi_1(1)^*\psi_1(1)\,d^3\mathbf{r}_1 \int \psi_2(2)^*\psi_2(2)\,d^3\mathbf{r}_2$$

If ψ_2 is normalized, the integral in this equation equals unity and

$$\begin{pmatrix}\text{Probability of finding} \\ \text{particle 1 in } d^3\mathbf{r}_1\end{pmatrix} = \psi_1(1)^*\psi_1(1)\,d^3\mathbf{r}_1 = |\psi_1(1)|^2\,d^3\mathbf{r}_1 \tag{16.3-24}$$

The probability density for electron 1 is just that of its own orbital, independent of electron 2. An analogous equation can be written for electron 2.

If the antisymmetrized wave function of Eq. (16.3-21) is used, the expression must be integrated in the same way as Eq. (16.3-23) to obtain the probability density for particle 1. Only the first two terms in Eq. (16.3-21) survive, due to the orthogonality of the orbitals, and the result is

$$\begin{aligned}\begin{pmatrix}\text{Probability of finding} \\ \text{particle 1 in } d^3\mathbf{r}_1\end{pmatrix} &= |C|^2\left[|\psi_1(1)|^2 + |\psi_2(1)|^2\right]d^3\mathbf{r}_1 \\ &= \frac{1}{2}\left[|\psi_1(1)|^2 + |\psi_2(1)|^2\right]d^3\mathbf{r}_1 \end{aligned} \tag{16.3-25}$$

This probability is the average of what would occur if electron 1 occupied orbital 1 and what would occur if it occupied orbital 2. Since we cannot specify which orbital is occupied by the electron, this is a plausible result. An exactly analogous expression can be written for electron 2. The total probability of finding some electron in a volume $d^3\mathbf{r}$ is the sum of the probabilities for the two electrons:

$$\begin{aligned}\begin{pmatrix}\text{Probability of finding} \\ \text{an electron in } d^3\mathbf{r}_1\end{pmatrix} &= 2|C|^2\left[|\psi_1(\mathbf{r})|^2 + |\psi_2(\mathbf{r})|^2\right]d^3\mathbf{r} \\ &= \left[|\psi_1(\mathbf{r})|^2 + |\psi_2(\mathbf{r})|^2\right]d^3\mathbf{r} \end{aligned} \tag{16.3-26}$$

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 Ground State of the Helium Atom

The lowest-energy state of a system is called its **ground state**. Since the subshell of lowest orbital energy, the 1*s* subshell, contains two spin orbitals (one space orbital), both electrons can be in the 1*s* subshell. Our approximate ground-state wave function is

$$\begin{aligned}\Psi^{(0)}_{1s1s}(1,2) &= \Psi_{1s,1/2;1s,-1/2}(1,2) \\ &= C[\psi_{100,1/2}(1)\psi_{100,-1/2}(2) - \psi_{100,-1/2}(1)\psi_{100,1/2}(2)] \end{aligned} \tag{16.3-27}$$

where two sets of orbital subscripts are used because the orbital wave function contains two spin orbitals. This wave function is antisymmetric, and satisfies the Pauli exclusion principle. If the spin orbitals are written as products of space orbitals and spin functions, the spin part can be factored out:

$$\begin{aligned}\Psi^{(0)}(1,2) &= C\left[\psi_{100}(1)\alpha(1)\psi_{100}(2)\beta(2) - \psi_{100}(1)\beta(1)\psi_{100}(2)\alpha(2)\right] \\ &= C\psi_{100}(1)\psi_{100}(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \end{aligned} \tag{16.3-28}$$

To normalize the wave function, the constant C must be such that

$$1 = C^*C\int \Psi^{(0)}(1,2)^*\Psi^{(0)}(1,2)\,dq_1'\,dq_2' \tag{16.3-29}$$

where the coordinates of both particles are integrated. Since we have introduced spin functions, an integration over the independent variables of the spin functions as well as over the space coordinates is indicated. We regard dq'_1 and dq'_2 as representing both space and spin coordinates:

$$dq'_1 = d^3\mathbf{r}_1\, d^s(1) \tag{16.3-30}$$

where $d^3\mathbf{r}_1$ is the volume element in ordinary space, and $d^s(1)$ is the "volume element" of the unspecified spin coordinates. We do not explicitly integrate over the unspecified spin coordinates, but define the spin functions α and β to be normalized and orthogonal to each other:

$$\int \alpha(1)^*\alpha(1)\, d^s(1) = \int \beta(1)^*\beta(1)\, d^s(1) = 1 \quad \text{(by definition)} \tag{16.3-31}$$

and

$$\int \beta(1)^*\alpha(1)\, d^s(1) = \int \alpha(1)^*\beta(1)\, d^s(1) = 0 \quad \text{(by definition)} \tag{16.3-32}$$

We use these definitions when an integration over spin coordinates is indicated instead of explicitly carrying out an integration.

The two-electron wave function in Eq. (16.3-28) is substituted into the normalization integral of Eq. (16.3-29). The integral can be factored, since the space and spin coordinates of each particle occur in separate factors:

$$\begin{aligned} 1 = C^*C \int \psi_{100}(1)^*\psi_{100}(1)\, d^3\mathbf{r}_1 \int \psi_{100}(2)^*\psi_{100}(2)\, d^3\mathbf{r}_2 \\ \times \int [\alpha(1)\beta(2) - \beta(1)\alpha(2)]^*[\alpha(1)\beta(2) - \beta(1)\alpha(2)]\, d^s(1)\, d^s(2) \end{aligned} \tag{16.3-33}$$

Since the hydrogenlike orbitals are normalized, the integrals over the space coordinates equal unity, and we have, after multiplying out the terms and factoring the spin integrals:

$$\begin{aligned} 1 = C^*C\Bigg\{\Bigg[\int \alpha(1)^*\alpha(1)\, d^s(1) \int \beta(2)^*\beta(2)\, d^s(2) \\ + \int \beta(1)\beta(1)\, d^s(1) \int \alpha(2)^*\alpha(2)\, d^s(2) \\ - \int \alpha(1)^*\beta(1)\, d^s(1) \int \beta(2)^*\alpha(2)\, d^s(2) \\ - \int \beta(1)^*\alpha(1)\, d^s(1) \int \alpha(2)^*\beta(2)\, d^s(2)\Bigg]\Bigg\} \end{aligned} \tag{16.3-34}$$

where we have factored the double integrals. Each of the first two terms in the final equation above gives unity because of the defined normalization of the spin functions. The last two terms give zero because of the defined orthogonality of the spin functions, so that if we choose C to be real and positive,

$$C = \sqrt{\frac{1}{2}} \tag{16.3-35}$$

The energy eigenvalue for our zero-order ground-state wave function is the sum of two hydrogenlike orbital energies:

$$E^{(0)}_{1s1s} = E_1(\mathrm{HL}) + E_1(\mathrm{HL}) = 2(-13.60\,\mathrm{eV})Z^2 \tag{16.3-36a}$$

For helium, $Z = 2$, so that

$$E^{(0)}_{1s1s} = -108.8\,\mathrm{eV} \tag{16.3-36b}$$

This approximate energy eigenvalue is seriously in error, since the experimental value is $-79.0\,\text{eV}$. Since 1 eV is equivalent to $96.5\,\text{kJ}\,\text{mol}^{-1}$, an error of 30 eV is a very large error, larger than chemical bond energies. We obtain better approximations in the next chapter.

Excited States of the Helium Atom

States of higher energy than the ground state are called **excited states**. For excited states represented by orbital wave functions, there are two cases: (1) both electrons occupy the same space orbital with different spin functions, and (2) the two electrons occupy different space orbitals, either with the same or different spin functions. A statement of which 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. This superscript can equal either 1 or 2. The **subshell configuration** is specified by writing the designation of each subshell with a right superscript giving the number of electrons occupying orbitals of that subshell. The maximum value of this superscript is 2 for an s subshell, 6 for a p subshell, 10 for a d subshell, and so on. The configuration of the ground state of helium is $(1s)^2$ (subshell and detailed configurations are the same with s subshells). Two of the many possible excited configurations are $(1s)^1(2s)^1$ and $(1s)^1(2p0)^1$ (detailed) or $(1s)^1(2p)^1$ (subshell). A superscript equal to unity is often omitted, so that $(1s)(2s)$ means the same as $(1s)^1(2s)^1$.

If both electrons occupy the same space orbital, a wave function for an excited state is similar to that of the ground state, with the antisymmetric spin factor. For the configuration $(2s)^2$:

$$\Psi_{2s2s} = \frac{1}{\sqrt{2}}\psi_{2s}(1)\psi_{2s}(2)[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \tag{16.3-37}$$

For the configuration $(1s)^1(2s)^1$, there are four states, since each electron has two choices, spin up and spin down. Four antisymmetric wave functions are:

$$\Psi_1 = \frac{1}{\sqrt{2}}[\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)]\alpha(1)\alpha(2) \tag{16.3-38a}$$

$$\Psi_2 = \frac{1}{\sqrt{2}}[\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)]\beta(1)\beta(2) \tag{16.3-38b}$$

$$\Psi_3 = \frac{1}{2}[\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)][\alpha(1)\beta(2) + \beta(1)\alpha(2)] \tag{16.3-38c}$$

$$\Psi_4 = \frac{1}{2}[\psi_{1s}(1)\psi_{2s}(2) + \psi_{2s}(1)\psi_{1s}(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)] \tag{16.3-38d}$$

All of these functions are eigenfunctions of the $\hat{L}^2$ and $\hat{S}^2$ operators, although we do not prove that fact.

Exercise 16.18

Show that Ψ_3 and Ψ_4 satisfy the zero-order Schrödinger equation and find the energy eigenvalue. Show that these functions are normalized if the orbitals are normalized.

Angular Momentum in the Helium Atom. Russell–Saunders Coupling

It is a theorem of both classical and quantum mechanics that the total angular momentum of an isolated system is conserved. If no external forces act on the system, its total angular momentum does not change in time. A conserved quantity 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 the same name. The total angular momentum is always a good quantum number for an isolated atom or molecule, and for atoms in the first part of the periodic table the orbital and spin angular momenta can be assumed to be good quantum numbers. This assumption is called **Russell–Saunders coupling**.

The sum of two angular momenta is a vector sum. Consider an atom with two electrons. Let $\mathbf{l}_1$ and $\mathbf{s}_1$ be the orbital and spin angular momenta of electron 1, and let $\mathbf{l}_2$ and $\mathbf{s}_2$ be the orbital and spin angular momenta of electron 2. We will now use lower-case letters for angular momenta of single electrons, and capital letters for angular momenta of multielectron atoms. The total orbital and spin angular momenta of the helium atom are vector sums of the contributions of the individual electrons:

$$\mathbf{L} = \mathbf{l}_1 + \mathbf{l}_2 \tag{16.3-39}$$

$$\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2 \tag{16.3-40}$$

The total angular momentum of the atom is

$$\mathbf{J} = \mathbf{L} + \mathbf{S} \tag{16.3-41}$$

The eigenvalues of the $\hat{J}^2$, $\hat{J}_z$, $\hat{L}^2$, $\hat{L}_z$, $\hat{S}^2$, and $\hat{S}_z$ operators follow the same pattern as other angular momenta:

$$\hat{J}^2\Psi = \hbar^2 J(J+1)\Psi \tag{16.3-42}$$

$$\hat{J}_z\Psi = \hbar M_J\Psi \tag{16.3-43}$$

$$\hat{L}^2\Psi = \hbar^2 L(L+1)\Psi \tag{16.3-44}$$

$$\hat{L}_z\Psi = \hbar M_L\Psi \tag{16.3-45}$$

$$\hat{S}^2\Psi = \hbar^2 S(S+1)\Psi \tag{16.3-46}$$

$$\hat{S}_z\Psi = \hbar M_S\Psi \tag{16.3-47}$$

Figure 16.14 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, the energy levels are characterized by the values of L and S. The orbital angular momentum quantum number L is a nonnegative integer. The spin angular momentum quantum number S is a nonnegative integer or half-integer. Each set of states corresponding to a particular value of L and a particular value of S is called a **term**. A **Russell–Saunders term symbol** is assigned to each term. The principal part of the symbol is a letter giving the value of L, as follows:

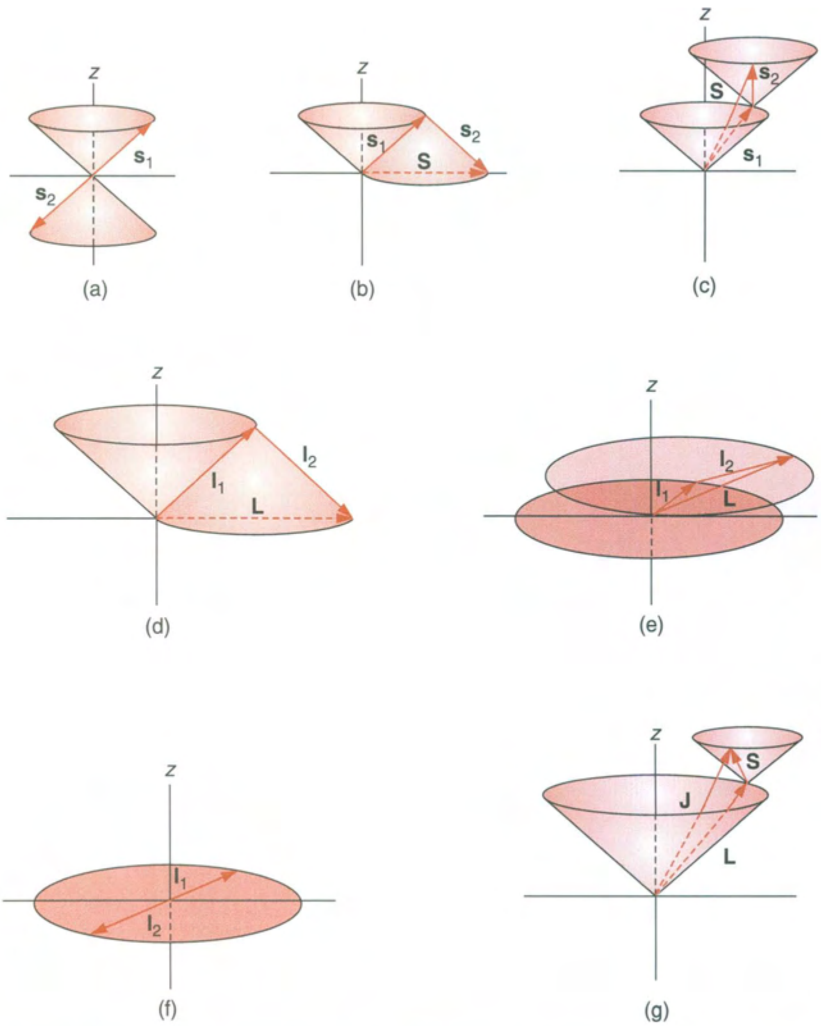

Figure 16.14. Examples of Vector Addition of Angular Momenta. These examples show how angular momenta add vectorially to give sums that follow the standard pattern for an angular momentum. (a) Two electron spins: $m_{s1} = 1/2$, $m_{s2} = -1/2$, $M_S = 0$, $S = 0$. (b) Two electron spins: $m_{s1} = 1/2$, $m_{s2} = -1/2$, $M_S = 0$, $S = 1$. (c) Two electron spins: $m_{s1} = 1/2$, $m_{s2} = 1/2$, $M_S = 1$, $S = 1$. (d) Two *p* electrons' orbital angular momenta: $l_1 = 1$, $m_1 = 1$, $l_2 = 1$, $m_2 = -1$, $M_L = 0$, $L = 1$. (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: $L = 1$, $M_L = 1$, $S = 1/2$, $M_S = 1/2$, $M_J = 3/2$, $J = 3/2$.

Value of L	Symbol
0	S
1	P
2	D
3	F
4	G
etc.	

From this point on the symbols are in alphabetical order.

A left superscript is attached that has the value $2S + 1$. For our two sets of states we will show that we have ${}^3S$ and ${}^1S$ (pronounced "triplet S" and "singlet S.") In addition to the terms "singlet" for $S = 0$ and "triplet" for $S = 1$, we use "doublet" for $S = 1/2$, "quartet" for $S = 3/2$, etc. The value of the left superscript is called the **multiplicity** of the term, and is equal to the number of values of M_S that occur since M_S ranges from S to $-S$. A right subscript giving the value of J is also sometimes used.

We now investigate the values of the quantum numbers for particular configurations. Since the angular momenta are vectors, their operators are expressed as vector sums. For two electrons,

$$\hat{L}^2 = (\hat{l}_{x1} + \hat{l}_{x2})^2 + (\hat{l}_{y1} + \hat{l}_{y2})^2 + (\hat{l}_{z1} + \hat{l}_{z2})^2 \tag{16.3-48}$$

$$\hat{L}_z = \hat{l}_{z1} + \hat{l}_{z2} \tag{16.3-49}$$

$$\hat{S}^2 = (\hat{s}_{x1} + \hat{s}_{x2})^2 + (\hat{s}_{y1} + \hat{s}_{y2})^2 + (\hat{s}_{z1} + \hat{s}_{z2})^2 \tag{16.3-50}$$

$$\hat{S}_z = \hat{s}_{z1} + \hat{s}_{z2} \tag{16.3-51}$$

The $\hat{L}_2$ and $\hat{S}^2$ expressions are not easy to use because they contain terms that do not commute with each other, and we will not obtain explicit expressions for them.[5] We can find the values of M_L and M_S, and from these infer the values of L and S using the fact that M_L ranges from $+L$ to $-L$ and that M_S ranges from $+S$ to $-S$. For two electrons, since the z components of two vectors add algebraically,

$$\boxed{M_L = m_1 + m_2} \tag{16.3-52}$$

and

$$\boxed{M_S = m_{s1} + m_{s2}} \tag{16.3-53}$$

EXAMPLE 16.7

Find the values of the quantum numbers M_L and M_S for each of the wave functions in Eq. (16.3-38a)–(16.3-38d).

Solution

$$\begin{aligned}\hat{L}_z\Psi_1 &= \left(\hat{l}_{z1} + \hat{l}_{z2}\right)\Psi_1 = \frac{1}{\sqrt{2}}\left[\hat{l}_{z1}\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\hat{l}_{z2}\psi_{1s}(2)\right]\alpha(1)\alpha(2)\\ &= 0 + 0 = 0\end{aligned}$$

so that $M_L = 0$. All of the other wave functions also contain only s orbitals, so that $M_L = 0$ for all of them.

$$\begin{aligned}\hat{S}_z\Psi_1 &= (\hat{s}_{z1} + \hat{s}_{z2})\Psi_1\\ &= \frac{1}{\sqrt{2}}(\psi_{1s}(1)\psi_{1s}(2) - \psi_{1s}(1)\psi_{1s}(2))(\hat{s}_{z1}\alpha(1)\alpha(2) + \alpha(1)\hat{s}_{z2}\alpha(2))\\ &= \frac{1}{\sqrt{2}}(\psi_{1s}(1)\psi_{1s}(2) - \psi_{1s}(1)\psi_{1s}(2))\left(\frac{\hbar}{2}\alpha(1)\alpha(2) + \alpha(1)\frac{\hbar}{2}\alpha(2)\right)\\ &= \left(\frac{\hbar}{2} + \frac{\hbar}{2}\right)\Psi_1 = \hbar\Psi_1\end{aligned}$$

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[5] Levine, *op. cit.*, pp. 292ff (Note 3).

so that Ψ_1 corresponds to $M_S = 1$. We carried out the operations, but could have simply identified the m_s values and added them.

Similarly,

$$\hat{S}_z\Psi_2 = \left(-\frac{\hbar}{2}-\frac{\hbar}{2}\right)\Psi_2 = -\hbar\Psi_2$$

so that $M_S = -1$ for Ψ_2.

$$\begin{aligned}\hat{S}_z\Psi_3 &= \frac{1}{2}[\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)] \\ &\quad \times [\hat{s}_{z1}\alpha(1)\beta(2) + \hat{s}_{z1}\beta(1)\alpha(2) + \alpha(1)\hat{s}_{z2}\beta(2) + \beta(1)\hat{s}_{z2}\alpha(2)] \\ &= \frac{1}{2}[\psi_{1s}(1)\psi_{2s}(2) - \psi_{2s}(1)\psi_{1s}(2)] \\ &\quad \times \left[\left(\frac{\hbar}{2}\right)\alpha(1)\beta(2) + \left(\frac{-\hbar}{2}\right)\beta(1)\alpha(2) + \alpha(1)\left(\frac{-\hbar}{2}\right)\beta(2) + \beta(1)\left(\frac{\hbar}{2}\right)\alpha(2)\right] \\ &= 0\end{aligned}$$

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.

We have enough states that we can have a ^3S term ($L = 0$, $S = 1$), with $M_S = 1$, 0, and -1, plus a ^1S term ($L = 0$, $S = 0$) with $M_S = 0$. The wave functions in Eq. (16.3-38) are eigenfunctions of the $\hat{S}^2$ operator. We state the eigenvalues without proof:

$$\hat{S}^2\alpha(1)\alpha(2) = 2\hbar^2\alpha(1)\alpha(2) \tag{16.3-54}$$

$$\hat{S}^2\beta(1)\beta(2) = 2\hbar^2\beta(1)\beta(2) \tag{16.3-55}$$

$$\hat{S}^2[\alpha(1)\beta(2) + \beta(1)\alpha(2)] = 2\hbar^2[\alpha(1)\beta(2) + \beta(1)\alpha(2)] \tag{16.3-56}$$

$$\hat{S}^2[\alpha(1)\beta(2) - \beta(1)\alpha(2)] = 0 \tag{16.3-57}$$

The first three functions correspond to the triplet term and the fourth corresponds to the singlet term. The symmetric spin factor in Eq. (16.3-56) belongs to the triplet, and the antisymmetric spin factor in Eq. (16.3-57) is the singlet. This is the general pattern.

We can infer the values of L and S as follows: Since the only value of M_L is zero, there are only S states, with $L = 0$. We begin with the largest value of M_S, which is 1 in this case. 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. 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.

EXAMPLE 16.8

Enumerate the states in the (1*s*) (2*p*) configuration.

Solution

With the 1*s* orbital and one of the *p* orbitals, we can construct either a symmetric space factor or an antisymmetric space factor. For example, using the $2p1$ orbital we have

$$\Psi_s = \frac{1}{\sqrt{2}}\left[\psi_{1s}(1)\psi_{2p1}(2) + \psi_{2p1}(1)\psi_{1s}(2)\right] \tag{16.3-58}$$

and

$$\Psi_{\mathrm{a}} = \frac{1}{\sqrt{2}}\left[\psi_{1s}(1)\psi_{2p1}(2) - \psi_{2p1}(1)\psi_{1s}(2)\right] \tag{16.3-59}$$

There is only one antisymmetric spin factor, and it must be combined with the symmetric space factor, so the symmetric space factor leads to only 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, but with $S = 1$ for each one. The $2p0$ and the $2p, -1$ orbitals each combine with the $1s$ orbital in exactly the same way as the $2p1$ orbital, to make one symmetric space factor and one antisymmetric space factor. Each corresponds to four states for a total of 12 states.

The space factors of Eqs. (16.3-58) and (16.3-59) both correspond to $M_L = 1$. The analogous factors containing the $2p0$ orbital correspond to $M_L = 0$, and those containing the $2p, -1$ orbital correspond to $M_L = -1$. These three values of M_L correspond to $L = 1$ with no states left over, so that only P terms occur. Each triplet spin factor combines with each one of the three antisymmetric space factors to give the nine states of the ^{3}P term, and the singlet spin factor combines with each one of the symmetric space factors to give the three states of the ^{1}P term.

The states 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 enough states for each possible term. These entries are shown in Table 16.4. 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. The largest values of M_L and M_S are identified, which must be equal to the largest values of L and S. The states with the appropriate values of M_L and M_S for this term are marked and then the largest remaining values of M_L and M_S are identified and marked off. The process is continued until all states have been assigned to terms. In this case, all states are assigned when the ^{3}P and ^{1}P terms are found.

Exercise 16.19

By explicit operation with $\hat{L}_z = \hat{L}_{z1} + \hat{L}_{z2}$, shows that the eigenvalues of the two space factors in Eq. (16.3-58) and Eq. (16.3-59) both equal $\hbar$, corresponding to $M_L = 1$.

Table 16.4. Terms for the $(1s)(2p)$ Configuration of the He Atom for Example 16.8

Values						Terms	
m_1	m_2	m_{s1}	m_{s2}	M_L	M_S	^{3}P	^{1}P
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	

In order to finish characterizing our electronic states, we can give the values of J, the quantum number for the total angular momentum, and M_J, the quantum number for its z component. Since **J** is the sum of **L** and **S**,

$$\hat{J}_z = \hat{L}_z + \hat{S}_z \tag{16.3-60}$$

Therefore,

$$M_J = M_L + M_S \tag{16.3-61}$$

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

$$J_{\text{max}} = L + S \tag{16.3-62}$$

The smallest value of J is

$$J_{\text{min}} = |L - S| \tag{16.3-63}$$

J must be nonnegative.

***Exercise 16.20**

Tabulate the M_L and M_S values of the 12 states of Example 16.8. Show that the following terms occur:

$$^1\text{P}_1, \quad ^3\text{P}_1, \quad ^3\text{P}_2, \quad ^3\text{P}_0$$

Hint: Use the list of quantum numbers in Table 16.4 and assign values of M_J. The largest value of M_J is equal to the largest value of J. Assign the states to the different values of J in the same way as was done in Example 16.8 with L and S.

16.4 Atoms with More Than Two Electrons

Our discussion of larger atoms will be similar to that of the helium atom, neglecting the electron–electron repulsion. In Chapter 17 we will describe the approximate inclusion of this repulsion.

The Lithium Atom in Zero Order

A lithium atom has three electrons and a nucleus with three protons. The Hamiltonian operator for a lithium atom with stationary nucleus is

$$\hat{H} = -\frac{\hbar^2}{2m}(\nabla_1^2 + \nabla_2^2 + \nabla_3^2) + \frac{1}{4\pi\varepsilon_0}\left(-\frac{3e^2}{r_1} - \frac{3e^2}{r_2} - \frac{3e^2}{r_3} + \frac{e^2}{r_{12}} + \frac{e^2}{r_{13}} + \frac{e^2}{r_{23}}\right) \tag{16.4-1}$$

As in the helium atom treatment, the zero-order Hamiltonian omits the electron–electron repulsion terms, giving

$$\hat{H}^{(0)} = \hat{H}_{\text{HL}}(1) + \hat{H}_{\text{HL}}(2) + \hat{H}_{\text{HL}}(3) \tag{16.4-2}$$

where the hydrogenlike Hamiltonians correspond to $Z = 3$. The zero-order approximation always leads to a wave function that is a product of orbitals:

$$\Psi^{(0)} = \psi_1(1)\psi_2(2)\psi_3(3) \tag{16.4-3}$$

The three orbitals are hydrogenlike orbitals with $Z = 3$, so that the zero-order wave function without antisymmetrization but with inclusion of spin is

$$\Psi^{(0)} = \psi_{n_1 l_1 m_1 m_{s1}}(1)\psi_{n_2 l_2 m_2 m_{s2}}(2)\psi_{n_3 l_3 m_3 m_{s3}}(3) \tag{16.4-4}$$

The subscripts on the subscripts indicate the fact that the quantum numbers do not necessarily have the same value for each orbital.

The electronic energy of the atom is the sum of three hydrogenlike energy eigenvalues with $Z = 3$. From Eq. (16.2-19),

$$\begin{aligned} E^{(0)} = E^{(0)}_{n_1 n_2 n_3} &= E_{n_1}(\mathrm{HL}) + E_{n_2}(\mathrm{HL}) + E_{n_3}(\mathrm{HL}) \\ &= -(13.60\ \mathrm{eV})\left(\frac{3^2}{n_1^2} + \frac{3^2}{n_2^2} + \frac{3^2}{n_3^2}\right) \end{aligned} \tag{16.4-5}$$

Exercise 16.21

Carry out the steps to obtain Eqs. (16.4-4) and (16.4-5).

Antisymmetrization

The orbital wave function of Eq. (16.4-4) can be antisymmetrized by including one term corresponding to each possible order of the orbital labels for a fixed order of particle labels. Each term that is generated from the first term by one permutation of a pair of indexes has a negative sign, and each term that is generated by two permutations of pairs of indexes has a positive sign. The antisymmetrized function is

$$\begin{aligned} \Psi = \frac{1}{\sqrt{6}}[&\psi_1(1)\psi_2(2)\psi_3(3) - \psi_2(1)\psi_1(2)\psi_3(3) - \psi_1(1)\psi_3(2)\psi_2(3) \\ &- \psi_3(1)\psi_2(2)\psi_1(3) + \psi_3(1)\psi_1(2)\psi_2(3) + \psi_2(1)\psi_3(2)\psi_1(3)] \end{aligned} \tag{16.4-6}$$

where we abbreviate the quantum numbers by writing 1 instead of n_1, l_1, m_1, m_{s1}, etc.

Exercise 16.22

Show that the function produced by exchanging particle labels 1 and 3 in Eq. (16.4-6) 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 (this is the Pauli exclusion principle).

EXAMPLE 16.9

If orbitals ψ_1 and ψ_3 are the same function, show that the wave function of Eq. (16.4-6) vanishes.

Solution

$$\begin{aligned}\Psi &= \frac{1}{\sqrt{6}}[\psi_1(1)\psi_2(3)\psi_1(3) - \psi_2(1)\psi_1(2)\psi_1(3) - \psi_1(1)\psi_1(2)\psi_2(3) \\ &\quad - \psi_1(1)\psi_2(2)\psi_1(3) + \psi_1(1)\psi_1(2)\psi_2(3) + \psi_2(1)\psi_1(2)\psi_1(3)] \\ &= 0\end{aligned}$$

Exercise 16.23

Show that the wave function of Eq. (16.4-6) 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. Each term will factor, but there will be 36 terms. 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.

Slater Determinants

There is another notation that can be used to write the antisymmetrized wave function of Eq. (16.4-6). A **determinant** is a quantity derived from a square matrix by a certain set of multiplications, additions and subtractions. 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 the coordinates on which the orbitals depend. The wave function of Eq. (16.4-6) is equal to the determinant:

$$\Psi = \frac{1}{\sqrt{6}}\begin{vmatrix} \psi_1(1) & \psi_1(2) & \psi_1(3) \\ \psi_2(1) & \psi_2(2) & \psi_2(3) \\ \psi_3(1) & \psi_3(2) & \psi_3(3) \end{vmatrix} \qquad (16.4\text{-}7)$$

The Slater determinant is named after John C. Slater, 1900–1976, a prominent American physicist who made various contributions to atomic and molecular quantum theory.

which is called a **Slater determinant**. There is a brief introduction to matrices and determinants in Appendix B.

Exercise 16.24

Use the rule of Eq. (B-89) of Appendix B for expanding a three-by-three determinant to show that the function of Eq. (16.4-7) is the same as that of Eq. (16.4-6):

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. (16.4-7) are identical, and the determinant vanishes, in agreement with the Pauli exclusion principle.

For the ground state, we must choose three different spin orbitals with the minimum possible sum of orbital energies, since the zero-order energy is equal to the sum of the orbital energies. This practice of choosing the ground-state configuration with the minimum sum of orbital energies is called the **Aufbau principle**, from the German word for "building-up". For the lithium atom, we choose the two 1*s* spin orbitals and one spin orbital from the second shell. In zero order, all of the 2*s* and 2*p* orbitals have the same energy, but we anticipate the fact that higher-order calculations will give a lower energy for the 2*s* subshell than for the 2*p* subshell and choose one of the 2*s* spin orbitals. The zero-order energy of the ground state is, from Eq. (16.2-21),

$$\begin{aligned} E_{\text{gs}}^{(0)} &= E_{1s1s2s}^{(0)} = 2E_1(\text{HL}) + E_2(\text{HL}) \\ &= (-13.60\,\text{eV})\left(2\frac{3^2}{1^2} + \frac{3^2}{2^2}\right) = -275.4\,\text{eV} \end{aligned} \tag{16.4-8}$$

This value is seriously in error, as was the zero-order value for helium. It differs from the experimental value of $-203.5\,\text{eV}$ by 35%.

The antisymmetrized zero-order wave function can be written

$$\Psi^{(0)} = \frac{1}{\sqrt{6}}\begin{vmatrix} \psi_{1s}(1)\alpha(1) & \psi_{1s}(2)\alpha(2) & \psi_{1s}(3)\alpha(3) \\ \psi_{1s}(1)\beta(1) & \psi_{1s}(2)\beta(2) & \psi_{1s}(3)\beta(3) \\ \psi_{2s}(1)\alpha(1) & \psi_{2s}(2)\alpha(2) & \psi_{2s}(3)\alpha(3) \end{vmatrix} \tag{16.4-9}$$

The 2*s*-spin-down orbital could have been chosen instead of the 2*s*-spin-up orbital. We therefore have two states of equal energy instead of a single ground state. 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.

Exercise 16.25

Consider the excited-state configuration (1*s*)(2*s*)(3*s*) for a lithium atom.

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.

Atoms with More Than Three Electrons

The treatment of the other atoms in zero order is similar 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

$$\hat{H} = -\frac{\hbar^2}{2m}\sum_{i=1}^{Z}\nabla_i^2 - \frac{Ze^2}{4\pi\varepsilon_0}\sum_{i=1}^{Z}\frac{1}{r_i} + \frac{e^2}{4\pi\varepsilon_0}\sum_{i=2}^{Z}\sum_{j=1}^{i-1}\frac{1}{r_{ij}} \tag{16.4-10}$$

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. (16.4-10) are a sum of hydrogenlike one-electron Hamiltonian operators, and the double sum is a sum of terms like those that we have neglected with helium and lithium. The zero-order Hamiltonian operator is sum of hydrogenlike Hamiltonians (with those terms neglected):

$$\hat{H}^{(0)} = \sum_{i=1}^{Z} \hat{H}_{\mathrm{HL}}(i) \tag{16.4-11}$$

The time-dependent Schrödinger equation corresponding to this Hamiltonian can be solved by separation of variables, using the trial function

$$\Psi^{(0)} = \psi_1(1)\psi_2(2)\psi_3(3)\psi_4(4)\cdots\psi_Z(Z) = \prod_{i=1}^{Z} \psi_i(i) \tag{16.4-12}$$

where the symbol $\prod$ stands for a product of factors, just as the $\sum$ symbol stands for a sum of terms. Since the terms in the zero-order Hamiltonian are hydrogenlike Hamiltonians, the factors $\psi_1(1), \psi_2(2), \psi_3(3)$, etc. are all hydrogenlike orbitals and the energy eigenvalue is a sum of hydrogenlike orbital energies:

$$\psi_i(i) = \psi_{n_i l_i m_i m_{si}}(i) \tag{16.4-13}$$

$$E^{(0)} = E_{n_1}(\mathrm{HL}) + E_{n_2}(\mathrm{HL}) + \cdots = \sum_{i=1}^{Z} E_{n_i}(\mathrm{HL}) \tag{16.4-14}$$

where n_i, l_i, etc., are values of the quantum numbers for hydrogenlike orbitals. Just as with the helium and lithium atoms, the zero-order wave functions and energies of Eqs. (16.4-13) and (16.4-14) are very poor approximations.

We must antisymmetrize the orbital wave function of Eq. (16.4-12). This can be done by writing a Slater determinant with one row for each spin orbital and one column for each electron:

$$\Psi = \frac{1}{\sqrt{Z!}} \begin{vmatrix} \psi_1(1) & \psi_1(2) & \psi_1(3) & \psi_1(4) & \cdots & \psi_1(Z) \\ \psi_2(1) & \psi_2(2) & \psi_2(3) & \psi_2(4) & \cdots & \psi_2(Z) \\ \psi_3(1) & \psi_3(2) & \psi_3(3) & \psi_3(4) & \cdots & \psi_3(Z) \\ \psi_4(1) & \psi_4(2) & \psi_4(3) & \psi_4(4) & \cdots & \psi_4(Z) \\ \cdots & \cdots & \cdots & \cdots & \cdots & \cdots \\ \psi_Z(1) & \psi_Z(2) & \psi_Z(3) & \psi_Z(4) & \cdots & \psi_Z(Z) \end{vmatrix} \tag{16.4-15}$$

where the $1/\sqrt{Z!}$ factor normalizes the wave function, assuming that all orbitals are normalized and orthogonal to each other, and where we have abbreviated the quantum numbers. The Pauli exclusion principle must be followed. No two spin orbitals can be the same, or two rows of the determinant would be identical, causing the wave function to vanish.

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 computation can be simplified by noting that the contributions to M_L and M_S for any completely filled subshell vanish. For example, the only term symbol that occurs for the ground state of an inert gas (He, Ne, Ar, etc.) is ^1S. Since the hydrogenlike orbitals in the same shell all have the same energy, many of the terms are degenerate in zero order, but will have different energies when better approximations are used.

In the next chapter, we will discuss approximations beyond the zero-order approximation that will give better values of atomic energies. We will usually use the orbital approximation. We will find that the orbitals in different subshells in the same shell do not correspond to the same energy, and will use the facts about the orbital energies to understand the periodic chart of the elements.

Summary of the Chapter

The time-independent Schrödinger equation for a general two-particle central-force system 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 one particle relative to the other.

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 a set of functions called spherical harmonic functions. These functions are also eigenfunctions of the operator for the square of the orbital angular momentum and its z component, with eigenvalues given by

$$\hat{L}^2 Y_{lm} = \hbar l(l+1)Y_{lm}$$

and

$$\hat{L}_z Y_{lm} = \hbar m Y_{lm}$$

The solution to the equation for the radial factor $R(r)$ was presented for the hydrogen atom, giving a set of wave functions with two quantum numbers: n, the principal quantum number, and l, the same quantum number as in the spherical harmonic functions. The hydrogenlike atom was defined, with a single electron, but with Z protons in the nucleus. The energy eigenvalues of the hydrogenlike atom depend only on the principal quantum number:

$$E = E_n = -\frac{(13.60\,\text{eV})Z^2}{n^2}$$

where Z was the number of protons in the nucleus.

An intrinsic electronic angular momentum of the electron was introduced. This angular momentum corresponds to a spinning motion of the electron in addition to its orbital motion. It corresponds to fixed magnitude and two possible z projections, $\hbar/2$ and $-\hbar/2$.

In the "zero-order" approximation, the repulsions between electrons were neglected. The energy eigenfunctions of the helium atom were products of one hydrogenlike orbital for each electron. These orbital wave functions were antisymmetrized to conform to the physical indistinguishability of the electrons, producing the Pauli exclusion principle, which states that no two electrons can occupy the same orbital in any orbital wave function. Similar wave functions were discussed for multielectron atoms. By utilizing the Pauli exclusion principle, possible electron configurations and term symbols can be computed.

PROBLEMS

Problems for Section 16.1

16.26. Using formulas in Appendix F, write the formulas for the spherical harmonic functions Y_{43} and Y_{42}.

16.27. 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) $\Theta_{22}(\theta)$.

16.28. Sketch the nodal surfaces for the spherical harmonic functions: (a) Y_{10}, (b) Y_{22}, (c) Y_{31}, (d) Y_{21}.

***16.29.** Transform the expression for $\Theta_{11}\Phi_{1y}$ to Cartesian coordinates. Show that this function is an eigenfunction of the operator $\hat{L}_y$ and find its eigenvalue.

Problems for Section 16.2

16.30. a. Sketch the nodal surfaces for the first five energy eigenfunctions for a particle in a three-dimensional spherical hard box. Hint: The spherical harmonic functions are the same, and the pattern of nodes is the same as with the hydrogen atom.

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.

***16.31. 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 2*s* state.

c. Calculate the percent difference between the energy of a $^4\mathrm{He}^+$ ion and a $^3\mathrm{He}^+$ ion in the 2*s* state.

16.32. A positronium atom is a hydrogenlike 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 1*s* state. Describe the classical motion of the two particles about the center of mass. Find the value of the Bohr radius for positronium.

***16.33.** Calculate the angle between the *z* axis and each of the cones of possible directions of the orbital angular momentum for $l = 2$.

16.34. 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.

***16.35.** Calculate $\langle r \rangle$ for the 2*s* and 2*p* states of a hydrogenlike atom. Comment on your answer.

16.36. a. Find the value of the distance *b* such that there is a 95% chance that an electron in a hydrogen atom in the 1*s* state is no further from the nucleus than the distance *b*.

b. Find the ratio of the 1*s* wave function at $r = b$ to the same function at $r = 0$.

c. Repeat parts (a) and (b) for 90% probability instead of 95%.

***16.37.** For a hydrogen atom in a 1*s* state, find the probability that the electron is no farther from the nucleus than (a) *a*, (b) 2*a*, (c) 3*a* where *a* is the Bohr radius.

16.38. Calculate $\langle z \rangle$ and σ_z for the electron in a hydrogen atom in the 1*s* state. Explain the meaning of the values.

***16.39.** Calculate the expectation values of p_x and of p_x^2 for the electron in a hydrogen atom in the 1*s* state. Why does $\langle p_x^2 \rangle$ not equal $\langle p_x \rangle^2$?

16.40. Calculate the expectation value for the kinetic energy of a hydrogenlike atom in the 1*s* state.

16.41. 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.

16.42. Find the most probable value of the electron's distance from the nucleus for a hydrogen atom in the 1*s*, the 2*s*, and the 2*p* states.

16.43. a. Construct a graph of the radial distribution function for the 3*d* 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.

16.44. a. Draw a rough picture of the nodal surfaces of each of the real 3*d* orbitals. From these, draw rough pictures of the orbital regions.

b. Do the same for the complex 3*d* orbitals (eigenfunctions of $\hat{L}_z$).

16.45. Using formulas in Appendix F, verify the formula given in Table 16.2 for R_{32}.

16.46. a. Construct the formula representing R_{40}, using formulas in Appendix F.

b. Construct a graph of the radial distribution function for the 4*s* state.

Problems for Section 16.3

16.47. 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. (16.3-38a).

16.48. **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 case 1 and which belong to case 2 as defined in Chapter 15.

16.49. **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.

16.50. If the spin angular momentum vector for one electron with spin up lies in the y–z plane, and the spin angular momentum vector for another electron with spin down also lies in the y–z plane, find the magnitude and direction of their vector sum. To what values of S and M_S (if any) does this vector sum correspond?

*16.51. Find the possible term symbols for the subshell configuration $(2p)(3d)$ for the helium atom.

16.52. Find the possible term symbols for the subshell configuration $(1s)(3d)$ for the helium atom. Which will probably have the lowest energy?

Problems for Section 16.4

*16.53. Find the possible term symbols for the ground state of the chlorine atom.

16.54. Find the ground-state electron configuration and the possible term symbols for the following atoms: (a) C, (b) Se, (c) Ar, (d) Mg.

*16.55. Find the possible term symbols for the following configurations of the Be atom:

a. $(1s)^2(2s)^2$ (ground state)

b. $(1s)^2(2s)(3s)$ (an excited state)

c. $(1s)(2s)(3s)(4s)$ (an excited state)

16.56. Find the term symbols for:

a. Li (ground state)

b. F (ground state)

c. Mg (ground state)

General Problems

*16.57. 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 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 ψ_{6d0} (ψ_{620}) wave function.

d. The number of nodal cones in the real part of the ψ_{6p1} (ψ_{611}) wave function.

16.58. Consider 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.

16.59. 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.

h. Electrons in a multielectron atom move exactly like electrons in a hydrogenlike atom with the appropriate nuclear charge.

17

The Electronic States of Atoms. II. Higher-Order Approximations for Multielectron Atoms

OBJECTIVES

After studying this chapter, the student should:

1. Understand the basic ideas behind the variation method, the perturbation method, and the self-consistent field method;
2. be able to solve simple problems using the variation and perturbation methods;
3. understand the Aufbau principle and its relationship to the periodic table of the elements;
4. be able to solve problems related to electron configurations and term symbols of multielectron atoms.

PRINCIPAL FACTS AND IDEAS

1. The interelectron repulsions are included in approximation methods that go beyond the zero-order orbital approximation.
2. The variation theorem 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, leaving only the error due to neglect of electron correlation.
5. The electronic structure of multielectron atoms can be described in terms of the approximation schemes.
6. The structure of the periodic table of the elements can be understood in terms of higher-order orbital approximations.

17.1 The Variation Method and Its Application to the Helium Atom

The zero-order orbital approximation that was employed in Chapter 16 neglects the interelectron repulsions, with the result that each electron is independent of the other electrons and occupies a hydrogenlike orbital in a product wave function. There are three principal approximation schemes that go beyond this approximation. The first scheme is the **variational method**, which is based on the **variation theorem**.

The Variation Theorem

The expectation value of the energy for a state corresponding to a wave function ψ is given by Eq. (15.4-1):

$$\langle E\rangle = \frac{\int \psi^* \hat{H}\psi \, dq}{\int \psi^* \psi \, dq} \tag{17.1-1}$$

where $\hat{H}$ is the correct Hamiltonian operator for 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:*

$$\frac{\int \varphi^* \hat{H}\varphi \, dq}{\int \varphi^* \varphi \, dq} \geq E_{gs} \quad \text{(variation theorem)} \tag{17.1-2}$$

where φ is any function obeying the same boundary conditions as the correct wave functions and depending on the same coordinates and where $\hat{H}$ must be the correct Hamiltonian. The 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 17.10.

The Variation Method

The variation theorem suggests the **variation method** for finding an approximate ground-state energy and wave function. First 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 **variational energy**, and is usually denoted by W. Next, find the member of the family that gives a lower (more negative) value of W than any other member of the family. Since W can never be more negative than the correct ground-state energy, 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 application of the variation method uses a family of functions that can be represented by a single formula containing one or more variable parameters. Such as family of functions is called a **variation function** or a

variation trial function. The variational energy W is calculated as a function of the parameters, and the minimum value of W is found by the methods of calculus.

Application of the Variation Method to the Helium Atom[1]

Let us first use the zero-order orbital wave function of Eq. (16.3-28) as a variation trial function. This is a single function, so no minimization can be done. It is normalized so that the variational energy is

$$W = \frac{1}{2}\int \psi_{100}(1)^*\psi_{100}(2)^*[\alpha(1)\beta(2) - \beta(1)\alpha(2)]^*\hat{H}\psi_{100}(1)\psi_{100}(2) \times [\alpha(1)\beta(2) - \beta(1)\alpha(2)]\,dq_1'\,dq_2' \qquad (17.1\text{-}3)$$

where $\hat{H}$ is the correct Hamiltonian operator, and where dq_1' and dq_2' indicate integration over space and spin coordinates. The space orbital ψ_{100} is a hydrogenlike $1s$ orbital with $Z = 2$.

Since the helium-atom Hamiltonian operator is independent of the spin coordinates, the spin factor is not operated on and 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. The result is

$$W = \int \psi_{100}(1)^*\psi_{100}(2)^*\left[\hat{H}_{\mathrm{HL}}(1) + \hat{H}_{\mathrm{HL}}(2) + \frac{e^2}{4\pi\varepsilon_0 r_{12}}\right]\psi_{100}(1)\psi_{100}(2)\,dq \qquad (17.1\text{-}4)$$

where we use the symbol dq to stand for $d^3\mathbf{r}_1\,d^3\mathbf{r}_2$. The entire Hamiltonian, not the zero-order approximate Hamiltonian, must be used in Eq. (17.1-4).

The $\hat{H}_{\mathrm{HL}}(1)$ and $\hat{H}_{\mathrm{HL}}(2)$ terms in the Hamiltonian operator give ground-state energy eigenvalues for a hydrogenlike atom.

Exercise 17.1

Show that the $\hat{H}_{\mathrm{HL}}(1)$ term in Eq. (17.1-4) yields a contribution to W equal to $E_1(\mathrm{HL})$ and that the $\hat{H}_{\mathrm{HL}}(2)$ term yields an equal contribution.

We now have

$$W = 2E_1(\mathrm{HL}) + \int \psi_{100}(1)^*\psi_{100}(2)^*\left(\frac{e^2}{4\pi\varepsilon_0 r_{12}}\right)\psi_{100}(1)\psi_{100}(2)\,dq \qquad (17.1\text{-}5)$$

Evaluation of the integral in this equation is tedious and we given only the result:[2]

$$W = 2E_1(\mathrm{HL}) + \frac{5Ze^2}{8(4\pi\varepsilon_0 a)} = 2E_1(\mathrm{HL}) - \frac{5}{8}\langle\mathcal{V}\rangle_{\mathrm{HL}(1s)} \qquad (17.1\text{-}6)$$

where $\langle\mathcal{V}\rangle_{\mathrm{HL}(1s)}$ is the expectation value of the potential energy for the hydrogenlike atom in its ground state. The variational energy is, using Eq. (16.2-12),

$$W = -2\frac{Z^2e^2}{2(4\pi\varepsilon_0 a)} + \frac{5Ze^2}{8(4\pi\varepsilon_0 a)} = -108.8\,\mathrm{eV} + 34.0\,\mathrm{eV} = -74.8\,\mathrm{eV} \qquad (17.1\text{-}7)$$

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[1] Our treatment follows that in J. C. Davis, Jr., *Advanced Physical Chemistry*, The Ronald Press, New York, 1965, pp. 221ff.

[2] I. N. Levine, *Quantum Chemistry*, 4th ed., Prentice-Hall, Englewood Cliffs, N. J., 1991, pp. 230ff.

where we have put in the value $Z = 2$ in the calculation of the numerical value. This result is more positive than the correct value of $-79.0\,\text{eV}$, as the variation theorem guaranteed. The error is approximately $4\,\text{eV}$, which is much better than the error of $-30\,\text{eV}$ obtained with the zero-order approximation. This improvement in the energy value was not obtained by changing the wave function. Our wave function is still the zero-order wave function obtained by complete neglect of the interelectron repulsion. The improvement came from using the complete Hamiltonian operator in calculating the variational energy. The zero-order energy was calculated using only the zero-order Hamiltonian, and is not required to conform to the variation theorem.

We now use a variational trial function that represents a family of functions. We replace the nuclear charge Z in the hydrogenlike $1s$ orbitals by a variable parameter, Z'. The modified $1s$ space orbital is

$$\psi'_{100} = \psi'_{100}(Z') = \frac{1}{\sqrt{\pi}}\left(\frac{Z'}{a}\right)^{3/2} e^{-Z'r/a} \tag{17.1-8}$$

where a is the Bohr radius. The orbital depends on the value of Z', and we label it with a prime ($'$). It is still normalized. The variation trial function is

$$\varphi = \varphi(Z') = \psi'(1)\psi'(2)\frac{1}{\sqrt{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)] \tag{17.1-9}$$

where we omit the subscripts on the orbital symbols. There is a physical motivation for choosing this variation function. As an electron moves about in the atom, there is some probability that the other electron will be somewhere between the first electron and the nucleus, "shielding" the first electron somewhat from the full nuclear charge and causing it to move as though the nucleus had a smaller charge. Therefore, a value of Z' smaller than 2 should produce a better approximation than the value $Z = 2$ used to obtain the value of $-74.8\,\text{eV}$ in Eq. (17.1-7).

The wave function of Eq. (17.1-9) is substituted into Eq. (17.1-1) to calculate the variational energy. The correct number of protons, $Z = 2$, not the value of Z', must be used in the Hamiltonian operator. The variational energy is

$$\begin{aligned} W = &\int \psi'(1)^*\psi'(2)^* \\ &\times \left[\hat{\mathscr{K}}(1) - \frac{Ze^2}{4\pi\varepsilon_0 r_1} + \hat{\mathscr{K}}(2) - \frac{Ze^2}{4\pi\varepsilon_0 r_2} + \frac{e^2}{4\pi\varepsilon_0 r_{12}}\right]\psi'(1)\psi'(2)\,dq \end{aligned} \tag{17.1-10}$$

where $\hat{\mathscr{K}}$ 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

$$\begin{aligned} \iint \psi'(1)^*\psi'(2)^*\hat{\mathscr{K}}(1)\psi'(1)\psi'(2)\,d^3\mathbf{r}_1\,d^3\mathbf{r}_2 &= \int \psi'(1)^*\hat{\mathscr{K}}(1)\psi'(1)\,d^3\mathbf{r}_1 \\ &= Z'^2\langle\mathscr{K}_{\text{H}}\rangle_{1s} = -Z'^2E_1(\text{H}) \end{aligned} \tag{17.1-11}$$

where $\langle\mathscr{K}_{\text{H}}\rangle_{1s}$ is the expectation value of the kinetic energy of the hydrogen (not hydrogenlike) atom in the $1s$ state, and where we have used the fact that the expectation value of the kinetic energy equals the negative of the total energy (see Section 16.2). We have used the fact that the integral over the coordinates of particle 2 can be factored out, and the assumption that the orbital $\psi'(2)$ is normalized so that this integral equals unity. The factor Z'^2 comes from the fact that the orbital $\psi'(1)$ is the $1s$ orbital for an effective nuclear charge equal to $Z'e$.

The second term in the Hamiltonian operator in Eq. (17.1-10) gives

$$\begin{aligned}\text{Contribution to } W &= \int \psi'(1)^*\psi'(2)^* \frac{Ze^2}{4\pi\varepsilon_0 r_1}\psi'(1)\psi'(2)\,dq \\ &= ZZ'\langle \mathcal{V}_{\mathrm{H}}\rangle_{(1s)} = 2ZZ'E_1(\mathrm{H})\end{aligned} \qquad (17.1\text{-}12)$$

where $\langle \mathcal{V}\rangle_{\mathrm{H}(1s)}$ is the expectation value of the potential energy of a hydrogen (not hydrogenlike) atom in the $1s$ state. We have a factor of Z from the original factor Z in the Hamiltonian, and a factor of Z' from use of the $1s$ orbital that corresponds to a nuclear charge of $Z'e$. The final equality comes from Eq. (16.2-27).

Exercise 17.2

Show that Eq. (17.1-12) is correct.

The next two terms in the Hamiltonian operator in Eq. (17.1-10) are just like the first two, except that the roles of particles 1 and 2 are interchanged. After the integrations are done, this interchange makes no difference, and these two terms give contributions equal to those of the first two terms. The last term is the same as in Eq. (17.1-6) except that the orbitals correspond to the nuclear charge of $Z'e$ instead of Ze, so that its contribution is

$$\int \psi'(1)^*\psi'(2)^*\left(\frac{e^2}{4\pi\varepsilon_0 r_{12}}\right)\psi'(1)\psi'(2)dq = -\frac{5}{4}Z'E_1(\mathrm{H}) \qquad (17.1\text{-}13)$$

The final result is

$$W = E_1(\mathrm{H})\left(-2Z'^2 + 4ZZ' - \frac{5}{4}Z'\right) \qquad (17.1\text{-}14)$$

The variational energy is a function of a parameter, because our variation function was a family of functions expressed by a formula with a parameter.

Exercise 17.3

Verify eq. (17.1-14).

We find the minimum value of W by differentiating with respect to the variable parameter Z' and setting this derivative equal to zero:

$$0 = E_1(\mathrm{H})\left(-4Z' + 4Z - \frac{5}{4}\right)$$

This equation is satisfied by

$$Z' = Z - \frac{5}{16} \qquad (17.1\text{-}15)$$

For $Z = 2$, $Z' = 27/16 = 1.6875$. Our optimized helium atom wave function corresponds to a shielding of the nucleus so that an electron moves as though there were an effective nuclear charge of 1.6875 protons instead of 2 protons. This is equivalent to saying that one electron has a 31.25% probability of being between the nucleus and the other electron. This electron density acts as though it were located at the nucleus, since a theorem of electrostatics asserts that a spherically symmetric distribution of charge

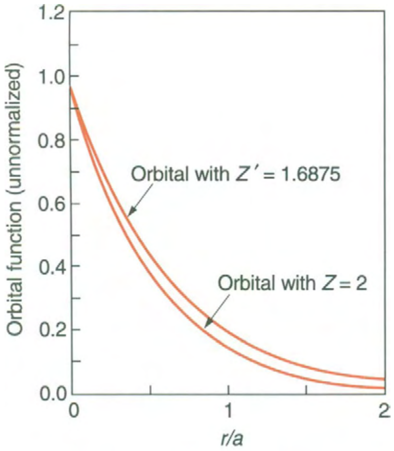

Figure 17.1. Zero-Order and Variationally Obtained Orbitals for the Ground State of the Helium Atom. This diagram shows how the two orbitals compare, with the effect of shielding making the variationally obtained orbital extend farther from the nucleus.

produces an electric field outside of the charge distribution exactly like that of a point charge of the same size as the total distributed charge. Figure 17.1 shows the zero-order 1*s* orbital (with $Z = 2$) and the variational orbital we have just obtained, with $Z' = 1.6875$. The variable on the horizontal axis is the distance from the nucleus divided by the Bohr radius a.

The minimum value of W is

$$\begin{aligned} W &= (-13.60\,\text{eV})[-2(1.6875)^2 + 4(2)(1.6875) - \frac{5}{4}(1.6875)] \\ &= -77.5\,\text{eV} \end{aligned} \tag{17.1-16}$$

This value differs from the experimental value of $-79.0\,\text{eV}$ by 1.5 eV, an error of 2%, corresponding to $145\,\text{kJ mol}^{-1}$. Our result is still not accurate enough for quantitative chemical purposes. More accurate values can be obtained by choosing more complicated variation functions. Hylleraas used the variation function[3]

$$\varphi = Ce^{-Z''r_1/a}e^{-Z''r_2/a}(1 + br_{12}) \tag{17.1-17}$$

This is not an orbital wave function because of the dependence of the final factor on r_{12}, the distance between the electrons. This function gave a variational energy equal to $-78.7\,\text{eV}$ 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 variational functions have been used, and have given excellent agreement with experiment.[4]

The presence of the factor $(1 + br_{12})$ introduces a dependence on the interelectron distance. In a one-term orbital wave function, the probability density of each electron is independent of the position of any other electrons as in Eq. (16.3-24), and there is no electron correlation. The wave function of Eq. (17.1-17) gives a larger probability density for larger separations of the electrons. This inclusion of explicit dependence on interelectron distance is called **dynamical electron correlation**. An antisymmetrized orbital wave function can also exhibit correlation if it has an antisymmetric space factor like the triplet wave functions of Eq. (16.3-38) or Eq. (16.3-59), since an antisymmetrized space factor vanishes if two electrons are at the same location and has a small magnitude if they are near to each other. This effect is called **statistical correlation**.

Exercise 17.4

Consider the antisymmetrized orbital wave function

$$\Psi = C[\psi_1(1)\psi_2(2) - \psi_2(1)\psi_1(2)]$$

where ψ_1 and ψ_2 are any two different space orbitals. Show that the wave function vanishes if both electrons are at the same location.

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[3] E. A. Hylleraas, *Z. Physik*, **65**, 209 (1930).

[4] T. Koga, *J. Chem. Phys.*, **94**, 5530 (1991).

17.2 The Perturbation Method and Its Application to the Helium Atom

This method is the second of the three most commonly used approximation schemes. It is applied to a problem in which the Hamiltonian operator can be separated into two terms.

$$\hat{H} = \hat{H}^{(0)} + \hat{H}' \tag{17.2-1}$$

such that $\hat{H}^{(0)}$ gives a Schrödinger equation that can be solved:

$$\hat{H}^{(0}\Psi^{(0)} = E^{(0)}\Psi^{(0)} \tag{17.2-2}$$

This equation is called the **unperturbed equation** or the **zero-order equation**. The wave function $\Psi^{(0)}$ and the energy eigenvalue $E^{(0)}$ are called the **zero-order wave function** or the **unperturbed wave function** and the **zero-order energy eigenvalue** or the **unperturbed energy eigenvalue**. The term $\hat{H}'$ in the Hamiltonian operator is called the **perturbation**. The best results are obtained if the perturbation term is small compared to other terms in the Hamiltonian operator.

For the helium atom, $\hat{H}^{(0)}$ is the same as the zero-order Hamiltonian in Chapter 16, and $\hat{H}'$ represents the interelectron repulsion energy. This energy in a helium atom is not small compared with the total energy, but we proceed. We first construct a new Hamiltonian operator in which the perturbation terms is multiplied by a fictitious parameter, λ:

$$\hat{H} = \hat{H}^{(0)} + \lambda\hat{H}' \tag{17.2-3}$$

The new Schrödinger equation is

$$\hat{H}(\lambda)\Psi(\lambda) = E(\lambda)\Psi(\lambda) \tag{17.2-4}$$

where the energy eigenvalue and the energy eigenfunction now depend on λ. It seems at first that we are further complicating an already intractable problem by introducing a new independent variable. However, we will express energies and wave functions as power series in λ, and will sometimes obtain useful information by using only a few terms in the series.

Consider a particular energy eigenfunction Ψ_n and its energy eigenvalue E_n, assumed to be nondegenerate. We assume that the energy eigenvalues and energy eigenfunctions can be represented by a power series in λ:

$$E_n = E_n^{(0)} + E_n^{(1)}\lambda + E_n^{(2)}\lambda^2 + \cdots \tag{17.2-5}$$

$$\Psi_n = \Psi_n^{(0)} + \Psi_n^{(1)}\lambda + \Psi_n^{(2)}\lambda^2 + \cdots \tag{17.2-6}$$

We use superscripts on the coefficients instead of subscripts because we already have subscripts on our eigenvalues and eigenfunctions. The idea of the perturbation method is to obtain only a few coefficients (often just two) in Eqs. (17.2-5) and (17.2-6) and to hope that a partial sum containing these terms gives a useful approximation to the entire series when we let $\lambda = 1$. Figure 17.2 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.

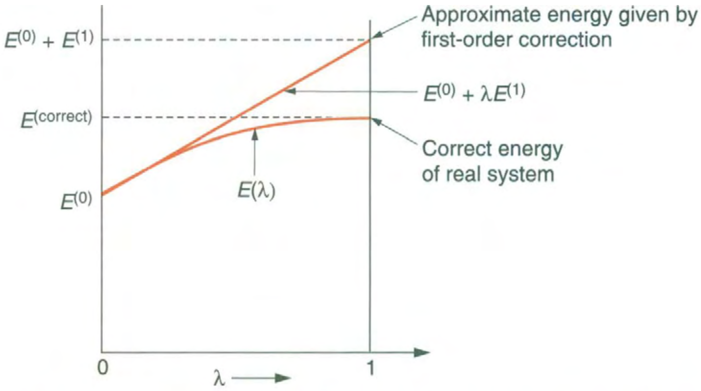

Figure 17.2. An Energy Eigenvalue as a Function of λ for a Hypothetical System. This diagram shows how the fictitious parameter λ is used in the perturbation method. Only the value $\lambda = 1$ has physical meaning, corresponding to the actual system. $\lambda = 0$ corresponds to a soluble problem with part of the Hamiltonian operator omitted (the zero-order problem).

Appendix G contains a derivation of the formula for the first-order correction to the energy, $E_n^{(1)}$. The result contains only the zero-order wave function:

$$\boxed{E_n^{(1)} = \int \Psi_n^{(0)*}\hat{H}'\Psi_n^{(0)}\,dq} \tag{17.2-7}$$

We now apply first-order perturbation to the ground state of the helium atom, for which

$$\hat{H}^{(0)} = \hat{H}_{\mathrm{HL}}(1) + \hat{H}_{\mathrm{HL}}(2) \tag{17.2-8}$$

$$\hat{H}' = \frac{e^2}{4\pi\varepsilon_0 r_{12}} \tag{17.2-9}$$

The zero-order ground-state energy $E_{1s1s}^{(0)}$ is given by Eq. (16.3-12) and $\Psi_{1s1s}^{(0)}$ is given by Eq. (16.3-28). Integration over the spin coordinates in Eq. (17.2-7) yields

$$E_{1s1s}^{(1)} = \int \psi_{100}(1)^*\psi_{100}(2)^*\left(\frac{e^2}{4\pi\varepsilon_0 r_{12}}\right)\psi_{100}(1)\psi_{100}(2)\,d^3\mathbf{r}_1\,d^3\mathbf{r}_2 \tag{17.2-10}$$

This result is the same as the integral in Eq. (17.1-5), so that our perturbation method result to first order is the same as the result we obtained with the variation method using the unmodified zero-order wave function as our variation function:

$$E_{1s1s}^{(0)} + E_{1s1s}^{(1)} = -108.8\,\mathrm{eV} + 34.0\,\mathrm{eV} = -74.8\,\mathrm{eV} \tag{17.2-11}$$

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, and we do not discuss them. 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:[5]

$$E_{1s1s}^{(2)} = -4.3\,\mathrm{eV} \tag{17.2-12}$$

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[5] C. W. Scherr and R. E. Knight, *Rev. Mod. Phys.*, **35**, 436 (1963).

so that the second-order value of the energy is −79.1 eV, within 0.1 eV of the experimental value, −79.0 eV. Since the perturbation method is different from the variation method, the second-order 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.[6]

17.3 The Self-Consistent Field Method

The third general approximation method is the **self-consistent field** method (abbreviated SCF) introduced in 1928 by Hartree.[7] The goal of this method is similar to that of the variation method in that it seeks to optimize a wave function. It differs in two ways: first, the search is not restricted to any particular family of functions; second, it deals only with orbital wave functions. It allows the form of the orbital functions to be varied, and is capable of finding the best possible orbital approximation. The SCF method is extensively used in modern quantum chemistry. We do not discuss this method in detail, but illustrate its use by applying it to the ground state of the helium atom. The ground state of helium is a singlet state, and the antisymmetrization is in the spin factor of the wave function. We can proceed with the space factor of the wave function, omitting the spin factor, since the Hamiltonian contains no spin dependence.

The zero-order orbitals satisfied Eqs. (16.3-10) and (16.3-11), which omit the potential energy of electron–electron repulsion. We add a correction term to Eq. (16.3-10) to represent this potential energy. If electron 2 were fixed at location $\mathbf{r}_2$.

$$-\frac{\hbar^2}{2m}\nabla_1^2\psi(1)-\frac{Ze^2}{4\pi\varepsilon_0 r_1}\psi_1(1)+\frac{e^2}{4\pi\varepsilon_0 r_{12}}\psi_1(1)=E_1\psi_1(1) \tag{17.3-1}$$

where r_{12} is the distance between the fixed position of electron 2 and the variable position of electron 1 and where E_1 is a new orbital energy. If electron 2 is not at a fixed position, but occupies the normalized orbital $\psi_2(2)$, then its probability of being found in the volume element $d^3\mathbf{r}_2$ is

$$(\text{Probability})=\psi_2(2)^*\psi_2(2)\,d^3\mathbf{r}_2=|\psi_2(2)|^2\,d^3r_2 \tag{17.3-2}$$

We now replace the electron–electron repulsion term in the Hamiltonian of Eq. (17.3-1) by a weighted average over all positions of electron 2, obtaining

$$-\frac{\hbar^2}{2m}\nabla_1^2\psi(1)-\frac{Ze^2}{4\pi\varepsilon_0 r_1}\psi_1(1)+\left[\int\frac{e^2}{4\pi\varepsilon_0 r_{12}}|\psi_2(2)|^2\,d^3r_2\right]\psi_1(1)=E_1\psi_1(1) \tag{17.3-3}$$

This is an **integrodifferential equation**, since it has both derivatives and an integral in it. After the integration, the integral term depends only on the coordinates of electron 1, so that the equation has a solution if the orbital for electron 2 is a known function. However, at this point both $\psi_1(1)$ and $\psi_2(2)$ are unknown functions (both are ψ_{1s} function if we are discussing the ground state).

The integrodifferential equation is solved by iteration (successive approximations). The first step is to replace the orbital under the integral by the zero-order function or

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[6] C. W. Scherr and R. E. Knight, *loc. cit.* (Note 5).

[7] D. R. Hartree, *Proc. Cambridge Phil. Soc.*, **24**, 89, 111, 426 (1928).

some other known function. The $\psi_{1s}(1)$ orbital that results from solving this equation is called the first-order solution $\psi_{1s}^{(1)}(1)$. The equation that it obeys is

$$-\frac{\hbar^2}{2m}\nabla_1^2\psi_{1s}^{(1)}(1) - \frac{Ze^2}{4\pi\varepsilon_0 r_1}\psi_{1s}^{(1)}(1) + \left[\int \frac{e^2}{4\pi\varepsilon_0 r_{12}}|\psi_{1s}^{(0)}(2)|^2\, d^3r_2\right]\psi_{1s}^{(1)} = E_{1s}^{(1)}\psi_{1s}^{(1)}(1) \tag{17.3-4}$$

where $E_{1s}^{(1)}$ is a new approximation to the orbital energy. It is found that the integral in this equation depends only on r_1, not on θ_1 and ϕ_1, so the θ_1 and ϕ_1 dependence can be separated from the r_1 dependence. It is ordinarily not possible to solve Eq. (17.3-4) analytically, but an accurate numerical representation of $\psi_{1s}^{(1)}(1)$ can be obtained.

The next iteration (repetition) is carried out by replacing $\psi_{1s}^{(0)}(2)$ under the integral sign by $\psi_{1s}^{(1)}(2)$ and denoting the new unknown function by $\psi_{1s}^{(2)}(1)$. This equation is solved, and the resulting solution is used under the integral for the next iteration, and so forth. The equation for the jth iteration is

$$-\frac{\hbar^2}{2m}\nabla_1^2\psi_{1s}^{(j)}(1) - \frac{Ze^2}{4\pi\varepsilon_0 r_1}\psi_{1s}^{(j)}(1) + \left[\int \frac{e^2}{4\pi\varepsilon_0 r_{12}}|\psi_{1s}^{(j-1)}(2)|^2\, d^3r_2\right]\psi_{1s}^{(j)}(1) = E_{1s}^{(j)}\psi_{1s}^{(j)}(1) \tag{17.3-5}$$

Successive approximations converge to the best possible orbital approximation. When additional iterations produce only negligible changes in the orbital function and the energy, we say that the integral term provides a self-consistent contribution to the force on electron 1, or a **self-consistent field**. At this point, the iteration is stopped and we assume that we are close to the best possible orbitals.

In the SCF method, the expectation value of the energy is not the sum of the orbital energies, because the potential energy of electron–electron repulsion has been included in Eq. (17.3-3) for each electron. Since both orbitals are obtained from this equation, the sum of the two orbital energies includes the interelectron repulsion energy twice. We correct for this double inclusion by subtracting the expectation value of the interelectron repulsion energy from the sum of the orbital energies. If n iterations have been carried out, the expectation value of the energy is

$$\begin{aligned} E(\text{atom}) &= 2E_{1s}^{(n)} - \int \frac{e^2}{4\pi\varepsilon_0 r_{12}}|\psi_{1s}^{(n)}(1)|^2|\psi_{1s}^{(n)}(2)|^2\, d^3\mathbf{r}_1\, d^3\mathbf{r}_2 \\ &= 2E_{1s}^{(n)} - J_{1s1s} \end{aligned} \tag{17.3-6}$$

The integral J_{1s1s} is called a **Coulomb integral** because it represents at approximate expectation value of a Coulomb (electrostatic) repulsion energy between two electrons.

Roothaan modified the Hartree–Fock method by representing the orbitals by linear combinations of functions similar to Eq. (15.2-13) instead of by numerical representations.[8] Clementi and Roetti expressed the unknown orbitals as a linear combination of **Slater-type orbitals** (STOs). Each Slater-type orbital is a product of r raised to some power, an exponential factor, and the correct spherical harmonic angular functions. Using this expression instead of a numerical representation to evaluate the integrals in the self-consistent-field method, they obtained an energy for the ground state of the helium atom equal to −77.9 eV.[9]

The Slater-type orbitals are named after the same John C. Slater after whom the Slater determinants are named.

The self-consistent field method converges to the best orbital wave function, but it does not include any dynamical electron correlation. The difference between the best

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[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).

energy calculated with an orbital wave function and the correct nonrelativistic energy 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.

17.4 Excited States of the Helium Atom

Excited states of atoms are generally harder to treat than ground states. The variation theorem applies only to ground states, so it cannot be used for excited states in its original form. There is an **extended variation theorem**, which states that the calculated variational 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, etc.[10] Unfortunately, the correct ground-state energy eigenfunction is not generally known, so that a family of functions exactly orthogonal to it cannot be chosen. 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 variational energy from this family might be a good approximation to the energy of the first excited state. In other cases, even if the ground-state wave function is not known, some known property, such as being a spherically symmetric function, might permit construction of a trial function that is exactly orthogonal to it.

Degenerate Perturbation Theory

The perturbation method as described earlier in this chapter does not apply to a zero-order state that has the same energy as other zero-order states of the system (the degenerate case). For example, the zero-order orbital energies of the $2s$ and $2p$ hydrogenlike orbitals are all equal, to that all of the zero-order states of the $(1s)(2s)$ and $(1s)(2p)$ helium configurations have the same energy. A version of the perturbation method has been developed to handle the degenerate case. We will describe this method only briefly and present some results for the first excited states of the helium atom.[11]

There is no guarantee that the wave functions that we first obtain with the zero-order solution are in correspondence with the correct wave functions in the degenerate case. If not, the smooth dependence on the parameter λ depicted in Figure 17.2 will not occur. The first task of the degenerate perturbation method is to find the **correct zero-order wave functions**, the ones that are in one-to-one correspondence with the exact wave functions. As the fictitious parameter λ is increased from a value of zero to a value of unity, each correct zero-order function smoothly turns into one of the exact functions

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[10] Levine, *op. cit.*, pp. 193ff (Note 2).

[11] Levine, *op. cit.*, pp. 241ff (Note 2).

without getting mixed up with other functions. We express the correct zero-order wave functions as linear combinations of the degenerate "initial" zero-order wave functions:

$$\Psi^{(0)}_{n(\mathrm{new})} = \sum_{j=1}^{g} c_{nj}\Psi^{(0)}_{j} \tag{17.4-1}$$

In order to find the c_{nj} coefficients that define the correct zero-order functions, one must solve a set of homogeneous linear simultaneous equations that are somewhat similar to a set of equations described in Appendix H. Every equation of such a set consists only of terms each of which is proportional to one of the coefficients to be found. These equations are "trivially" satisfied if all of the coefficients equal zero. An equation that must be satisfied for a nontrivial solution of these equations to exist is called a **secular equation.**[12] Solution of the secular equation gives the first-order corrections to the energies as well as allowing solution of the equations for the c_{nj} coefficients for each correct zero-order function. It turns out that the wave functions of Eq. (16.3-38) are the correct zero-order functions for the $(1s)(2s)$ configuration, and three sets of similar functions are the correct zero-order functions for the $(1s)(2p)$ configuration.

Figure 17.3 shows the results of calculations to first order and to third orders for the energies of the four levels that result from the $(1s)(2s)$ and the $(1s)(2p)$ configurations.[13] We observe the following facts: (1) Each triplet state has a lower energy than the corresponding singlet state. (2) The $(1s)(2s)$ configuration gives states of lower energy than the $(1s)(2p)$ configuration. That is, the orbital energies of the $2p$ subshell are higher than the orbital energies of the $2s$ subshell. The same behavior is found by experiment generally to be true for atoms with more than two electrons, and it is also found in higher shells that the orbital energies of a d subshell lie higher than those of the orbital energies of the p subshell in the same shell, etc.

It is possible to explain the difference in the subshell energies on the basis of shielding. An electron in the $1s$ orbital of a ground-state helium atom moves as though the nuclear charge were reduced, due to the shielding of the positive nuclear charge by the negative charge of the other electron. Electrons in other shells are similarly shielded by other electrons that are present. An electron in a $2s$ orbital spends more time close to the nucleus than one in a $2p$ orbital, as shown in the radial distribution functions of Figure 16.13b. An electron in a $2s$ orbital will experience less shielding and its energy will be lower than one in a $2p$ orbital, in agreement with the results shown in Figure 17.3.

It is possible to explain the difference in the energies of the singlet and triplet states on the basis of statistical correlation. The singlet state wave functions have symmetric space factors, since the spin factors are antisymmetric. Statistical correlation is not found in symmetric space factors. In the triplet state wave functions, the spin factor is symmetric, so the space factor is antisymmetric, giving statistical correlation, as in Exercise 17.4. The electrons have lower probability of being found close together than of being far apart when the system is in a triplet state. Since close proximity of two electrons corresponds to higher potential energy, a triplet state has a lower energy than a singlet state with the same space orbitals. We will use these explanations involving shielding and statistical correlation again in discussing multi-electron atoms, although this analysis is oversimplified. It also is found that the antisymmetric space factor corresponds to lower probability that the electrons will be far apart, as well as to a lower

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[12] Levine, *op. cit.*, pp. 238ff (Note 2).

[13] Levine, *op. cit.*, pp. 247ff (Note 2).

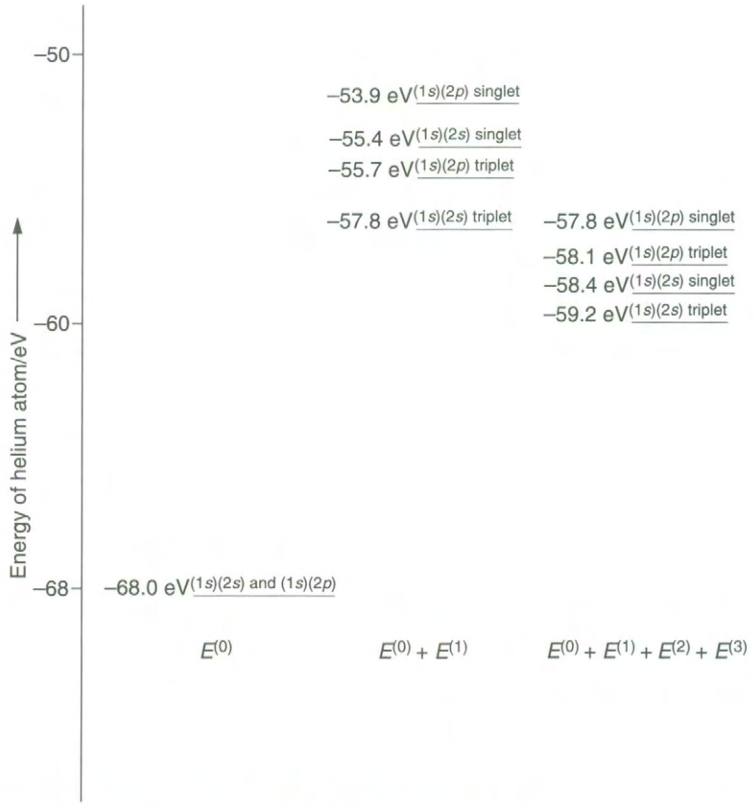

Figure 17.3. Approximate Energies of Helium Excited States. These excited state are the same as those found in perturbation theory. It is assumed that perturbation theory is capable of finding all of the actual states, even if the correct energies cannot be calculated exactly.

probability that they will be close together. There is also a higher probability that the electrons will be found close to the nucleus, and this fact may be a controlling factor.[14]

Exercise 17.5

Sketch a qualitative energy level diagram for the excited states of the $(1s)(3s)$, $(1s)(3p)$, and $(1s)(3d)$ configurations for the helium atom.

The self-consistent-field method must also be modified in order to treat excited states of the helium atom, because two different space orbitals can be involved. In this case two simultaneous integrodifferential equations must be solved by iteration. Furthermore, an antisymmetrized wave function requires two terms in the space factor of the wave function. The original self-consistent-field method of Hartree did not provide for antisymmetrization. The method was modified by Fock[15] to include antisymmetrization.

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[14] Levine, *op. cit.*, pp. 303ff (Note 2).

[15] V. Fock, *Zf. Phys.*, **61**, 126 (1930).

17.5 Atoms with More Than Two Electrons

The discussion of other atoms is similar to that of helium. In zero order, electron–electron repulsions are neglected, and in higher-order calculations these repulsions are treated with the same approximation methods as in the helium atom.

Higher-Order Approximations for the Lithium Atom

The zero-order wave function for the ground state of the lithium atom was written in Section 16.4. An application of the variation method to the lithium atom ground state uses an orbital wave function containing hydrogenlike orbitals with variable orbital exponents (variable effective nuclear charges) similar to that used with helium except that different effective nuclear charges are used in the 1*s* and 2*s* orbitals. The minimum in the variational energy, -201.2 eV, is found to occur with effective nuclear charges of 2.686 protons for the 1*s* orbitals and 1.776 protons for the 2*s* orbital.[16] This variational energy differs from the correct value of -203.5 eV by 1%. The difference in the two effective nuclear charges corresponds to the fact that an electron occupying a 2*s* orbital is on the average farther from the nucleus than an electron occupying a 1*s* orbital, so that there is a larger probability that other electrons are found between it and the nucleus than is the case with a 1*s* electron. The effective charge for the 2*s* orbital corresponds to 1.224 electrons being found between the nucleus and the 2*s* electron, while a 1*s* electron appears to have 0.314 electron between itself and the nucleus.

The effective nuclear charge seen by the 1*s* electrons is nearly the same as would be seen by the 1*s* electrons in a heliumlike atom with three protons in the nucleus, since the minimum in the variational energy of Eq. (17.1-14) occurs at $Z' = 2.6875$ if $Z = 3$. A 1*s* electron in a lithium atom is shielded primarily by the other 1*s* electron, and sees almost no shielding due to the 2*s* electron. Since the 2*s* electron on the average is found farther away from the nucleus than the 1*s* electron, this result is plausible.

***Exercise 17.6**

a. Find the value of $\langle r \rangle$ for an electron in a hydrogenlike 1*s* orbital with $Z = 2.686$.

b. Find the value of $\langle r \rangle$ for an electron in a hydrogenlike 2*s* orbital with $Z = 1.776$.

In further variational calculations, the 2*p* orbital is found to be higher in energy than the 2*s* orbitals, so that the ground configuration is $(1s)^2(2s)$, not $(1s)^2(2p)$. The 2*p* electron is more effectively screened from the nuclear charge than is a 2*s* electron. However, an electron in a 2*p* orbital is not on the average farther from the nucleus than one in a 2*s* orbital for the same nuclear charge (see Problem 16.35). It is not just the average distance from the nucleus, but the entire radial probability distribution that determines the effectiveness of the shielding. The 2*s* orbital is nonzero for $r = 0$, while the 2*p* orbitals vanish for $r = 0$, so an orbital in a 2*s* orbital has a greater probability of being found close to the nucleus, where the shielding is least effective, than does an electron in a 2*p* orbital. Figure 16.10b shows that the radial probability distribution for the 2*s* orbital has a "hump" close to the nucleus that the 2*p* orbital does not have. We say that the 2*s* orbital is more "penetrating" toward the nucleus than are the 2*p* orbitals.

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[16] Levine, *op. cit.*, pp. 274ff (Note 2).

The **ionization potential** can be used to obtain an estimate of the effective nuclear charge for the outermost electron in an atom. 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 changed much 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 electron.[17] In the case of lithium, we have already seen that the effective charge seen by the 1s electrons is nearly unaffected by the presence of the 2s electron, so this condition is fairly well met.

EXAMPLE 17.1

Find the effective nuclear charge seen by the 2s electron in lithium from the ionization potential, which is 124 kcal mol^{-1}. Compare this value with the value of 1.776 obtained with the variational method.

Solution

The ionization potential in electronvolts 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 2s orbital is given by Eq. (16.2-10) as

$$E_2 = -\frac{(17.6\,\mathrm{eV})Z'^2}{4}$$

where Z' is the effective nuclear charge. Setting this energy equal to 5.38 eV gives $Z' = 1.26$, which is in only rough agreement with the value of 1.776 obtained by the variational 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. This value is considerably less accurate than the value obtained by the simple variational calculation.[18] The Hartree–Fock method is the most successful of the three common approximation methods. A careful Hartree–Fock–Roothaan calculation leads to a ground-state energy of −202.3 eV, differing from the correct value by only 0.6%.[19] This error 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 configurations, a method that is known as **configuration interaction**, abbreviated CI. For example, for the ground state of the lithium atom, one could use

$$\Psi = c_1\Psi_{1s1s2s} + c_2\Psi_{1s2s2s} + c_3\Psi_{1s1s3s} + \cdots \tag{17.5-1}$$

where c_1, c_2, and c_3, etc., are variable parameters and the Ψs represent Slater-determinant wave functions with the given configurations. The variational energy is minimized with respect to these parameters. Although it is not obvious from inspection of Eq. (17.5-1) that Ψ includes dynamical correlation, it does in fact depend on

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[17] Levine, *op. cit.*, p. 475 (Note 2).

[18] Levine, *op cit.*, p. 274ff (Note 2).

[19] F. L. Pilar, *Elementary Quantum Chemistry*, McGraw-Hill, New York, 1968, p. 336.

interelectron distances, a fact that we discuss briefly in the next chapter. Unfortunately, the process converges slowly, so that many configurations must be used to get good accuracy. Using large computers, atomic and molecular calculations have been constructed with as many as a million configurations.

Atoms with More Than Three Electrons

The higher-order approximate treatment of the other atoms is similar to the helium and lithium treatments. All three approximations schemes can be applied, but the most accurate work has been done with the Hartree–Fock–Roothaan method and configuration interaction. The optimum orbitals appear to be in one-to-one correspondence with the hydrogenlike orbitals. Figure 17.4 shows approximate orbital energies in neutral atoms, obtained by an approximation scheme called the Thomas–Fermi method. This method gives orbital energies that generally agree with those from the Hartree–Fock method. Notice that logarithmic scales are used in the figure. Several things are apparent: First, the orbitals in the same shell but in different subshells have different energies, with higher values of l corresponding to higher energies; second, all of the orbitals in a given subshell have the same energy; third, the energies depend strongly on the nuclear charge, with some pairs of curves crossing and recrossing as a function of

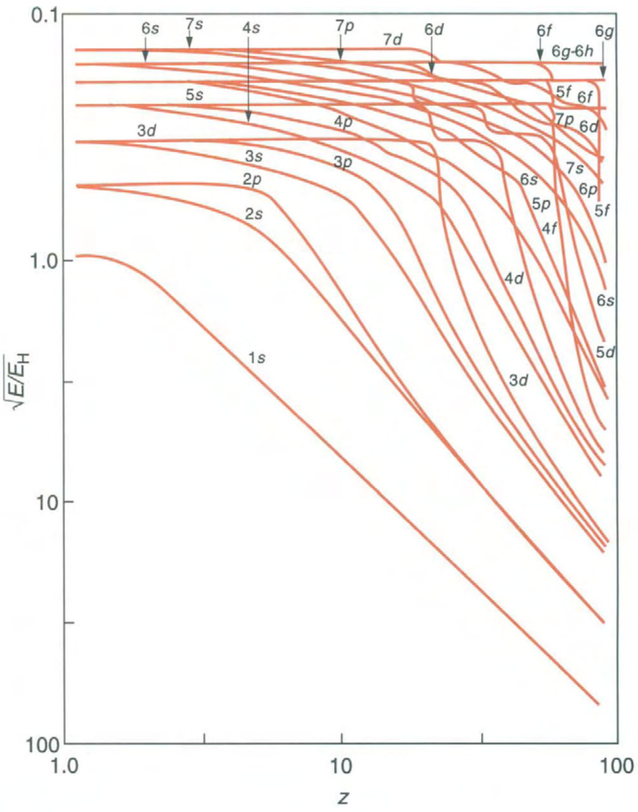

Figure 17.4. Approximate Orbital Energies in Neutral Atoms. The axes in this diagram are logarithmic. The order of occupation of subshells can only approximately be determined from this diagram. From R. Latter, *Phys. Rev.*, **99**, 510 (1955).

the nuclear charge. The energy differences between subshells in the same shell can be ascribed to differences in shielding. An electron in an *s* orbital spends more time close to the nucleus than an electron in a *p* orbital and is less effectively shielded from the nucleus by other electrons, giving it a lower orbital energy. Similarly, an electron in a *p* orbital is less effectively shielded than an electron in a *d* orbital, and so on. All of the orbitals in a subshell have the same orbital energy because they all contain the same radial factor.

Using Figure 17.4 or some equivalent source of orbital energies, it is now possible to determine the ground-level configuration for any neutral atom, using the Aufbau principle that was introduced in Chapter 16. This principle states that the ground-state configuration is obtained by choosing the lowest-energy set of orbitals compatible with Pauli exclusion. For the first 18 elements, the subshell energies lie in the increasing order 1*s*, 2*s*, 2*p*, 3*s*, 3*p*. For example, the subshell configuration of the ground state of argon is $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6$. From Figure 17.4 we see that beyond atomic number 15, the 3*d* orbital energy is higher than that of the 4*s*. Therefore, elements 19 (potassium) and 20 (calcium) in their ground states have the 4*s* orbitals occupied in preference to the 3*d* orbitals. Beyond atomic number 23, the figure shows the 4*s* energy above the 3*d* energy. However, it is found experimentally that most of the transition elements from scandium (element 23) through zinc (element 30) have two electrons occupying the 4*s* spin orbitals in their ground levels, although chromium (element 24) and copper (element 29) have only one 4*s* electron. Assuming the energies in the figure to be essentially correct, it appears that other factors besides orbital energy, principally the correlation energy, are important in determining the ground-level configuration.

The correct ground-level configuration for most elements can be obtained from the scheme of Figure 17.5, which shows the "**diagonal mnemonic device**" or the "**diagonal rule**." To determine the order of orbitals for the Aufbau principle, one follows the diagonal paths from upper right to lower left, moving top to bottom from one diagonal to the next. 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 to be occupied by the electrons of a given atom. The diagonal mnemonic device is equivalent to the "$\boldsymbol{n+l}$ **rule**," which states that subshells of a given value of $n + l$ are occupied

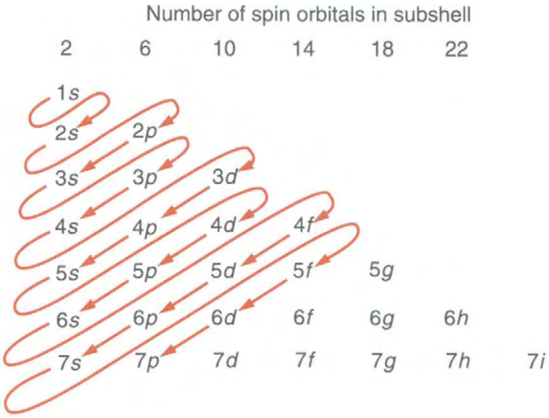

Figure 17.5. The Diagonal Mnemonic Device for Applying the Aufbau Principle to Neutral Atoms. Following the arrows in the diagram gives the order of occupation of subshells in neutral atoms. Exceptions are given in Table 17.1.

before those of the next higher value of $n + l$, and that within a given value of $n + l$, the subshells are occupied in the order of increasing n.

EXAMPLE 17.2

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 giving an inert gas configuration as part of the configuration. The Mn configuration is sometimes abbreviated as $[\mathrm{Ar}](3d)^5(4s)^2$, where [Ar] stands for the ground-level configuration of argon.

*Exercise 17.7

Give the ground-level configuration of the elements: (a) S, (b) Ta, (c) Hg.

Table 17.1 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 d subshell having 5 or 10 electrons instead of having 4 or 9 electrons. These exceptions to the rule apparently correspond to the fact that a half-filled or filled subshell is more stable than otherwise expected, possibly because the orbital regions of the real d orbitals are well separated from each other, allowing electrons to have a fairly

Table 17.1 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	$[\mathrm{Kr}](4d)^9(5s)^1$
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	$[\mathrm{Rn}](5f)^{14}(6d)^1(7s)^2$

low energy of repulsion when occupying these orbitals in preference to another choice of orbitals. There has been some discussion about whether lanthanum and actinium are also exceptions to the diagonal mnemonic rule. Lanthanum has sometimes been assigned a $5d$ electron in the ground level, and actinium has been assigned a $6d$ electron. However, from an analysis of spectroscopic observations, it appears that lanthanum has a $4f$ electron in its ground state and that actinium has a $5f$ electron, as predicted by the diagonal rule.[20]

The diagonal mnemonic rule does not necessarily apply to ions, since the shielding is different for ions than for neutral atoms. For example, the iron atom has six $3d$ electrons and two $4s$ electrons, in conformity with the diagonal rule. The Ni^{2+} ion, with the same number of electrons, has eight $3d$ electrons and no $4s$ electrons. The correct electron configuration for positive ions can usually be obtained by finding the configuration of the neutral atom and then removing electrons from the outer shell instead of the subshell to which the last electrons were added.

For those elements with partially filled subshells, the detailed configuration and the values of the quantum numbers L and S of the ground level can be predicted, using rules due to Hund. **Hund's first rule** is: *For the same value of L, 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 second rule is applied only after the first rule has been applied. These rules are quite reliable for ground levels, but less reliable for other levels.[21] There is also a third rule, which states that for subshells that are more than half filled, higher values of J correspond to lower energies, and that for subshells that are less than half filled, lower values of J correspond to lower energies.

With several electrons, the operators for the squares of the total orbital and spin angular momentum are complicated, since the angular momenta are vector sums. We will not discuss them, but will work with the z components. The operators for the z components are algebraic sums of the one-electron operators:

$$\hat{L}_z = \sum_{i=1}^{Z} \hat{l}_{iz}, \qquad \hat{S}_z = \sum_{i=1}^{Z} \hat{s}_{iz} \tag{17.5-2}$$

The quantum numbers M_L and M_S are also algebraic sums:

$$M_L = \sum_{i=1}^{Z} m_i \tag{17.5-3}$$

$$M_S = \sum_{i=1}^{Z} m_{si} \tag{17.5-4}$$

For any given detailed configuration, the possible values of M_L and M_S can be determined by algebraic addition as was done in Chapter 16. 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 from the fact that M_L ranges from $-L$ to $+L$, and that M_S ranges from $-S$ and $+S$. The ground-level term can then be determined from Hund's rules.

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[20] W. B. Jensen, *J. Chem. Educ.*, **59**, 635 (1982).

[21] Levine, *op. cit.*, pp. 303ff (Note 2).

EXAMPLE 17.3

Using Hund's first and second rules, find the ground-level term symbol for the nitrogen atom.

Solution

The ground-level configuration is $(1s)^2(2s)^2(2p)^3$. Applying Hund's first rule, we seek the largest value that S can have. The filled $1s$ and $2s$ subshells make no net contribution to L or S, because the subshells are filled and their m_s values add to zero. 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 smallest is $-3/2$. Therefore, the largest value of S is 3/2, and this will be the ground-level value.

Since we are looking for values of M_L, we use the space orbitals that are eigenfunctions of the $\hat{l}_z$ operators, the ψ_{2p1}, ψ_{2p0}, and $\psi_{2p,-1}$ orbitals. Each of these is occupied by one electron, so $M_L = 1 + 0 - 1 = 0$, and the only value of L is zero. The term symbol is ^{4}S (quartet S). There is no need to apply Hund's second rule, since only one value of L can occur with the value of S that we found.

***Exercise 17.8**

Find the ground-level term symbols for (a) Be, (b) B, (c) C, (d) O, and (e) F.

The explanation of Hund's first rule is the same as the explanation for the fact that the triplet levels were lower in energy than the singlet levels in helium, discussed in Chapter 16. The higher values of S correspond to more electrons occupying states of parallel spins, which means that they occupy a larger number of space orbitals. Occupying different orbitals lowers the probability that the electrons will be found close together, thus lowering the potential energy.

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 increasing order of atomic mass, there was a repetition, or periodicity, of chemical and physical properties. For example, lithium, sodium, potassium, rubidium, and cesium all form oxides with the formula M_2O and chlorides with the formula MCl, while beryllium, magnesium, calcium, strontium, and barium all form oxides with the formula MO and chlorides with the formula MCl_2, where we abbreviate the symbol for the metal with the letter M.

Inside the front cover of this book is a modern periodic table. The elements are listed in order of atomic number, instead of atomic mass, except that some elements are listed separately at the bottom of the table. Elements in any given column exhibit similar chemical properties. There are several ways of numbering the columns, and the two most common ways are shown. One scheme, which is supposed to become the standard scheme, is to number the 18 columns from 1 to 18. The other is to number the columns 1A through 8A and 1B through 8B, as indicated. Three columns are grouped together as column 8B. This numbering corresponds closely to the numbering scheme used by Mendeleev, although the A and B columns were not distinguished in his table, which had only eight columns, with iron, cobalt and nickel together in one column. There is also another numbering scheme in which some of the A and B designations are interchanged. The elements in the columns labeled A are called **representative elements**, and those in the columns labeled B are called **transition elements** or

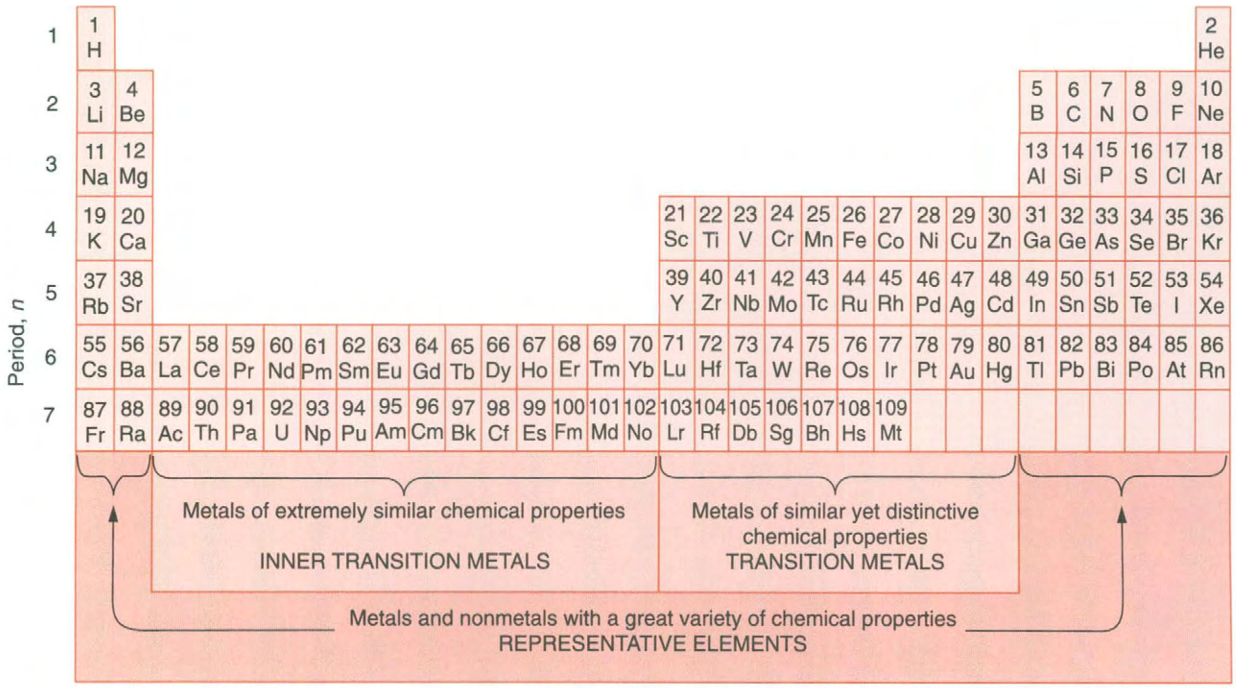

Figure 17.6. A Periodic Table of the Elements. This table is different from the periodic table inside the front cover in that all elements are listed in order of atomic number. The inner transition elements are given their own columns in the body of the table, instead of being placed underneath the body of the table.

transition metals. The two sets of 14 elements at the bottom of the chart are called **inner transition elements** or **inner transition metals**. Figure 17.6 shows a periodic table in which all elements are listed in order of increasing atomic number.

The elements following uranium (U, element 92) in the table do not occur in the earth's crust, but have been synthesized in nuclear reactors.[22] The elements after lawrencium, element 103, were given temporary names: element 104 was unnilquadrium, element 105 was unnilpentium, etc., based on the Latin version of the atomic numbers. Some of these names have been replaced, although there has been disagreement about what the names should be. The names of elements 104–109 that have been accepted by the International Union of Pure and Applied Chemistry are[23]

Atomic number	Symbol	Name
104	Rf	Rutherfordium
105	Db	Dubnium
106	Sg	Seaborgium
107	Bh	Bohrium
108	Hs	Hassium
109	Mt	Meitnerium

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[22] *Chem. Eng. News*, March 13, 1995, p. 35.

[23] *Chem. Eng. News*, August 21, 1995, p. 4, IUPAC news release, August 30, 1997.

Many elements were unknown at the time of Mendeleev. These elements included the inert gases, most of the inner transition elements, and others scattered about the table, such as scandium, gallium, and germanium. However, Mendeleev had sufficient confidence in the periodicity principle that he left blank spaces in the table for undiscovered elements. Mendeleev listed the elements in order of atomic mass, because the concept of atomic number was unknown. There are cases in which a larger atomic mass occurs before a small atomic mass (Ar and K, Co and Ni, Te and I). However, Mendeleev had an incorrect value for the atomic mass of tellurium, he listed Fe, Co, and Ni together in his column 8, and argon had not been discovered. He might have been unaware of these reversals of order.

The form of the periodic table was first explained by Niels Bohr, who also introduced the modern "long" form of the chart with 18 columns. The similarity of chemical properties of the elements in a given column is due to the similarity of their electron configurations in the outermost shell (**the valence shell**). For example, sodium and potassium both easily lose one electron because sodium has only one electron in its valence shell (the third shell) and potassium has only one electron in its valence shell (the fourth shell). 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 10 columns, corresponding to the 10 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.

The general chemical behavior of an element can be predicted from its first ionization potential and its electron affinity. The **ionization potential** (also called ionization energy) is the energy required to remove one electron. The **electron affinity** is the energy required to remove the extra electron from a singly charged negative ion of the element. It is therefore equal to the amount of energy given off in forming a negative ion, and is positive if a gaseous atom spontaneously attracts an electron. Those with relatively high ionization potential will also have relatively high electron affinities (except for the inert gases). Those elements with relatively small values of the ionization potential will tend to lose electrons when combining chemically. Those elements with high electron affinities will tend to gain electrons when combining chemically.

Figure 17.7 shows the first ionization potential of the elements as a function of atomic number. The elements with the highest ionization potentials are the inert gases, which have eight electrons in the valence shell (except for helium). A similar graph of the electron affinity would show that the elements of column 7A, the halogens, have the greatest electron affinity. In other words, if the halogen achieves the same configuration as an inert gas by gaining an electron, it becomes relatively stable. The elements with the lowest ionization potentials are the elements in column 1A, the alkali metals, which have a single electron in the *s* subshell of the valence shell. It is relatively easy to remove an electron from an atom of an alkali metal, giving the inert gas configuration in the shell just below the valence subshell.

Figure 17.7 shows several additional elements, such as beryllium, nitrogen, magnesium, phosphorus, zinc, and mercury, which have higher ionization potentials than their immediate neighbors. All of these elements have ground-level configurations with all subshells completely filled (beryllium, magnesium, zinc, and mercury), or with all subshells filled except for a half-filled valence subshell (nitrogen and phosphorus). We conclude that not only is a filled subshell relatively stable, but also that a half-filled subshell is relatively stable. We have already mentioned this behavior in some exceptions to the diagonal rule, such as chromium and copper.

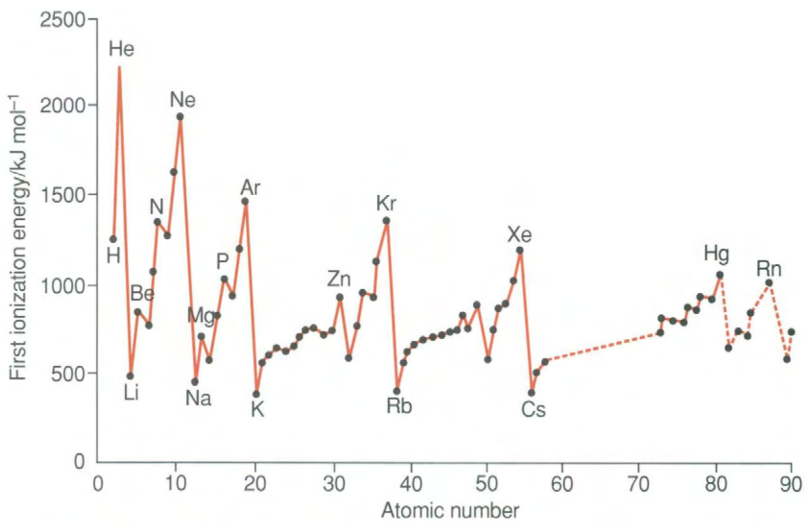

Figure 17.7. First Ionization Potentials of the Elements. The trends in the table and their relation to position in the periodic chart are understood in terms of electron configurations. Moving from left to right in one row of the periodic chart corresponds to increasing the number of protons in the nucleus, holding the electrons more tightly, but without increasing the number of occupied shells. Moving from top to bottom in the periodic chart corresponds to moving to shells farther from the nucleus, lessening the attraction of the electrons to the nucleus, which is shielded by the electrons in the inner shells.

By Hund's first rule, a subshell that is half full or less than half full in the ground level will have each electron occupying a different space orbital, in order to have parallel spins, resulting in the state of maximum M_S. A half-filled subshell therefore has one electron occupying each space orbital, and has the same electron charge distribution as a full subshell except for having only half as much total charge. **Unsöld's theorem** asserts that the charge distribution in a filled hydrogenlike subshell is spherically symmetric (independent of θ and ϕ). This theorem also must hold for a half-filled subshell.

Exercise 17.9

For hydrogenlike 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.

There are a number of additional chemical and physical properties, including atomic size, melting temperature, and electronegativity, that can be correlated with electron configuration and thus with position in the periodic table.

Summary of the Chapter

This chapter introduced three approximation schemes and discussed their application to atoms with two or more electrons. The first approximation scheme was the variation method, in which a variation trial function is chosen to minimize the approximate ground-state energy. 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 approximation corresponds to introduction of electron correlation, a dependence of the wave function on the interelectronic distance.

The next approximation method discussed was the perturbation method. To apply this method, the Hamiltonian must be written as $\hat{H}^{(0)} + \hat{H}'$, where $\hat{H}^{(0)}$ represents a Hamiltonian of a Schrödinger equation that can be solved. The term $\hat{H}'$ is called the perturbation term. The perturbation term is arbitrarily multiplied by a fictitious parameter λ, so that $\lambda = 1$ corresponds to the actual case. The method is based on representations of the energy eigenvalues and energy eigenfunctions as power series in λ and approximation of the series by partial sums. In the helium atom treatment the interelectronic repulsive potential energy was treated as the perturbation term in the Hamiltonian operator. The method gave useful results for excited states.

The third approximation scheme was the self-consistent-field method of Hartree and Fock. In this method an optimum orbital wave function is sought without restricting the search to a single family of functions. For the helium atom the interelectronic replusive 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.

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 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. The 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 interelectron 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 the stable configuration with fully occupied s and p subshells.

PROBLEMS

Problems for Section 17.1

17.10. Prove the variational 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 variational energy and use eigenfunction and orthogonality properties.

17.11. Calculate the variational energy of a particle in a one-dimensional box of length a, with the following trial functions:

- *__a.__ $\varphi(x) = Ax(a - x)$
- *__b.__ $\varphi(x) = Ax^2(a^2 - x^2)$
- **c.** $\varphi(x) = Ax^3(a^3 - x^3)$

Calculate the percent error for each trial function.

17.12. Calculate the variational 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.

17.13. Using the variation method, calculate the energy of the ground state of an anharmonic oscillator with potential energy $\mathscr{V} = kz^2/2 + bz$, where k and b are constants. Use the trial function

$$\varphi = C(\psi_0 + c_1\psi_1)$$

where ψ_0 and ψ_1 are the first energy eigenfunctions. Using Eq. (17.1-2), notice that the constant C cancels out of the variational energy. Minimize the energy with respect to c_1.

17.14. Using the variation method, calculate the energy of the ground state of an anharmonic oscillator with potential energy function $\mathscr{V} = kz^2/2 + cz^4$, where k and c are constants. Use the following variational trial functions, minimizing the energy with respect to the parameter b in each case.

a. $\dfrac{A}{b^2 + z^2}$

b. Ae^{-bz^4}

***17.15.** 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 variational calculation.

b. What energy in eV is required to remove both electrons?

17.16. 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. 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 variational 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.

Problems for Section 17.2

***17.17. 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:

$$\mathscr{V}(z) = \begin{cases} \infty & \text{if } z < 0 \text{ or } a < z \\ bz & \text{if } 0 < z < a \end{cases}$$

b. An electron in a one-dimensional box of length 10.00 Å is transported to a very large planet on which the acceleration due to gravity is $6.00 \times 10^{18}\ \mathrm{m\,s^{-1}}$. The box is placed in a vertical position. Find the energy of the electron in first order.

17.18. Using first-order perturbation, calculate the energy of the ground state of an anharmonic oscillator with potential energy $\mathscr{V} = kz^2/2 + bz$, where k and b are constants. Compare your answer with that of Problem 17.13.

***17.19.** 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 and c are constants.

17.20. Using first-order perturbation, calculate the energy of the ground state of a system with the potential energy:

$$\mathscr{V}(z) = \begin{cases} \infty & \text{if } \ z < -a \text{ or } a < z \\ kz^2/2 & \text{if } \ -a < z < a \end{cases}$$

17.21. Consider a system such that one of the wave functions happens to be an eigenfunction of the perturbation term in the Hamiltonian. Show that first-order perturbation gives an exact solution to the Schrödinger equation.

Problems for Section 17.4

17.22. Write all of the term symbols for the $(1s)(2p)$ excited configuration of He.

17.23. Write all of the term symbols for the $(1s)(3d)$ excited configuration of He.

Problems for Section 17.5

17.24. Using the values for the orbital exponents (effective number of protons in the nucleus) in Section 17.4, 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.

***17.25.** Write the ground-state electron configurations by subshells for the following elements: (a) Fe, (b) Rn, (c) Tc, (d) Rb.

17.26. Using Hund's rules, write the ground term symbol for each of the elements in Problem 17.25.

***17.27.** 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.

17.28. 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.

*17.29. 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 $3s$ electron in a sodium atom in its ground state. State any assumptions.

17.30. Which of the elements in the first two rows of the periodic table have electronic charge distributions that are spherically symmetric?

*17.31. For each of the first 18 elements of the periodic table, give the number of unpaired electrons in the ground state.

17.32. Use the expression for the time-dependent wave function to show that the real hydrogenlike energy eigenfunctions correspond to standing waves while the complex hydrogenlike energy eigenfunctions correspond to traveling waves. Say how the traveling waves move. Show that both types of energy eigenfunctions correspond to stationary states.

General Problems

17.33. Prove an extended variational theorem: If the trial function φ is orthogonal to ψ_0, the correct ground-state wave function, the variational energy cannot be lower than the correct energy of the first excited state, E_1. See Problem 17.10.

17.34. 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.

17.35. 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.

17.36. **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 $\hat{H}' = bx$, where b is a 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. Obtain a formula for the ground-state energy of the particle of part (a), using the variation method and the trial function $\varphi = Ax^n(a-x)$.

e. 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 $b = -1.60 \times 10^{-11}\,\mathrm{J\,m^{-1}}$. Evaluate the energy according to parts (a) and (c).

f. Evaluate the energy according to part (d) and find the optimum value of n.

17.37. An electric dipole consists of two charges of equal magnitude and opposite sign separated by a distance d. The magnitude of the electric dipole is defined to be the magnitude of each of the charges times the separation. When an 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

$$\boldsymbol{\mu}_{\text{induced}} = \alpha\mathcal{E}$$

where μ is the magnitude of the dipole moment and $\mathcal{E}$ is the magnitude of the electric field. The additional energy of the atom due to the induced dipole in the electric field is

$$E' = -\tfrac{1}{2}\alpha\mathcal{E}^2$$

For a hydrogen atom and for an electric field in the z direction, the Hamiltonian operator is

$$\hat{H} = \hat{H}^{(0)} + e\mathcal{E}z = e\mathcal{E}r\cos(\theta)$$

where $\hat{H}^{(0)}$ is the Hamiltonian in the absence of the field. The magnitude of the dipole moment is

$$\mu = e\mathcal{E}\langle z\rangle = e\mathcal{E}\langle r\cos(\theta)\rangle$$

a. Use the variation method to find the energy of a hydrogen atom in an electric field in the z direction with magnitude $\mathcal{E}$. Use the $1s$ wave function as the variation trial function. No minimization will be possible. Explain your result.

b. Use the variation method to find the energy of a hydrogen atom in an electric field in the z direction with magnitude $\mathcal{E}$. Use the variation trial function

$$\varphi = C(\psi_{1s} + c\psi_{2p_z})$$

The constant C will cancel out of the energy expression, Eq. (17.1-2). 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).

d. Use first-order perturbation to find the energy of a hydrogen atom in an electric field in the z direction with magnitude $\mathcal{E}$. Explain any difference between your result and that of part (a).

17.38. 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 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 variational energy equals the correct ground-state energy, the variational trial function must be equal to the correct ground-state wave function.

18

The Electronic States of Molecules

OBJECTIVES

After studying this chapter, the student should:

1. be familiar with and understand the properties of the electronic states of the hydrogen molecule ion;
2. be able to construct approximate wave functions and electron configurations or homonuclear diatomic molecules;
3. be able to use general properties of molecular orbitals, including criteria for formation of good bonding orbitals, to predict the qualitative properties of electronic states of heteronuclear diatomic molecules;
4. be able to describe qualitatively the bonding in a fairly small polyatomic molecule, including bond angles, bond polarities, and the dipole moment of the molecule, using the criteria for formation of good bonding orbitals;
5. be able to describe qualitatively the bonding in fairly small polyatomic molecule, using the valence bond method;
6. be able to assign molecules to point groups and use some of the elementary applications of group theory to molecular wave functions;
7. be familiar with some of the semi-empirical molecular orbital calculation schemes and be able to use commercially available computer programs to carry out these calculations.

PRINCIPAL FACTS AND IDEAS

1. In the Born–Oppenheimer approximation, the nuclei 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 further approximations.
3. Molecular orbitals can be represented approximately as linear combinations of atomic orbitals (LCAO-MOs).
4. The electronic states of homonuclear diatomic molecules can be described with a common set of LCAO-MOs.
5. The valence bond method is an alternative to the molecular orbital method.
6. Heteronuclear diatomic molecules are described with molecular orbitals that differ from those of homonuclear diatomic molecules.
7. Qualitative descriptions of the electronic states of molecules can be obtained by using general criteria for forming good bonding LCAO molecular orbitals.
8. The electronic structure of polyatomic molecules can be described with LCAO molecular orbitals.
9. Group theory can be used to obtain useful information about molecular orbitals and wave functions.
10. Various semi-empirical and ab initio techniques exist for carrying out molecular orbital calculations.

18.1

The Born–Oppenheimer Approximation. The Hydrogen Molecule Ion

In a two-particle system such as the hydrogen atom, the Schrödinger equation can be solved in closed form (with solutions that can be represented by formulas). This is done as in Chapter 16 by separating the Schrödinger equation for two particles into one equation for the motion of the center of mass and another for the relative motion. For atoms with more than one electron we had to resort to approximations, including the assumption that in studying the electronic motion in atoms the nucleus was stationary.

Our study of the electronic motion in molecules is based on a similar assumption, the **Born–Oppenheimer approximation**,[1] which is the assumption that the nuclei are stationary when the electronic motion is studied. Fixed bond distances and bond angles are assumed and a Hamiltonian operator is written for electronic motion only. This is a good approximation, since electrons move so rapidly that they adapt to a new electronic wave function as soon as the nuclei move to a new location or conformation.

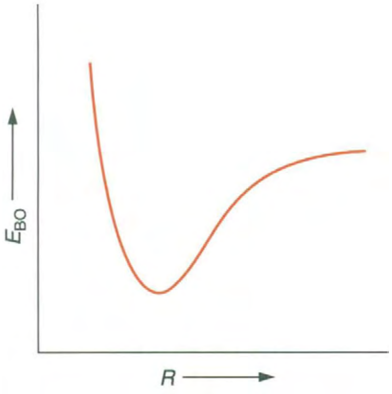

Figure 18.1 Born–Oppenheimer Energy as a Function of Internuclear Distance for a Diatomic Molecule (Schematic). This energy is the total energy of the molecule in the Born–Oppenheimer approximation. It consists of the electronic energy (kinetic plus potential), plus the energy of repulsion of the nuclei for each other.

The energy of the molecule with stationary nuclei is called the Born–Oppenheimer energy. Figure 18.1 shows schematically the ground-state Born–Oppenheimer energy of a diatomic molecule, which depends only on the internuclear distance, R. With polyatomic molecules, the Born–Oppenheimer energy depends on all of the internuclear distances and bond angles. Since the Born–Oppenheimer energy is a function of nuclear positions but not their velocities, it acts as a potential energy for molecular vibrations. Molecular rotations are usually studied with the assumption that the molecule is locked in the conformation of lowest energy (the equilibrium conformation). To a good approximation, the kinetic energy of nuclear motion can be added to the Born–Oppenheimer energy to obtain the total energy of the molecule. We return to study of the nuclear motions in Chapter 19.

The Schrödinger Equation for the Hydrogen Molecule Ion

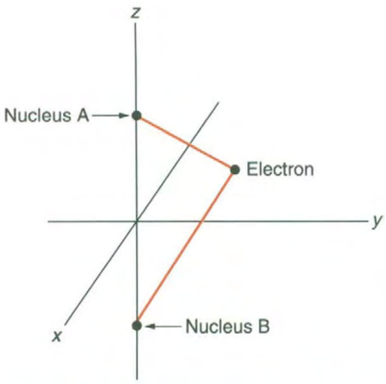

Figure 18.2 The Hydrogen Molecule Ion (H_2^+) System. This system is the simplest molecule, having only one electron. It is the only molecule for which the Schrödinger equation can be solved in the Born–Oppenheimer approximation without any additional appproximations.

The simplest molecular system is the hydrogen molecule ion, H_2^+, consisting of two nuclei and a single electron, as depicted in Figure 18.2. We apply the Born–Oppenheimer approximation, assuming that the nuclei are stationary with one nucleus at position A on the z axis and the other nucleus at position B on the z axis and with the origin of coordinates midway between the nuclei. The Born–Oppenheimer Hamiltonian operator for the hydrogen molecule ion is

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{R} - \frac{1}{r_A} - \frac{1}{r_B}\right) \tag{18.1-1}$$

where ∇^2 is the Laplacian operator for the electron's coordinates, m is the electron mass, R 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 assumed to be fixed. Since

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[1] Max Born and J. Robert Oppenheimer, *Ann. Phys.*, **84**, 457 (1927).

the internuclear distance R is constant in the Born–Oppenheimer approximation, the potential energy $\mathcal{V}_{\mathrm{nn}}$ of internuclear repulsion is a constant:

$$\frac{e^2}{4\pi\varepsilon_0 R} = \mathcal{V}_{\mathrm{nn}} = \text{constant} \tag{18.1-2}$$

We exclude $\mathcal{V}_{\mathrm{nn}}$ from the electronic energy and write

$$\hat{H} = \hat{H}_{\mathrm{el}} + \mathcal{V}_{\mathrm{nn}} \tag{18.1-3}$$

$$\hat{H}_{\mathrm{el}} = -\frac{\hbar^2}{2m}\nabla^2 + \frac{e^2}{4\pi\varepsilon_0}\left(-\frac{1}{r_{\mathrm{A}}} - \frac{1}{r_{\mathrm{B}}}\right) \tag{18.1-4}$$

The electronic Schrödinger equation is

$$\hat{H}_{\mathrm{el}}\psi_{\mathrm{el}} = E_{\mathrm{el}}\psi_{\mathrm{el}} \tag{18.1-5}$$

where E_{el} is the electronic energy eigenvalue. A constant added to a Hamiltonian operator does not change the energy eigenfunctions and results in adding that constant to the energy eigenvalues. (See Exercise 14.22.) We can write

$$E_{\mathrm{BO}} = E_{\mathrm{el}} + \mathcal{V}_{\mathrm{nn}} \tag{18.1-6}$$

where E_{BO} is the Born–Oppenheimer energy.

The variables can be separated in Eq. (18.1-5) by transforming to a coordinate system that is called confocal polar elliptical coordinates. We will not discuss the solution,[2] but will present some facts about the ground state and first excited state. We call the energies and orbitals of these states the "exact Born–Oppenheimer" energies and orbitals. They contain no approximations other than the Born–Oppenheimer approximation.

Figure 18.3 shows the Born–Oppenheimer energy as a function of R for the two states. The lower curve has a minimum at $R = 1.06 \times 10^{-10}\ \mathrm{m} = 106\ \mathrm{pm}$. This value of R is denoted by R_{e} and is called the **equilibrium internuclear distance**. We consider the molecule to be chemically bonded in the ground state with a bond order of 1/2, since there is one shared electron. For large values of R the energy approaches a constant value. The difference in energy between this constant value and the value of the energy at $R = R_{\mathrm{e}}$ is denoted by D_{e} and is called the **dissociation energy** of the molecule. For the $\mathrm{H_2}^+$ ion, D_{e} is equal to 2.8 eV. The first excited state has an energy that decreases monotonically as R increases. If the molecule is in the first excited state it will dissociate, forming a hydrogen atom and an H^+ ion.

Molecular Orbitals

The eigenfunctions of the Hamiltonian of Eq. (18.1-5) are one-electron wave functions that correspond to electronic motion around both nuclei. They are **molecular orbitals.** Figure 18.4 shows qualitatively the orbital regions for the ground state and first excited state. There is some similarity between the ground-state orbital region and that of the 1s orbital region for the hydrogen atom and between the orbital region of the first excited state and that of the $2p_z$ orbital of the hydrogen atom. If the mathematical limit is taken as R approaches zero, a hypothetical single atom called the **united atom** is obtained. The united atom for $\mathrm{H_2}^+$ is the He^+ ion with a single electron and $Z = 2$. In this limit

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[2] D.R. Bates, K. Ledsham and A. L. Stewart, *Phil. Trans. Roy. Soc.* **A246**, 215 (1963).

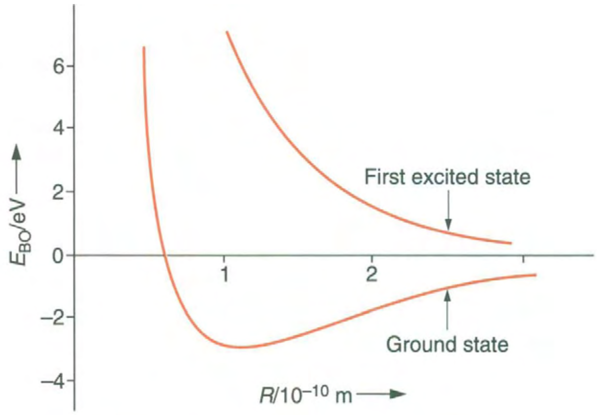

Figure 18.3 The Born–Oppenheimer Energy of the Ground State and First Excited State of the Hydrogen Molecule Ion as a Function of Internuclear Distance. This figure shows the results of solving the Schrödinger equation repeatedly for different internuclear distances in the Born–Oppenheimer approximation and then drawing a smooth curve through the energy eigenvalues as a function of internuclear distance. Both the ground state and the first excited state are shown.

the ground-state molecular orbital turns into the united-atom 1*s* He^+ orbital, and the first excited-state molecular orbital turns into the united-atom $2p_z$ He^+ orbital.

The ground-state orbital has no nodes except at infinite distance from the nuclei, while the first excited-state orbital has a nodal surface between the nuclei. A wave function with more nodes generally corresponds to a higher energy than one with fewer nodes. A molecular orbital without a nodal surface between the nuclei generally corresponds to an electronic energy with a minimum value as a function of *R* and it is called a **bonding molecular orbital**. An orbital with a nodal surface between the nuclei generally corresponds to an electronic energy that decreases monotonically as *R* increases and is called an **antibonding molecular orbital**.

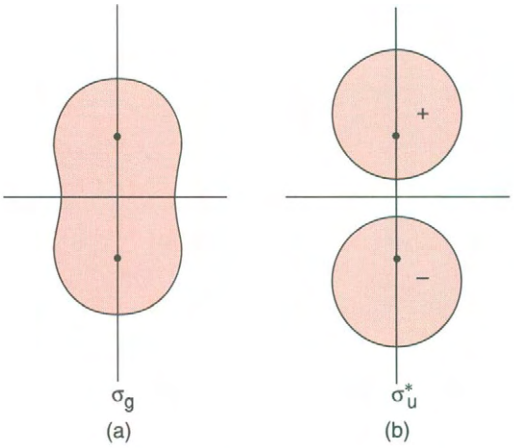

Figure 18.4 The Orbital Regions for the Hydrogen Molecule Ion (Schematic). (a) The ground state. (b) The first excited state. These sketches show the important qualitative properties of these two orbitals. The ground state corresponds to a standing wave with no nodes, and the first excited state corresponds to a standing wave with a nodal plane between the nuclei.

The orbital angular momentum operators $\hat{L}^2$ and $\hat{L}_z$ commute with the electronic Hamiltonian of the hydrogen atom, and energy eigenfunctions could be found that were eigenfunctions of these two operators. The operator $\hat{L}^2$ does not commute with the electronic Hamiltonian of the $H_2{}^+$ molecule because all directions are not equivalent due to the two fixed nuclei. However, $\hat{L}_z$ does commute with the electronic Hamiltonian operator if the nuclear axis is chosen as the z axis. The energy eigenfunctions can be eigenfunctions of $\hat{L}_z$, although not necessarily of $\hat{L}^2$. The eigenvalues of $\hat{L}_z$ follow the same pattern as in the atomic case:

$$\hat{L}_z\psi = \hbar m\psi \tag{18.1-7}$$

where the quantum number m equals any integer and where ψ represents an energy eigenfunction. The magnitude of m is not bounded by any quantum number l as for atoms. For molecular orbitals, we define a nonnegative quantum number λ:

$$\lambda = |m| \tag{18.1-8}$$

A nonzero value of λ corresponds to two states because m can be either positive or negative. Each level for $\lambda \neq 0$ has a degeneracy equal to 2 (is "doubly degenerate").

Atomic orbitals corresponding to $l = 0$ were called s orbitals, orbitals with $l = 1$ were called p orbitals, etc. For molecular orbitals we use the following Greek-letter designations:

Value of λ	Symbol
0	σ
1	π
2	δ
3	ϕ
etc.	

Both the ground-state orbital and the first excited-state orbital of the hydrogen molecule ion are σ (sigma) orbitals.

Symmetry Properties of the Molecular Orbitals

There is an important class of operators that can commute with the Born–Oppenheimer electronic Hamiltonian operator for a molecule and can be used to characterize the symmetry properties of molecules and of molecular orbitals. These operators are **symmetry operators**, which move points from one location to another in three-dimensional space. Each symmetry operator is classified and named by the way it moves a point. For each operator, there is a **symmetry element**, which is a point, line, or plane with respect to which the symmetry operation is performed.

The symmetry operators that commute with the Born–Oppenheimer Hamiltonian of a given molecule are said to belong to the molecule. The electronic energy eigenfunctions of the molecule can also be eigenfunctions of these operators. For diatomic molecules, we consider several symmetry operators. The **inversion operator**, $\hat{i}$, is defined to move a point on a line through the origin of coordinates to a location that is at the same distance from the origin as the original location. If the cartesian coordinates of the original location are (x, y, z), the inversion operator moves the point to $(-x, -y, -z)$. For a general operation, we denote the final coordinates by (x', y', z'), so that for the inversion operator $x' = -x$, $y' = -y$, and $z' = -z$. We denote the operation by the equation

$$\hat{i}(x, y, z) = (x', y', z') = (-x, -y, -z) \tag{18.1-9}$$

The symmetry element for the inversion operator is the origin. Since there is only one origin, there is only one inversion operator. **Point symmetry operators** are symmetry operators that leave a point at its original location if that location is at the origin. The inversion operator is an example of a point symmetry operator. The symmetry elements of point symmetry operators always include the origin.

A **reflection operator** is defined to move a point along 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 $\hat{\sigma}_\mathrm{h}$ reflects through a horizontal plane:

$$\hat{\sigma}_\mathrm{h}(x, y, z) = (x', y', z') = (x, y, -z) \tag{18.1-10}$$

There is only one horizontal plane through the origin, so there is only one $\hat{\sigma}_\mathrm{h}$ operator among the point symmetry operators. A symmetry operator that reflects through a vertical plane is denoted by $\hat{\sigma}_\mathrm{v}$. Since there are infinitely many vertical planes containing the origin, there are infinitely many $\hat{\sigma}_\mathrm{v}$ operators among the point symmetry operators. It is convenient to attach subscripts or other labels to distinguish them from each other.

*Exercise 18.1

Find the coordinates of the points resulting from the operations:

a. $\hat{i}(1, 2, 3)$

b. $\hat{\sigma}_\mathrm{h}(4, -2, -2)$

c. $\hat{\sigma}_{\mathrm{v}yz}(7, -6, 3)$ where $\hat{\sigma}_{\mathrm{v}yz}$ is the reflection operator that reflects through the yz plane.

Rotation operators cause a point to move as it would if it were part of a rigid body rotating about a specified axis, which is the symmetry element. The point moves around a circle that is centered on the axis of rotation and perpendicular to it. By convention, all rotations are counterclockwise when viewed from the end of the rotation axis that is designated as the positive end. There are infinitely many lines that pass through the origin, and for each rotation axis there can be rotations by infinitely many different angles. We consider only rotation operators that produce a full rotation (360°) when applied an integral number of times. A rotation operator that produces one full rotation when applied n times is denoted by $\hat{C}_n$. It is convenient to add subscripts to denote the axis. For example, the $\hat{C}_{4z}$ operator rotates by 90° about the z axis, and its effect on a point at (x, y, z) is

$$\hat{C}_{4z}(x, y, z) = (x', y', z') = (-y, x, z) \tag{18.1-11}$$

Figure 18.5 shows the effect of the operators $\hat{i}$, $\hat{\sigma}_\mathrm{h}$, and $\hat{C}_{4z}$ on a point in the first octant.

*Exercise 18.2

Find the following locations:

a. $\hat{C}_{2x}(1, 2, 3)$ (the axis of rotation is the x axis).

b. $\hat{C}_{3y}(1, 1, 1)$ (the axis of rotation is the y axis).

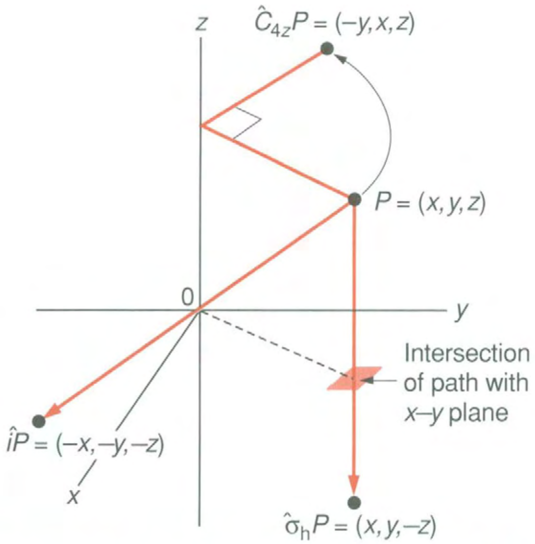

Figure 18.5 The Effect of the Symmetry Operators $\hat{i}$, $\hat{\sigma}_h$, and $\hat{C}_{4z}$. These mathematical operators move a point in three-dimensional space in ways defined in the text.

In addition to the above operators there is the **identity operator**, which does nothing. It is denoted by $\hat{E}$. The letter E is used because it is the first letter of the German word "Einheit," meaning "unity."

$$\hat{E}(x, y, z) = (x, y, z) \tag{18.1-12}$$

The Operation of Symmetry Operators on Functions

Ordinary mathematical operators operate on functions, not on isolated points. We define a mode of operation so that symmetry operators also operate on functions. Let $f(x, y, z)$ be some function of the coordinates x, y, and z, and let $\hat{O}$ be some symmetry operator that carries a point at (x, y, z) to a location (x', y', z'):

$$\hat{O}(x, y, z) = (x', y', z') \tag{18.1-13}$$

When the operator $\hat{O}$ operates on the function f it produces a new function g, defined to be the function that has the same value at the location (x', y', z') that the function f has at the location (x, y, z). If

$$\hat{O}f(x, y, z) = g(x, y, z) \tag{18.1-14}$$

then

$$g(x', y', z') = f(x, y, z) \tag{18.1-15}$$

A function can be an eigenfunction of a symmetry operator. The only eigenvalues that occur are $+1$ and -1.

EXAMPLE 18.1

Show that the hydrogenlike $1s$ orbital is an eigenfunction of the inversion operator $\hat{i}$. Find the eigenvalue.

Solution

$$\psi_{1s} = \sqrt{\frac{1}{\pi}}\left(\frac{Z}{a}\right)^{3/2} e^{-Zr/a}$$

where Z is the number of protons in the nucleus, a is the Bohr radius, and r is the distance from the nucleus:

$$r = (x^2 + y^2 + z^2)^{1/2}$$

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

$$\hat{i}\psi_{1s} = \psi_{1s}$$

The ψ_{1s} function is an eigenfunction of the inversion operator with eigenvalue 1.

Exercise 18.3

***a.** Determine the spherical polar coordinates of $\hat{i}P$ and $\hat{\sigma}_h P$ if P represents a point whose location is (r, θ, ϕ).

b. Show that the ψ_{2p_z} hydrogenlike orbital is an eigenfunction of the $\hat{\sigma}_h$ operator with eigenvalue -1.

The equilibrium nuclear conformations of many molecules are symmetrical. Our first use of symmetry operators is to apply them to the nuclei of a molecule in their equilibrium conformation. Our second use is to apply them to the electrons of the molecule or to an orbital function, leaving the nuclei fixed in their equilibrium positions. If a symmetry operator moves every nucleus to a location previously occupied by a nucleus of the same kind (same isotope of the same element) it belongs to the molecule. A symmetry operator that belongs to the molecule will not change the value of the potential energy when it is applied to the electrons with the nuclei fixed. It will bring every electron to a point in which it either is at the same distance from each nucleus as it was in its original position or is at the same distance from a different nucleus of the same kind. The operation of the inversion operator on the electron of an H_2^+ molecule ion is illustrated in Figure 18.6. This motion brings the electron to the same distance from nucleus A as it originally was from nucleus B and vice versa, and thus does not change the potential energy. Any symmetry operator that belongs to a molecule will not change the potential energy when it is applied to its electrons and will commute with the Born–Oppenheimer electronic Hamiltonian operator of that molecule.

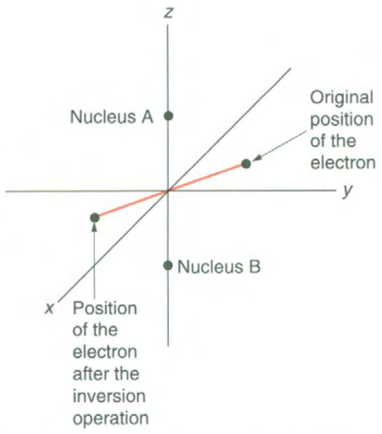

Figure 18.6 The Effect of the Symmetry Operator $\hat{i}$ on the electron of the H_2^+ Ion. This symmetry operator moves the electron so that its distance from nucleus B is the same as its original distance from nucleus A.

Exercise 18.4

Show that the symmetry operators $\hat{i}$, $\hat{\sigma}_h$, $\hat{C}_{nz}$, and $\hat{C}_{2a}$ belong to the H_2^+ molecule, where n is any positive integer and where a stands for any axis in the x–y plane. Show also that if these operators are applied to the electron position with fixed nuclei, the potential energy is unchanged.

A symmetry operator can operate on electronic wave functions as defined in Eq. (18.1-15), and electronic wave functions can be eigenfunctions of symmetry operators that commute with the electronic Hamiltonian operator. The ground-state electronic orbital of H_2^+ is an eigenfunction of each of the symmetry operators in Exercise 18.4, and each eigenvalue is equal to $+1$. The orbital of the first excited state is also an eigenfunction of these operators, but the eigenvalues of $\hat{i}$, $\hat{\sigma}_h$, and $\hat{C}_{2a}$ are equal to -1. An eigenfunction having an eigenvalue of $\hat{i}$ equal to $+1$ is denoted by a subscript g (from the German *gerade*, meaning "even") and an eigenvalue of $\hat{i}$ equal to -1 is denoted by a subscript u (from the German *ungerade*, meaning "odd"). An eigenvalue of $\hat{\sigma}_h$ 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 $\hat{\sigma}_h$ equal to $+1$, corresponding to a bonding orbital. The sigma orbitals are generally numbered from the lowest to the highest orbital energy, so the ground-state orbital of the hydrogen molecule ion is denoted by $\psi_{1\sigma_g}$ and the first excited state is denoted by $\psi_{2\sigma_u^*}$.

18.2 LCAO-MOs—Molecular Orbitals That Are Linear Combinations of Atomic Orbitals

The exact Born–Oppenheimer solutions to the Schrödinger equation for the hydrogen molecule ion 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. We define **molecular orbitals that are linear combinations of atomic orbitals**, abbreviated LCAO-MO. If $f_1, f_2, f_3, \ldots$ are a set of functions, then g is called a **linear combination** of these functions if it equals a sum of these functions times constant coefficients:

$$g = c_1 f_1 + c_2 f_2 + c_3 f_3 + \cdots \tag{18.2-1}$$

We say that the function g is **expanded** in terms of the set of **basis functions** $f_1, f_2, \ldots$. The coefficients $c_1, c_2, \ldots$ are called **expansion coefficients**. If the linear combination can be an exact representation of an arbitrary function obeying the same boundary conditions as the basis set, the basis set is said to be a **complete set**. In Chapter 15 we introduced the assumption that the set of all eigenfunctions of a hermitian operator is a complete set for expansion of any function obeying the same boundary conditions as the eigenfunctions. We will not attempt to use a complete set of functions for our LCAO-MOs, but will begin with a basis set consisting of two atomic orbitals centered on two different nuclei.

LCAO-MOs for the First Two States of the H_2^+ Molecule Ion

We seek LCAO-MO representations for the $\psi_{1\sigma_g}$ and $\psi_{2\sigma_u^*}$ molecular orbitals. 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. We take two hydrogenlike orbitals as our first basis set: one with r_A as its independent variable and one with r_B as its independent variable. We use the abbreviations:

$$\psi_{1sA} = \psi_{1s}(r_A) \tag{18.2-2a}$$

$$\psi_{1sB} = \psi_{1s}(r_B) \tag{18.2-2b}$$

The orbital ψ_{1sA} has its orbital region centered at location A and the orbital ψ_{1sB} has its orbital region centered at location B. We now form molecular orbitals that are linear combinations of the basis functions:

$$\psi_{\mathrm{MO}} = c_{\mathrm{A}}\psi_{1s\mathrm{A}} + c_{\mathrm{B}}\psi_{1s\mathrm{B}} \tag{18.2-3}$$

The number of possible independent linear combinations is always equal to the number of independent basis functions. We have two basis functions so it is possible to make two independent linear combinations. We seek two molecular orbitals that are approximations to the ground state orbital and the first excited state orbital of the $H_2{}^+$ ion.

There are at least two ways to find the appropriate values of c_{A} and c_{B} for the ground state. One procedure is to regard ψ_{MO} as a variational trial function and to minimize the variational energy as a function of c_{A} and c_{B}. We do not present this calculation, but the result is that the variational energy is minimized when $c_{\mathrm{A}} = c_{\mathrm{B}}$. An approximation to the first excited state is obtained when the energy has its maximum value, and this corresponds to $c = -c_{\mathrm{B}}$.[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 ground-state exact Born–Oppenheimer orbital is an eigenfunction of the inversion operator with eigenvalue +1. In order to obtain an LCAO-MO with this eigenvalue, we choose

$$c_{\mathrm{A}} = c_{\mathrm{B}} \tag{18.2-4}$$

Since the origin is midway between the two nuclei, inversion from any point leads to a point that is the same distance from nucleus B that the original point was from nucleus A and vice versa. If $c_{\mathrm{A}} = c_{\mathrm{B}}$ each term in the linear combination becomes equal to the original value of the other term, so that the molecular orbital is an eigenfunction of the inversion operator with eigenvalue 1 if $c_{\mathrm{A}} = c_{\mathrm{B}}$.

In order to obtain a molecular orbital with the same symmetry properties as the exact Born–Oppenheimer orbital of the first excited state, we must choose

$$c_{\mathrm{A}} = -c_{\mathrm{B}} \tag{18.2-5}$$

The symmetry properties are sufficiently fundamental that choosing the molecular orbitals to be their eigenfunctions leads to the same LCAO-MOs as the variation procedure. These LCAO-MOs are eigenfunctions of the other symmetry operators that belong to the $H_2{}^+$ molecule.

Exercise 18.5

a. Argue that $c_{\mathrm{A}} = c_{\mathrm{B}}$ leads to an eigenvalue of +1 for the $\hat{\sigma}_{\mathrm{h}}$ operator and for the $\hat{C}_{2a}$ operator, where $\hat{C}_{2a}$ is a rotation operator whose symmetry element lies somewhere in the x–y plane.
b. Argue that $c_{\mathrm{A}} = -c_{\mathrm{B}}$ leads to an eigenvalue of −1 for the $\hat{\sigma}_{\mathrm{h}}$ operator and for the $\hat{C}_{2a}$ operator.

We introduce the symbols for our two LCAO-MOs:

$$\psi_{\sigma_{\mathrm{g}}1s} = C_{\mathrm{g}}[\psi_{1s\mathrm{A}} + \psi_{1s\mathrm{B}}] \tag{18.2-6}$$

$$\psi_{\sigma_{\mathrm{u}}^{*}1s} = C_{\mathrm{u}}[\psi_{1s\mathrm{A}} - \psi_{1s\mathrm{B}}] \tag{18.2-7}$$

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[3] J. C. Davis, Jr., *Advanced Physical Chemistry*, The Ronald Press, New York, 1965, p. 404.

where the $1s$ subscripts indicate the atomic orbitals from which the LCAO-MOs were constructed. The value of the constants C_{g} and C_{u} can be chosen to normalize the molecular orbitals.

Figure 18.7 schematically shows the orbital regions for the $\sigma_{\mathrm{g}}1s\ LCAO-MO$ and the $\sigma_{\mathrm{u}}^{*}1s$ LCAO-MO, as well as the orbital regions for the $1s$ atomic orbitals. The intersection of the two atomic orbital regions is called the **overlap region**. This is the only region where both atomic orbitals differ significantly from zero. For the $\sigma_{\mathrm{g}}1s$ orbital the two atomic orbitals combine with the same sign in the overlap region, producing an orbital region characteristic of a bonding orbital with no nodal surfaces. For the $\sigma_{\mathrm{u}}^{*}1s$ orbital the atomic orbitals combine with opposite signs in the overlap region, canceling to produce a nodal surface between the nuclei, characteristic of an antibonding orbital. This addition and cancellation are similar to constructive and destructive interference of waves, but should not be interpreted as actual interference.

Figure 18.8 shows the electronic energy for each of these LCAO molecular orbitals along with the exact Born–Oppenheimer energies. The value of D_{e} for the $\sigma_{\mathrm{g}}1s$ orbital is equal to 1.76 eV, with a value of R_{e} equal to 1.32×10^{-10} m. As we expect from the variational theorem, the approximate energies lie above the exact energies for all values of R. The energies can be improved by "scaling" the atomic orbitals: that is, by replacing the atomic number Z in the orbital exponent by a variable parameter.

LCAO-MOs can be constructed that are linear combinations of more than two atomic orbitals. For example, for the ground state of the hydrogen molecule ion, we could write

$$\begin{aligned}\psi_{\mathrm{MO}} = {}& c_{1s\mathrm{A}}\psi_{1s\mathrm{A}} + c_{1s\mathrm{B}}\psi_{1s\mathrm{B}} + c_{2s\mathrm{A}}\psi_{2s\mathrm{A}} \\ & + c_{2s\mathrm{B}}\psi_{2s\mathrm{B}} + c_{2p_z\mathrm{A}}\psi_{2p_z\mathrm{A}} + c_{2p_z\mathrm{B}}\psi_{2p_z\mathrm{B}}\end{aligned} \tag{18.2-8}$$

When the variational energy is minimized with respect to the c coefficients, a better (lower) value is obtained than with the $\sigma_{\mathrm{g}}1s$ orbital. However, we will use linear combinations of only two atomic orbitals as much as possible, since we will content ourselves with qualitative description rather than quantitative calculation. The $2p_x$ and $2p_y$ atomic orbitals are not included in Eq. (18.2-8) because they have different

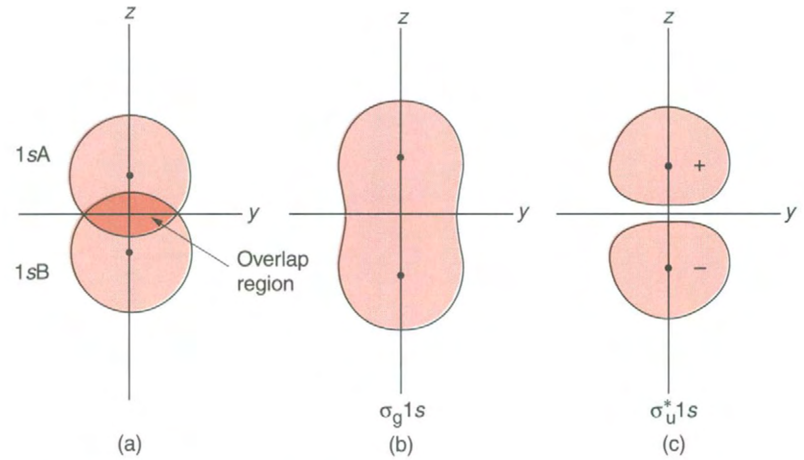

Figure 18.7 The Orbital Region for the $\sigma_{\mathrm{g}}1s$ and $\sigma_{\mathrm{u}}^{*}1s$ LCAO Molecular Orbitals. (a) The overlapping orbital regions of the $1s$A and $1s$B atomic orbitals. (b) The orbital region of the $\sigma_{\mathrm{g}}1s$ LCAO-MO. (c) The orbital Region of the $\sigma_{\mathrm{u}}^{*}1s$ LCAO-MO. The orbital regions of the LCAO molecular orbitals have the same general features as the "exact" Born Oppenheimer orbitals whose orbital regions were depicted in Figure 18.4.

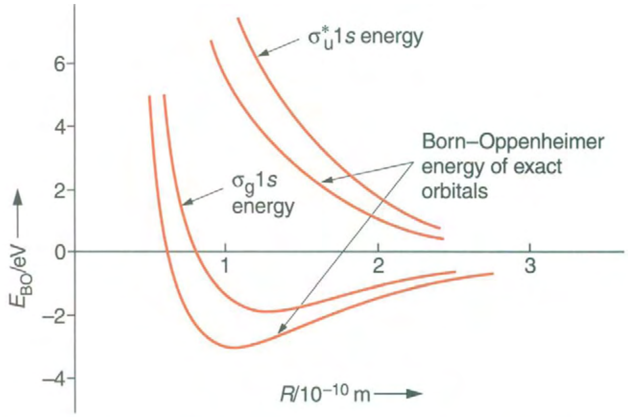

Figure 18.8 The Orbital Energies for the $\sigma_g 1s$ and $\sigma_u^* 1s$ LCAO Molecular Orbitals. This diagram shows qualitatively how the Born–Oppenheimer energies of the LCAO molecular orbitals compare with the Born Oppenheimer energies of the "exact" orbitals. The approximate orbital energies must lie above the corresponding exact energies for all internuclear distances.

symmetry about the bond axis than does the exact ground-state orbital. If they were included with nonzero coefficients, the LCAO-MO would not be an eigenfunction of the same symmetry operators as the exact orbitals.

Exercise 18.6

Argue that the $2p_x$ and $2p_y$ atomic orbitals are eigenfunctions of the $\hat{C}_{2z}$ 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 $\hat{C}_{2z}$ operator.

LCAO-MOs for Additional Excited States of $H_2{}^+$

The wave functions for additional excited states of $H_2{}^+$ are approximated by LCAO-MOs using higher-energy hydrogenlike orbitals. For example, two linear combinations of $2s$ orbitals that are eigenfunctions of the appropriate symmetry operators are

$$\psi_{\sigma_g 2s} = C_g[\psi_{2s}(r_A) + \psi_{2s}(r_B)] = C_g[\psi_{2sA} + \psi_{2sB}] \tag{18.2-9}$$

$$\psi_{\sigma_u^* 2s} = C_u[\psi_{2s}(r_A) - \psi_{2s}(r_B)] = C_u[\psi_{2sA} - \psi_{2sB}] \tag{18.2-10}$$

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 molecule dissociates from the $\sigma_g 2s$ state to a hydrogen nucleus and a hydrogen atom in the $2s$ state, as shown schematically in Figure 18.9.

Exercise 18.7

Draw sketches of the orbital regions for the functions in Eq. (18.2-9) and (18.2-10). Argue that the designations σ_g and σ_u^* are correct.

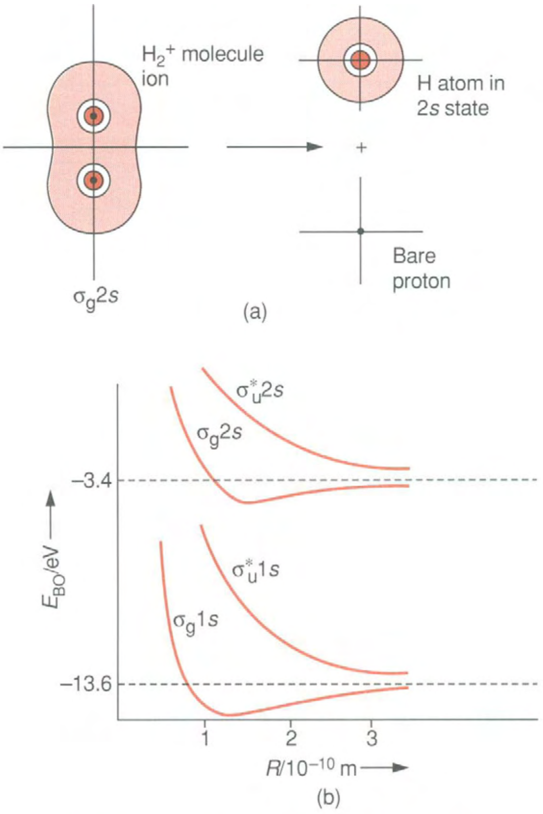

Figure 18.9 Dissociation of a Hydrogen Molecule Ion in the $\sigma_g 1s$ and $\sigma_g 2s$ States. (a) The orbital regions before and after dissociation. (b) The energy levels of the LCAO molecular orbitals as a function of internuclear distance. If a molecule in the $\sigma_g 2s$ state dissociates, an atom in a 2*s* state and a bare nucleus result. A molecule in the $\sigma_g 1s$ state dissociates to form an atom in the 1*s* state and a bare nucleus.

Normalization of the LCAO-MOs

To normalize the $\sigma_{\mathrm{g}}1s$ orbital we write

$$1 = |C_{\mathrm{g}}|^2 \int (\psi_{\mathrm{A}} + \psi_{\mathrm{B}})^*(\psi_{\mathrm{A}} + \psi_{\mathrm{B}})\, d^3\mathbf{r} \qquad (18.2\text{-}11)$$

where we abbreviate the 1*s*A and 1*s*B subscripts by A and B. The 1*s* atomic orbitals are real functions, so the complex conjugate symbol can be omitted. We will choose the normalization constant C_{g} to be real so that

$$1 = C_{\mathrm{g}}^2 \int (\psi_{\mathrm{A}}^2 + 2\psi_{\mathrm{A}}\psi_{\mathrm{B}} + \psi_{\mathrm{B}}^2)\, d^3\mathbf{r} \qquad (18.2\text{-}12)$$

The atomic orbitals ψ_{A} and ψ_{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:

$$\int \psi_{\mathrm{A}}\psi_{\mathrm{B}}\, d^3\mathbf{r} = S \qquad (18.2\text{-}13)$$

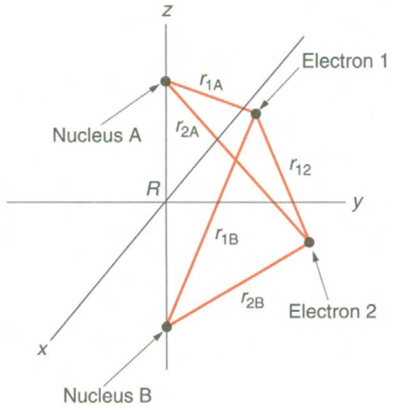

Figure 18.10 The Hydrogen Molecule System. This system is analogous to the helium in having two electrons. Our treatment of it is similar to the treatment of the helium atom, except for using molecular orbitals instead of atomic orbitals.

The integral S is called the **overlap integral** because the major contribution to its integrand comes from the overlap region. In other regions at least one of the factors in the integrand is small. Since the $1s$ orbitals are positive everywhere the overlap integral for two $1s$ orbitals is positive. Its value depends on R, approaching zero if the two nuclei are very far apart and approaching unity when R approaches zero since it then approaches a normalization integral. Similar overlap integrals can be defined for other pairs of atomic orbitals, and it is convenient to attach two subscripts to the symbol S to indicate which two orbitals are involved. The overlap integral in Eq. (18.2-13) would be denoted as $S_{1s,1s}$. For any normalized atomic orbitals, the values of overlap integrals must lie between -1 and $+1$, and approach zero as R is made large. If we had an overlap integral between a $1s$ and a $2p_z$ orbital on different nuclei, it would approach zero as the nuclei approach each other, because it would approach an othogonality integral instead of a normalization integral.

We now have

$$1 = C_g^2(1 + 2S + 1) \tag{18.2-14}$$

so that the normalized LCAO-MO is

$$\psi_{\sigma_g 1s} = \frac{1}{\sqrt{2 + 2S}}(\psi_A + \psi_B) \tag{18.2-15}$$

Exercise 18.8

Show that the normalization constant for the $\sigma_u^* 1s$ LCAO-MO is

$$C_u = \frac{1}{\sqrt{2 - 2S}} \tag{18.2-16}$$

18.3

Homonuclear Diatomic Molecules

Homonuclear diatomic molecules have two nuclei of the same kind. We discuss the homonuclear diatomic molecules of the first and second rows of the periodic table, and will base our discussion on the $H_2{}^+$ molecular orbitals in much the same way as we based our discussion of multielectron atoms on the hydrogen atom atomic orbitals in Chapters 16 and 17.

The Hydrogen Molecule

Figure 18.10 shows the hydrogen molecule, consisting of two nuclei at locations A and B and two electrons at locations 1 and 2. With its two electrons the hydrogen molecule bears the same relationship to the hydrogen molecule ion that the helium atom does to the hydrogen atom, and our treatment of it resembles that of the helium atom. We apply the Born–Oppenheimer approximation, assuming the nuclei to be fixed on the z axis with the origin at their center of mass. The distances between the particles are labeled as shown in the figure. The Born–Oppenheimer Hamiltonian operator is

$$\begin{aligned}\hat{H}_{\mathrm{el}} &= -\frac{\hbar^2}{2m}(\nabla_1^2+\nabla_2^2)+\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{R}-\frac{1}{r_{1\mathrm{A}}}-\frac{1}{r_{1\mathrm{B}}}-\frac{1}{r_{2\mathrm{A}}}-\frac{1}{r_{2\mathrm{B}}}+\frac{1}{r_{12}}\right)\\ &= \hat{H}_{\mathrm{HMI}}(1)+\hat{H}_{\mathrm{HMI}}(2)+\frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{R}+\frac{1}{r_{12}}\right)\end{aligned} \tag{18.3-1}$$

where $\hat{H}_{\mathrm{HMI}}(1)$ and $\hat{H}_{\mathrm{HMI}}(2)$ are hydrogen–molecule–ion electronic Hamiltonian operators denoted by $\hat{H}_{\mathrm{el}}$ in Eq. (18.1-4). The nuclear repulsion term (proportional to $1/R$) is included because the HMI Hamiltonian operators do not contain this term. This term is a constant in the Born–Oppenheimer approximation, since R 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 total Born–Oppenheimer energy, as in Eq. (18.1-6).

The LCAO-MO Treatment of the Hydrogen Molecule

The final term in the Hamiltonian operator, representing interelectron repulsion, prevents separation of the equation into two one-electron equations. We neglect this term as we did in the zero-order helium atom treatment, obtaining the zero-order electronic Hamiltonian operator:

$$\hat{H}^{(0)} = \hat{H}_{\mathrm{HMI}}(1)+\hat{H}_{\mathrm{HMI}}(2) \tag{18.3-2}$$

This zero-order Hamiltonian leads to a separation of variables with a trial function that is a product of two hydrogen-molecule-ion orbitals:

$$\Psi^{(0)} = \psi_1(1)\psi_2(2) \tag{18.3-3}$$

The zero-order Born–Oppenheimer energy is a sum of two hydrogen-molecule-ion electronic energies plus $\mathscr{V}_{\mathrm{NN}}$.

$$E^{(0)} = E_{\mathrm{HMI}}(1)+E_{\mathrm{HMI}}(2)+\mathscr{V}_{\mathrm{nn}} = E_{\mathrm{HMI}}(1)+E_{\mathrm{HMI}}(2)+\frac{e^2}{4\pi\varepsilon_0 R} \tag{18.3-4}$$

We could use the exact Born–Oppenheimer $H_2{}^+$ orbitals in this wave function. However, the zero-order orbital approximation is crude enough that no appreciable further damage is done by using the LCAO-MO orbitals instead of the exact Born–Oppenheimer orbitals.

To find the ground-state wave function we apply the Aufbau principle, choosing the lowest-energy LCAO-MOs compatible with the Pauli exclusion principle. Including the spin factor, the antisymmetrized and normalized zero-ground state wave function is

$$\psi^{(0)} = \frac{1}{\sqrt{2}}\psi_{\sigma_g 1s}(1)\psi_{\sigma_g 1s}(2)[\alpha(1)\beta(2)-\beta(1)\alpha(2)] \tag{18.3-5}$$

Electron configurations are assigned in much the same way as with atoms. This function corresponds to the electron configuration $(\sigma_g 1s)^2$, with two electrons occupying the $\sigma_g 1s$ bonding molecular space orbital. We say that the hydrogen molecule has a **single covalent bond** with one pair of shared electrons.

When calculations are done, the zero-order wave function gives a dissociation energy $D_e = 2.65\,\mathrm{eV}$ and equilibrium internuclear distance $R_e = 0.84\times10^{-10}\,\mathrm{m} = 84\,\mathrm{pm}$, compared with the experimental values of 4.75 eV and 74.1 pm. More accurate

Table 18.1. Summary of Results on the Hydrogen Molecule

	D_e/eV	R_e/pm
Experimental values	4.75	74.1
Molecular Orbital Methods		
Simple LCAO-MO	2.65	84
Simple LCAO-MO, 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 coordinates	4.75	
Self-Consistent Field Methods		
Best Hartree–Fock	3.64	74

Data from Ira N. Levine, *Quantum Chemistry*, 4th ed., Prentice-Hall, Englewood Cliffs, N. J., 1991.

values can be obtained using the perturbation method, variation method, or self-consistent field method. A variation function with variable orbital exponents in the atomic orbitals in the LCAO-MO wave function gives $D_e = 3.49\,\text{eV}$ and $R_e = 73.2\,\text{pm}$ with an orbital exponent corresponding to an apparent nuclear charge of 1.197 protons. A Hartree–Fock–Roothaan calculation gives $D_e = 3.64\,\text{eV}$ and $R_e = 74\,\text{pm}$.[4] The Hartree–Fock orbitals can be the best possible orbitals (no error except for the correlation error). The correlation error is approximately equal to 1.11 eV, assuming that this Hartree–Fock–Roothaan calculation approximates the best Hartree–Fock calculation.

Just as with atoms, configuration interaction (abbreviated CI) can be used to improve our description. A CI wave function using the two electron configurations $(\sigma_g 1s)^2$ and $(\sigma_u^* 1s)^2$ is

$$\Psi_{\text{CI}} = C_{\text{CI}}[\psi_{\sigma_g 1s}(1)\psi_{\sigma_g 1s}(2) + c_u \psi_{\sigma_u^* 1s}(1)\psi_{\sigma_u^* 1s}(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)] \tag{18.3-6}$$

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 $D_e = 4.02\,\text{eV}$ and $R_e = 75\,\text{pm}$. The inclusion of a single additional electron configuration has thus removed about one-third of the correlation error.[5] Table 18.1 summarizes some of the numerical results of calculations on the ground state of the hydrogen molecule.

Excited states of the hydrogen molecule correspond to electron configurations other than $(\sigma_g 1s)^2$. Some of these states are not bound states. In the electron configuration

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[4] Ira N. Levine, *Quantum Chemistry*, 4th ed., Prentice-Hall, Englewood Cliffs, N. J., 1991, pp. 385 ff.

[5] Levine, *op. cit.*, pp 385 ff (Note 4).

$(\sigma_g 1s)(\sigma_u^* 1s)$ 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.

Term Symbols for Homonuclear Diatomic Molecules

As with atoms, term symbols are used to designate electronic energy levels of homonuclear diatomic molecules. In the atomic case the main part of the term symbol was determined by the magnitude of the orbital angular momentum: the letter S stood for $L = 0$, the letter P for $L = 1$, D for $L = 2$, etc. The energy eigenfunctions of diatomic molecules are not necessarily eigenfunctions of $\hat{L}^2$ since this operator does not commute with the electronic Hamiltonian operator. We say that L is not a good quantum number or sometimes that $\hat{L}^2$ is not a good quantum number (even though it is an operator and not a quantum number). However, $\hat{L}_z$ does commute with the electronic Hamiltonian operator, and an energy eigenfunction can be an eigenfunction of $\hat{L}_z$:

$$\hat{L}_z \Psi = \hbar M_L \Psi \tag{18.3-7}$$

where M_L is the same quantum number as in the atomic case. In the orbital approximation, M_L is equal to the algebraic sum of the values of m for each occupied orbital, just as with atoms. We define a nonnegative quantum number Λ, equal to $|M_L|$. The main part of the molecular term symbol is a capital Greek letter, assigned according to the value of Λ:

Value of Λ	Symbol
0	Σ
1	Π
2	Δ
3	Φ
etc.	

In the ground state of diatomic hydrogen, both of the electrons occupy sigma orbitals so that the value of M_L is zero as is the value of Λ. The ground state corresponds to a Σ (sigma) term.

Since the nonrelativistic electronic Hamiltonian operator contains no spin, all of the spin angular momentum operators commute with it, and the energy eigenfunctions can be eigenfunctions of $\hat{S}^2$ and $\hat{S}_z$. The quantum number for the eigenvalue of $\hat{S}^2$ is called S (as with atoms) and is equal to a nonnegative integer or half-integer. A left superscript equal to $2S + 1$ is used on the term symbol just as in the atomic case. There will often be several degenerate states with the same values of Λ and S. These states make up a term, and the term symbol applies to all of them. The ground state of the hydrogen molecule is nondegenerate and constitutes a ${}^1\Sigma$ (singlet sigma) term.

The energy eigenfunctions of homonuclear diatomic molecules can be chosen to be eigenfunctions of the symmetry operators belonging to the molecule in the same way as can the individual orbitals. 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 $\hat{\sigma}_v$ 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 excited electron configuration $(\sigma_g 1s)(\sigma_u^* 1s)$ can correspond to two different terms, with the spins either paired or unpaired. The eigenvalue of the inversion operator is −1 for both terms since one orbital is g and the other is u. One term is a triplet while the other is a singlet, and the term symbols for this configuration are $^1\Sigma_u^+$ and $^3\Sigma_u^+$.

The Valence Bond Method for the Hydrogen Molecule

Orbital wave functions are not the only type of approximate wave functions that have been used for molecules. In 1927 Hitler and London[6] introduced a type of approximate wave function for the ground state of the hydrogen molecule that is now called the **valence bond function**:

$$\Psi_{VB} = C[\psi_{1sA}(1)\psi_{1sB}(2) + \psi_{1sB}(1)\psi_{1sA}(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)] \qquad (18.3\text{-}8)$$

where C is a normalizing factor. 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. The two terms make a symmetric space factor, which must be multiplied by an antisymmetric spin factor.

When the valence bond function of Eq. (18.3-8) is used to calculate the variational energy, the values $D_e = 3.20\,\text{eV}$ and $R_e = 80\,\text{pm}$ are obtained. These values are in better agreement with experiment than the values obtained from the simple LCAO-MO wave function of Eq. (18.3-5). In order to compare the simple LCAO-MO wave function with the simple valance bond wave function, we express the molecular orbitals in the wave function of Eq. (18.3-5) in terms of atomic orbitals. The space factor in the simple LCAO-MO function of Eq. (18.3-5) is

$$\begin{aligned}\frac{1}{\sqrt{2}}\psi_{\sigma_g 1s}(1)\psi_{\sigma_g 1s}(2) &= C_g^2[\psi_{1sA}(1) + \psi_{1sB}(1)][\psi_{1sA}(2) + \psi_{1sB}(2)] \\ &= C_g^2[\psi_{1sA}(1)\psi_{1sA}(2) + \psi_{1sB}(1)\psi_{1sB}(2) \\ &\quad + \psi_{1sA}(1)\psi_{1sB}(2) + \psi_{1sB}(1)\psi_{1sA}(2)] \qquad (18.3\text{-}9)\end{aligned}$$

The last two terms on the right-hand-side of Eq. (18.3-9) 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** since one term has both electrons on nucleus A while the other has them on nucleus B. The simple LCAO-MO wave function gives the ionic terms equal weight with the covalent terms, while the simple valence-bond function omits them completely. It is apparent that it is better to omit them completely than to include them with the same weight as the covalent terms. It is even better to include the ionic terms with reduced weight. A modified valence-bond wave function is:

$$\Psi_{MVB} = c_{VB}\Psi_{VB} + c_I\Psi_I \qquad (18.3\text{-}10)$$

where c_{VB} and c_I are variable parameters and where Ψ_I contains the ionic terms:

$$\Psi_I = [\psi_{1sA}(1)\psi_{1sA}(2) + \psi_{1sB}(1)\psi_{1sB}(2)][\alpha(1)\beta(2) - \beta(1)\alpha(2)] \qquad (18.3\text{-}11)$$

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[6] W. Heitler and F. London, *Z. Physik*, **4**, 455 (1927).

When the coefficients c_{VB} and c_{I} are optimized, this wave function is identical to the optimized configuration-interaction function of Eq. (18.3-6). This fact enables us to understand why configuration interaction can introduce dynamical electron correlation. Combining the two configurations in Eq. (18.3-6) introduces some cancellation of parts of the wave function corresponding to electrons being close together, producing the same wave function as in Eq. (18.3-10), which includes some electron correlation because Ψ_{VB} contains only terms in which the electrons are on different atoms and are thus fairly far apart.

*Exercise 18.9

By expressing the function of Eq. (18.3-6) in terms of atomic orbitals, show that it can be made to be the same as the function of Eq. (18.3-10). Express the parameters c_{VB} and c_{I} in terms of C_{CI} and c_{u}.

The distinction between the valence bond method and the LCAO-MO method at least partially disappears when improvements are made to the simple functions. However, the valence bond method has become less popular than the molecular orbital method. One reason is that it is possible to make further improvements to the molecular orbital method by adding more configurations, while additional improvements beyond addition of ionic terms to the simple valence bond functions are more difficult to design.

Diatomic Helium

The zero-order Born–Oppenheimer Hamiltonian operator for diatomic helium consists of four hydrogen-molecule-ion-like (HMIL) Hamiltonian operators with $Z = 2$ (the interelectron repulsions and constant internuclear repulsion are omitted):

$$\hat{H}^{(0)} = \hat{H}_{\mathrm{HMIL}}(1) + \hat{H}_{\mathrm{HMIL}}(2) + \hat{H}_{\mathrm{HMIL}}(3) + \hat{H}_{\mathrm{HMIL}}(4) \qquad (18.3\text{-}12)$$

The constant nuclear repulsion term $\mathcal{V}_{\mathrm{nn}}$ will be omitted now, but must be added to the energy eigenvalue at the end of the calculation. This molecular Hamiltonian leads to separation of variables with a wave function that is a product of four hydrogen-molecule-ion-like orbitals. Including spin functions, the non-antisymmetrized zero-order LCAO-MO ground state wave function is

$$\Psi^{(0)} = \psi_{\sigma_{\mathrm{g}}1s}(1)\psi_{\sigma_{\mathrm{g}}1s}(2)\psi_{\sigma_{\mathrm{u}}^{*}1s}(3)\psi_{\sigma_{\mathrm{u}}^{*}1s}(4)\alpha(1)\beta(2)\alpha(3)\beta(4) \qquad (18.3\text{-}13)$$

This wave function can be antisymmetrized without vanishing.

Exercise 18.10

Antisymmetrize the function of Eq. (18.3-13) by writing it as a 4-by-4 Slater determinant.

The wave function of Eq. (18.3-13) corresponds to the electron configuration $(\sigma_{\mathrm{g}}1s)^2(\sigma_{\mathrm{u}}^{*}1s)^2$, with two electrons occupying bonding orbitals and two occupying antibonding orbitals. The repulsive effect of the antibonding orbitals roughly cancels the attractive effect of the bonding orbitals. The molecule does not exist in the ground state, but has been observed in excited states.

We define a **bond order**:

$$\text{Bond order} = \text{BO} = \tfrac{1}{2}(n_{\text{bonding}} - n_{\text{antibonding}}) \qquad (18.3\text{-}14)$$

where n_{bonding} is the number of electrons occupying bonding orbitals and $n_{\text{antibonding}}$ is the number of electrons occupying antibonding orbitals. The division by 2 makes the bond order conform to the traditional definition of a single bond as having a pair of shared electrons, a double bond as having two pairs, and so on. The bond order of the diatomic helium molecule in its ground state is 0.

Homonuclear Diatomic Molecules with More Than Four Electrons

For homonuclear diatomic molecules of elements with more than four electrons, we will require additional molecular orbitals beyond the $\sigma_g 1s$ and $\sigma_u^* 1s$ orbitals. We now construct a set of additional approximate LCAO-MOs, as follows: (1) each LCAO-MO is a combination of two atomic orbitals of the same type centered on each of two nuclei; (2) each LCAO-MO is an eigenfunction of the symmetry operators belonging to the homonuclear diatomic molecules. For a given element, we will use the atomic orbitals for that element, since these orbitals correspond to the appropriate number of protons in each nucleus.

From each pair of atomic orbitals, two independent LCAO molecular orbitals can be constructed. In one of them (a bonding orbital) the two atomic orbitals will add in the overlap region, and in the other (an antibonding orbital) the two atomic orbitals will cancel in the center of the overlap region. We have already created the $\sigma_g 2s$ and the $\sigma_u^* 2s$ orbitals from the $2s$ atomic orbitals in Eq. (18.2-9) and Eq. (18.2-10). The electron configuration of diatomic lithium in the ground state is

$$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2$$

and that of diatomic beryllium 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.

There are six $2p$ atomic space orbitals on two nuclei, and six LCAO molecular space orbitals can be constructed from them. We use the real atomic orbitals, ψ_{2p_x}, ψ_{2p_y}, and ψ_{2p_z}, in order to make the orbital regions more compact. In order to obtain eigenfunctions of the symmetry operators, the two $2p_z$ orbitals can be combined, the two $2p_x$ orbitals can be combined, and the two $2p_y$ orbitals can be combined. We obtain the LCAO-MOs:

$$\psi_{\sigma_g 2p_z} = C(\psi_{2p_z\text{A}} - \psi_{2p_z\text{B}}) \tag{18.3-15a}$$

$$\psi_{\sigma_u^* 2p_z} = C(\psi_{2p_z\text{A}} + \psi_{2p_z\text{B}}) \tag{18.3-15b}$$

$$\psi_{\pi_u 2p_x} = C(\psi_{2p_x\text{A}} + \psi_{2p_x\text{B}}) \tag{18.3-15c}$$

$$\psi_{\pi_g^* 2p_x} = C(\psi_{2p_x\text{A}} - \psi_{2p_x\text{B}}) \tag{18.3-15d}$$

$$\psi_{\pi_u 2p_y} = C(\psi_{2p_y\text{A}} + \psi_{2p_y\text{B}}) \tag{18.3-15e}$$

$$\psi_{\pi_g^* 2p_y} = C(\psi_{2p_y\text{A}} - \psi_{2p_y\text{B}}) \tag{18.3-15f}$$

where the normalizing constant C can have a different value in each case. If we want to determine molecular term symbols, we use the complex $2p$ atomic orbitals instead of the real $2p$ orbitals because they are eigenfunctions of the $\hat{L}_z$ operator.

Figure 18.11 shows the orbital regions of the atomic orbitals and the LCAO-MOs. The $2p_z$ atomic orbitals produce a sigma molecular orbital since they correspond to $m = 0$ (they are the same as 210 orbitals). A difference of the $2p_z$ atomic orbitals produces the bonding orbital, while a sum produces an antibonding orbital. This comes from the fact that the orbital function has different signs in the two lobes of the atomic orbital region so that the negative lobe of one $2p_z$ orbital region points toward the positive lobe of the other. Some authors reverse the sign of one orbital or reverse the direction of the z axis for one orbital in order to write a positive sign in the bonding

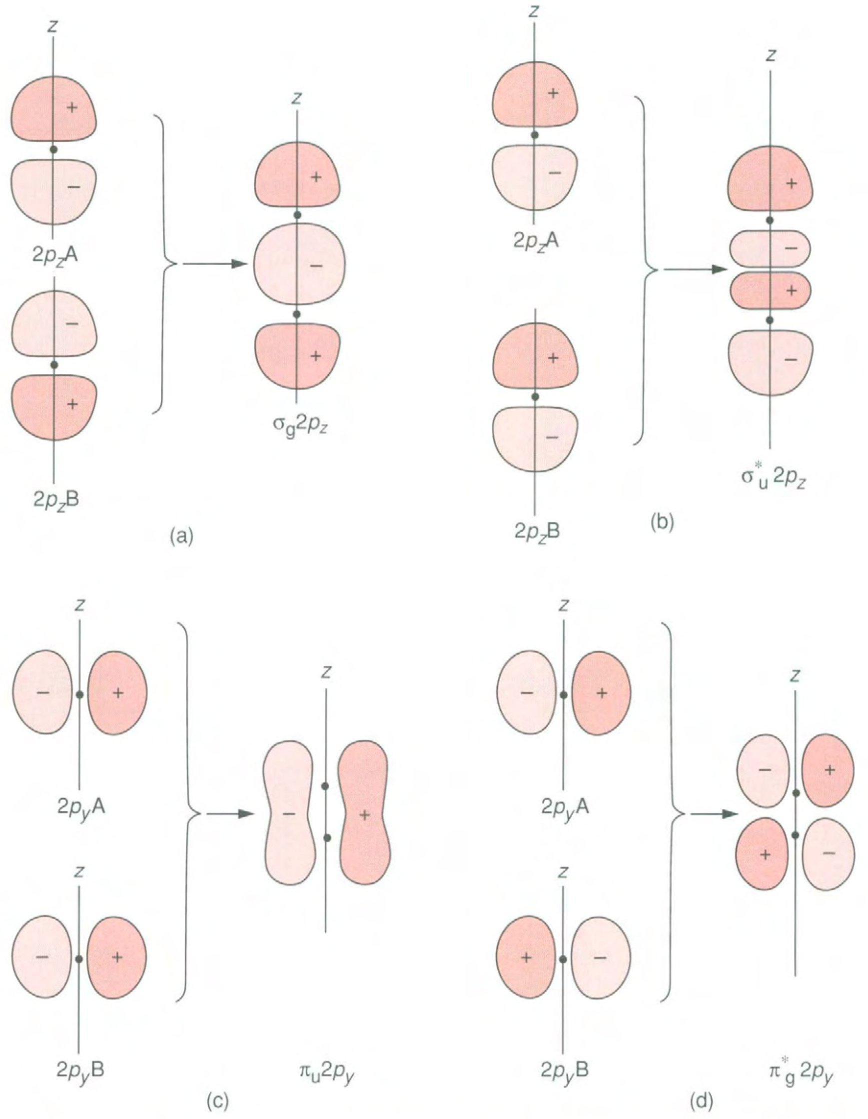

Figure 18.11 Orbital Regions for 2*p* Atomic Orbitals and LCAO Molecular Orbitals Made from Them. (a) **The $\sigma_g 2p_z$ LCAO-MO,** (b) **The $\sigma_u^* 2p_z$ LCAO-MO.** (c) **The $\pi_u 2p_y$ LCAO-MO.** (d) **The $\pi_g^* 2p_y$ LCAOMO.** This diagram shows how the orbital regions for bonding LCAOMOs arise from addition of atomic orbitals in the overlap regions and how the orbital regions for antibonding LCAOMO's arise from cancellation of atomic orbitals in the overlap regions.

orbital. The important thing is that the atomic orbitals must add and not cancel in the overlap region to make a bonding orbital.

The LCAO-MOs made from the $2p_x$ and $2p_y$ atomic orbitals are called π (pi) orbitals, even though they are not eigenfunctions of the $\hat{L}_z$ operator, because the $2p_x$ and $2p_y$ atomic orbitals are equivalent to linear combinations of the 211 and 21, -1 orbitals, which are eigenfunctions of the $\hat{L}_z$ operator. The bonding π orbitals are "u" instead of "g" because the two lobes of the $2p$ atomic orbitals have opposite signs, making the bonding orbitals eigenfunctions of the inversion operator with eigenvalue -1. If LCAO-MOs were constructed from the 211 and 21,-1 orbitals, the bonding orbitals would be designated as π_u211 (or π_u2pl) and $\pi_u21, -1$ and the antibonding orbitals would be designed as π_g^*211 and $\pi_g^*21, -1$.

Figure 18.12 shows a **correlation diagram**, in which the energies of the atomic orbitals and the simple LCAO molecular orbitals are shown schematically with line segments connecting the LCAO-MOs and the atomic orbitals from which they were constructed. From Figure 17.4 it is apparent that the atomic orbital energies depend on nuclear charges, so that the LCAO-MO energies also depend on nuclear charge as well as on internuclear distance. Although the $2p_x$, $2p_y$, and $2p_z$ atomic orbitals are at the same energy, the overlap for the $\sigma 2p$ LCAO-MOs is different from that of the $\pi 2p$ LCAO-MOs, and the $\sigma 2p$ energy is not equal to the $\pi_u 2p_x$ and $\pi_u 2p_y$ energies, although the $\pi_u 2p_x$ and $\pi_u 2p_y$ energies are equal to each other. The order of the LCAO-MO energies in the figure is correct for elements up 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. This difference in the relative energies of the $\sigma_g 2p_z$ orbital and the π_u orbitals is reasonable since in a sigma orbital the electron moves in a region more directly between the nuclei and would be

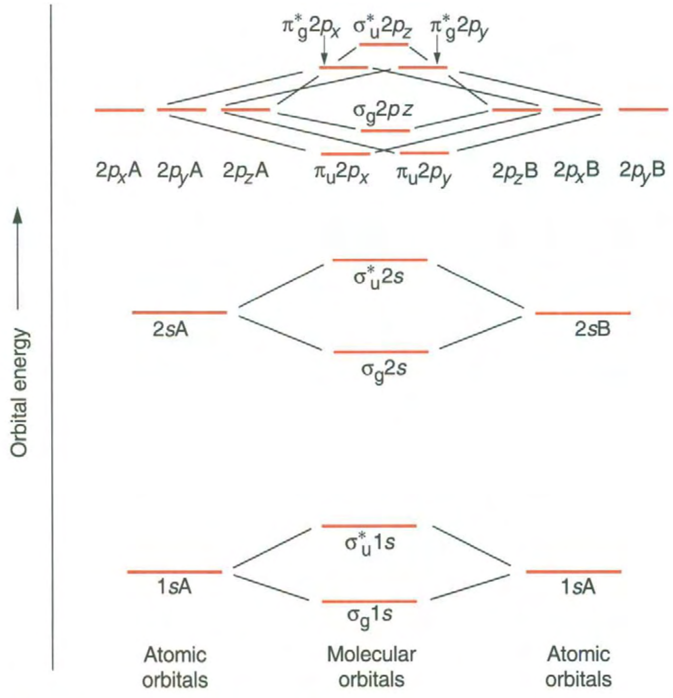

Figure 18.12 Correlation Diagram for Homonuclear Diatomic Molecules. This kind of diagram is an orbital energy level diagram in which the connections (correlations) between an LCAO-MO and the atomic orbitals making up the linear combination are displayed.

more effective in screening the nuclear charges from each other than in a π orbital. With the larger nuclear charges of the O and F atoms this screening is apparently more important than with the other atoms.

We can now write the ground-state electron configuration for all of the homonuclear diatomic molecules of elements of the first and second rows of the periodic chart, using the LCAO-MOs in Figure 18.12 and the Aufbau principle. These electron configurations are shown in Table 18.2. In boron and oxygen 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 to atoms. This agrees with the experimental fact that both diatomic boron and diatomic oxygen have triplet ground levels (two unpaired electrons). The detailed electron configurations in Table 18.2 convey all of the information conveyed by a non-antisymmetrized wave function. Two degenerate orbitals are analogous to a subshell and could be lumped together. The ground-state electron configuration of diatomic oxygen would then be written

$$(\sigma_{\mathrm{g}}1s)^2(\sigma_{\mathrm{u}}^*1s)^2(\sigma_{\mathrm{g}}2s)^2(\sigma_{\mathrm{u}}^*2s)^2(\sigma_{\mathrm{g}}2p)^2(\pi_{\mathrm{u}}2p)^4(\pi_{\mathrm{g}}^*2p)^2$$

This electron configuration does not explicitly show that the final two antibonding electrons occupy different orbitals.

EXAMPLE 18.2

Write an orbital wave function without antisymmetrization for the diatomic boron molecule in its ground level.

Solution

$$\begin{aligned}\Psi = {} & \psi_{\sigma_{\mathrm{g}}1s}(1)\alpha(1)\psi_{\sigma_{\mathrm{g}}1s}(2)\beta(2)\psi_{\sigma_{\mathrm{u}}^*1s}(3)\alpha(3)\psi_{\sigma_{\mathrm{u}}^*1s}(4)\beta(4)\\ & \times \psi_{\sigma_{\mathrm{g}}2s}(5)\alpha(5)\psi_{\sigma_{\mathrm{g}}2s}(6)\beta(6)\psi_{\sigma_{\mathrm{u}}^*2s}(7)\alpha(7)\psi_{\sigma_{\mathrm{u}}^*2s}(8)\beta(8)\\ & \times \psi_{\pi_{\mathrm{u}}2p_x}(9)\alpha(9)\psi_{\pi_{\mathrm{u}}2p_y}(10)\alpha(10)\end{aligned}$$

This wave function is one of the three triplet wave functions making up the ground level. Another has β spin functions instead of α for the final two factors, and a third would have the spin factor $\frac{1}{2}[\alpha(9)\beta(10) + \beta(9)\alpha(10)]$. There is also a singlet function corresponding to $\frac{1}{2}[\alpha(9)\beta(10) - \beta(9)\alpha(10)]$. (We have omitted a complete antisymmetrization.)

Table 18.2. Ground-State Electron Configurations of Diatomic Molecules

	Electron Configuration	Bond Order
H_2:	$(\sigma_{\mathrm{g}}1s)^2$	1
He_2:	$(\sigma_{\mathrm{g}}1s)^2(\sigma_{\mathrm{u}}^*1s)^2$	0
Li_2:	$(\sigma_{\mathrm{g}}1s)^2(\sigma_{\mathrm{u}}^*1s)^2(\sigma_{\mathrm{g}}2s)^2$	1
Be_2:	$(\sigma_{\mathrm{g}}1s)^2(\sigma_{\mathrm{u}}^*1s)^2(\sigma_{\mathrm{g}}2s)^2(\sigma_{\mathrm{u}}^*2s)^2$	0
B_2:	$(\sigma_{\mathrm{g}}1s)^2(\sigma_{\mathrm{u}}^*1s)^2(\sigma_{\mathrm{g}}2s)^2(\sigma_{\mathrm{u}}^*2s)^2(\pi_{\mathrm{u}}2p_x)(\pi_{\mathrm{u}}2p_y)$	1
C_2:	$(\sigma_{\mathrm{g}}1s)^2(\sigma_{\mathrm{u}}^*1s)^2(\sigma_{\mathrm{g}}2s)^2(\sigma_{\mathrm{u}}^*2s)^2(\pi_{\mathrm{u}}2p_x)(\pi_{\mathrm{u}}2p_y)^2$	2
N_2:	$(\sigma_{\mathrm{g}}1s)^2(\sigma_{\mathrm{u}}^*1s)^2(\sigma_{\mathrm{g}}2s)^2(\sigma_{\mathrm{u}}^*2s)^2(\pi_{\mathrm{u}}2p_x)(\pi_{\mathrm{u}}2p_y)^2(\sigma_{\mathrm{g}}2p_z)^2$	3
O_2:	$(\sigma_{\mathrm{g}}1s)^2(\sigma_{\mathrm{u}}^*1s)^2(\sigma_{\mathrm{g}}2s)^2(\sigma_{\mathrm{u}}^*2s)^2(\pi_{\mathrm{u}}2p_x)^2(\pi_{\mathrm{u}}2p_y)^2(\pi_{\mathrm{g}}^*2p_x)(\pi_{\mathrm{g}}^*2p_y)$	2
F_2:	$(\sigma_{\mathrm{g}}1s)^2(\sigma_{\mathrm{u}}^*1s)^2(\sigma_{\mathrm{g}}2s)^2(\sigma_{\mathrm{u}}^*2s)^2(\sigma_{\mathrm{g}}2p_z)^2(\pi_{\mathrm{u}}2p_x)^2(\pi_{\mathrm{u}}2p_y)^2(\pi_{\mathrm{g}}^*2p_x)^2(\pi_{\mathrm{g}}^*2p_y)^2$	1
Ne_2:	$(\sigma_{\mathrm{g}}1s)^2(\sigma_{\mathrm{u}}^*1s)^2(\sigma_{\mathrm{g}}2s)^2(\sigma_{\mathrm{u}}^*2s)^2(\sigma_{\mathrm{g}}2p_z)^2(\pi_{\mathrm{u}}2p_x)^2(\pi_{\mathrm{u}}p_y)^2(\pi_{\mathrm{g}}^*2p_x)^2(\pi_{\mathrm{g}}^*2p_y)^2(\sigma_{\mathrm{u}}^*2p_z)^2)$	0

Exercise 18.11

Write an orbital wave function without antisymmetrization 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 can be written for the ground states of homonuclear diatomic molecules from inspection of their electron configurations and use of Hund's first rule. For example, in the ground level of diatomic boron, the electron spins and orbital angular momentum projections occur in canceling pairs in the filled subshells. Only the electrons in the π orbitals make a contribution. By Hund's first rule, the two electrons occupy different space orbitals with unpaired spins. The orbital angular momentum projections cancel, making a triplet sigma term. The symmetry operators must be applied to all orbitals, and space orbitals occupied by two electrons are operated on once for each electron. The effect of operating twice always gives an eigenvalue of $+1$, so that we can ignore the orbitals occupied by two electrons. Both of the bonding π orbitals have eigenvalue -1 for the inversion operator, so their product has eigenvalue $+1$. A vertical mirror plane in the x–z will give eigenvalue $+1$ for the $\pi_u 2p_x$ orbital and eigenvalue -1 for the $\pi_u 2p_y$ orbital, so the term symbol is $^3\Sigma_g^-$. The eigenvalues would be reversed for a mirror plane in the y–z plane, but the result is the same when both orbitals are considered. The same vertical reflection plane must be used for all orbitals to determine whether the term is + or −.

An Alternative Set of Wave Functions

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 a pair of bonding and antibonding orbitals by the two atomic orbitals from which the LCAO-MOs were constructed. If this is done, electrons occupying atomic orbitals are counted as nonbonding and are omitted from bond order calculations.

EXAMPLE 18.3

Give the electron configuration for the ground state of diatomic carbon using nonbonding orbitals as much as possible.

Solution

The electron configuration is

$$(1sA)^2(1sB)^2(2sA)^2(2sB)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2.$$

The bond order is equal to 2, with four bonding electrons, no antibonding electrons, and eight nonbonding electrons.

Exercise 18.12

Using as many nonbonding orbitals as possible, give the ground-state electron configurations of diatomic boron and diatomic fluorine. Write the corresponding orbital wave function without antisymmetrization for each of these molecules.

Homonuclear Diatomic Molecules in the Valence Bond Approximation

For some homonuclear diatomic molecules satisfactory simple valence bond wave functions can be constructed. In this approximation two bonding electrons occupy a bonding factor constructed from two atomic orbitals on different nuclei, as in Eq. (18.3-8). We make maximum use of nonbonding orbitals since the valence bond theory has nothing analogous to antibonding orbitals. 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 18.4

Write a simple valence bond wave function for diatomic carbon in its ground state.

Solution

$$\begin{aligned}\Psi = {} & \psi_{1sA}(1)\alpha(1)\psi_{1sA}(2)\beta(2)\psi_{1sB}(3)\alpha(3)\psi_{1sB}(4)\beta(4) \\ & \times \psi_{2sA}(5)\alpha(5)\psi_{2sA}(6)\beta(6)\psi_{2sB}(7)\alpha(7)\psi_{2sB}(8)\beta(8) \\ & \times \sqrt{\frac{1}{2}}[\psi_{2p_xA}(9)\psi_{2p_xB}(10) + \psi_{2p_xB}(9)\psi_{2p_xA}(10)] \\ & \times [\alpha(9)\beta(10) - \beta(9)\alpha(10)] \\ & \times \sqrt{\frac{1}{2}}[\psi_{2p_yA}(11)\psi_{2p_yB}(12) + \psi_{2p_yB}(11)\psi_{2p_yA}(12)] \\ & \times [\alpha(11)\beta(12) - \beta(11)\alpha(12)] \end{aligned} \qquad (18.3\text{-}16)$$

A bonding factor corresponds to a single covalent bond so the bond order for diatomic carbon in the valence bond approximation is equal to 2, as in the LCAO-MO description. We have used bonding factors made with p orbitals to represent the double bond as two π bonds. The wave function in Example 18.4 is partially antisymmetrized, since the bonding factors and associated spin factors provide antisymmetrization between electrons 9 and 10 and also between electrons 11 and 12. If an improved valence bond wave function is desired, ionic terms can be added to the covalent terms in Eq. (18.3-16).

Exercise 18.13

a. Write a simple valence bond wave function for the ground state of diatomic fluorine.

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 LCAO-MO approximation by electron configurations other than the one arrived at using the Aufbau principle. Term symbols can be written for an excited electron configuration in much the same way as for the ground electron configuration.

Exercise 18.14

***a.** Write the term symbols that can occur for the diatomic beryllium electron configuration

$$(\sigma_g 1s)^2(\sigma_u^* 1s)^2(\sigma_g 2s)^2(\sigma_u^* 2s)(\sigma_u 2p).$$

***b.** Which term will have the lowest energy?
***c.** What is the bond order for this electron configuration?
d. Do you think the molecule could exist in this electron configuration?

18.4 Heteronuclear Diatomic Molecules

Heteronuclear diatomic molecules do not possess as high a degree of symmetry as homonuclear molecules, and we cannot evaluate coefficients in LCAO molecular orbitals by requiring that they have the proper symmetry. We illustrate the situation by an analysis of the simplest stable heteronuclear molecule, lithium hydride.

Lithium Hydride

Like the He_2 molecule, the LiH molecule has two nuclei and four electrons. We say that these molecules are **isoelectronic** (have the same number of electrons). Figure 18.13 shows the LiH system. The Born–Oppenheimer Hamiltonian operator for the LiH molecule in zero order (with the internuclear repulsion term omitted and the inter-electron repulsion term neglected) is

$$\hat{H}^{(0)} = \hat{H}_1(1) + \hat{H}_1(2) + \hat{H}_1(3) + \hat{H}_1(4) \tag{18.4-1}$$

where $\hat{H}_1(i)$ is the one-electron Hamiltonian operator for electron number i:

$$\hat{H}_1(i) = -\frac{\hbar^2}{2m}\nabla_i^2 + \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{r_{i\mathrm{H}}} + \frac{3}{r_{i\mathrm{Li}}}\right) \qquad (i = 1, 2, 3, 4) \tag{18.4-2}$$

Here $R_{i\mathrm{H}}$ is the distance from the hydrogen nucleus to electron number i and $r_{i\mathrm{Li}}$ is the distance from the lithium nucleus to electron number i. $\hat{H}_1$ is not a hydrogen-molecule-ion-like operator because the two nuclear charges are different. The zero-order Hamiltonian operator of Eq. (18.4-1) gives a Schrödinger equation in which the variables can be separated by assuming the wave function:

$$\Psi^{(0)} = \psi_1(1)\psi_2(2)\psi_3(3)\psi_4(4) \tag{18.4-3}$$

where each factor is a molecular orbital.

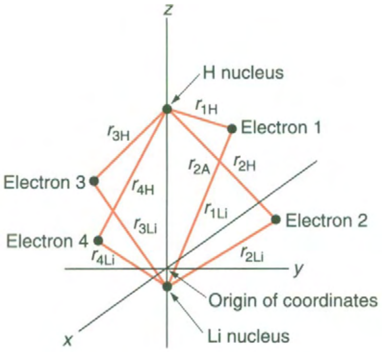

Figure 18.13. The LiH System. This system has two nuclei of different elements, and four electrons. The origin of coordinates is placed at the center of mass. The system is less symmetrical than a homonuclear diatomic molecule.

We seek LCAO representations of the molecular orbitals in Eq. (18.4-3). We take a basis set consisting of four space orbitals: the lithium $1s$, lithium $2s$, lithium $2p_z$, and hydrogen $1s$ atomic orbitals. This basis set is a **minimal basis set**, containing as few atomic orbitals as possible. These orbitals all have cylindrical symmetry about the bond axis (the z axis). This means that they are eigenfunctions with eigenvalue 1 of all rotation operators having the z axis as the symmetry element. The basis orbitals all correspond to $m = 0$. Any linear combination of them will be an eigenfunction of the symmetry operators that commute with the Hamiltonian operator and will be a σ orbital. The $2p_x$ and $2p_y$ lithium orbitals are not included in the basis set because they have different symmetry about the bond axis and do not correspond to the same value for the quantum number m as the other orbitals. The symmetry operators belonging to the molecule are all of the rotation operators about the bond axis and all of the $\hat{\sigma}_v$ operators. Our LCAO molecular orbitals can be eigenfunctions of these operators but would not be if the $2p_x$ and $2p_y$ orbitals were included.

Four independent LCAO-MOs can be made from our basis set of four orbitals:

$$\psi_{j\sigma} = c_{1s\mathrm{Li}}^{(j)}\psi_{1s\mathrm{Li}} + c_{2s\mathrm{Li}}^{(j)}\psi_{2s\mathrm{Li}} + c_{2p_z\mathrm{Li}}^{(j)}\psi_{2p_z\mathrm{Li}} + c_{1s\mathrm{H}}^{(j)}\psi_{1s\mathrm{H}} \qquad (j = 1, 2, 3, 4) \qquad (18.4\text{-}4)$$

The molecular orbitals are generally numbered from lowest to highest energy. We have added a σ subscript to indicate that all of these orbitals are σ orbitals. An additional subscript is added to the atomic orbitals and to the coefficients to show which atom the atomic orbital is taken from. Optimum values of the coefficients in the LCAO molecular orbitals can be obtained by the variation method or by the Hartree–Fock–Roothaan method.[7] Table 18.3 shows the results of a Hartree–Fock–Roothaan procedure for the four LCAO-MOs, and Figure 18.14 is a correlation diagram showing schematically the atomic and molecular orbital energies. By the Aufbau principle, the ground-state wave function is (without antisymmetrization)

$$\Psi_{g\sigma} = \psi_{1\sigma}(1)\alpha(1)\psi_{1\sigma}(2)\beta(2)\psi_{2\sigma}(3)\alpha(3)\psi_{2\sigma}(4)\beta(4) \qquad (18.4\text{-}5)$$

Let us now construct an approximate wave function that is qualitatively the same as that of Eq. (18.4-5) but contains simpler linear combinations. The 1σ LCAO-MO is almost exactly the same as the $1s$ lithium orbital, so we replace this LCAO-MO by the $1s$ lithium orbital, a nonbonding orbital. We now find a way to include no more than two atomic orbitals in each linear combination by changing our basis functions.

Hybrid Orbitals

The coefficients of the $2s$ lithium and $2p_z$ lithium orbitals in the 2σ LCAO-MO are roughly the same magnitude. This fact suggests a way to go back to our previous policy of including no more than two atomic orbitals in our LCAO-MOs. We define a **hybrid atomic orbital**:

$$\psi_{2sp,1} = N_1(-\psi_{2s} + \psi_{2p_z}) \qquad (18.4\text{-}6)$$

where N_1 is a normalizing constant. The designation $2sp$ is used because the new atomic orbital is a linear combination of the $2s$ and a $2p$ orbital, and the 1 suffix indicates that this is the first orbital of this type. There is another independent $2sp$ hybrid orbital that is orthogonal to the first $2sp$ hybrid orbital:

$$\psi_{2sp2} = N_2(-\psi_{2s} - \psi_{2p_z}) \qquad (18.4\text{-}7)$$

Table 18.3. 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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[7] C. C. J. Roothaan, *Rev. Mod. Phys.*, **23**, 69 (1951).

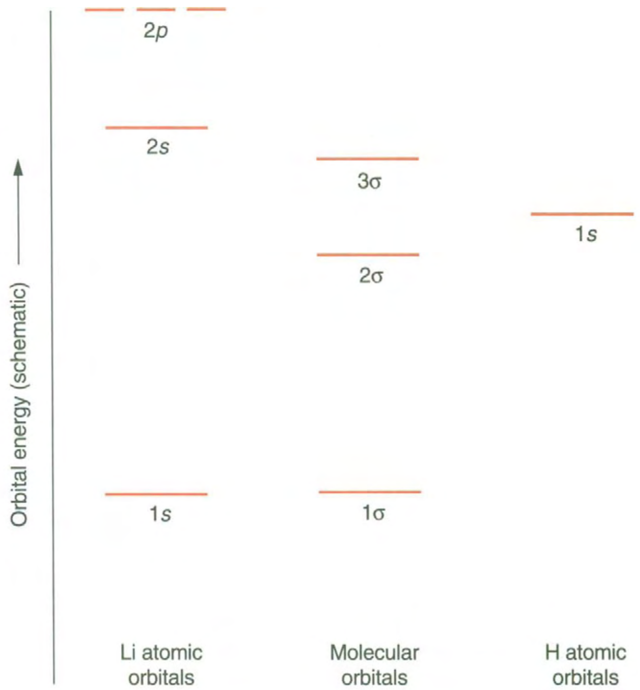

Figure 18.14. Correlation Diagram for the Lithium Hydride Molecule. Three molecular orbitals are shown. Only two of them are occupied in the ground state. The 1σ molecular orbital is essentially nonbonding, and the 2σ molecular orbital is essentially bonding. The molecule has a single bond, in contrast with the He_2 molecule, which has the same number of electrons, but has bond order zero.

Exercise 18.15

a. Using the fact that the $2s$ and $2p_z$ orbitals are normalized and orthogonal to each other, show that N_1 and N_2 both equal $\sqrt{1/2}$ if the hybrid orbitals are normalized.

b. Show that the $2sp,1$ and $2sp,2$ orbitals are orthogonal to each other.

Figure 18.15 shows cross sections of the orbital regions of the $2s$ and $2p_z$ orbitals and of the $2sp,1$ and $2sp,2$ hybrid orbitals. The $2s$ orbital function is negative in the outer part of its orbital region. 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. The orbital regions of the hybrid orbitals are therefore "directional," meaning that the orbital region extends farther in one direction than in other directions. 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 LCAO-MOs as linear combinations of no more than two atomic orbitals:

$$\psi_{1\sigma} = \psi_{1s\mathrm{Li}} \tag{18.4-8a}$$

$$\psi_{2\sigma} = c_{2sp,1\mathrm{Li}}\psi_{2sp,1\mathrm{Li}} + c_{1s\mathrm{H}}\psi_{1s\mathrm{H}} \approx -0.47\psi_{2sp,1\mathrm{Li}} - 0.88\psi_{1s\mathrm{H}} \tag{18.4-8b}$$

where we completely omit the $1s$Li orbital from the 2σ molecular orbital. In the second expression for the 2σ orbital the values of the coefficients were chosen to maintain

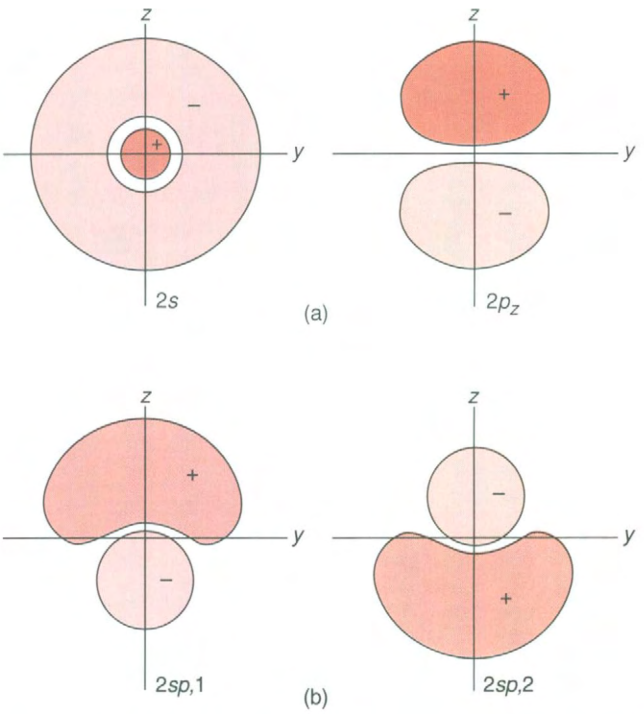

Figure 18.15. Orbital Regions for Nonhybridized and Hybridized Atomic Orbitals. (a) **The nonhybridized orbital regions.** (b) **The hybridized orbital regions.** This figure shows that the hybrid orbitals that are formed from one 2*s* atomic orbital and one 2*p* atomic orbital are directional. That is, each hybrid orbital has a lobe that extends farther from the nucleus and can give a larger overlap region. These two orbitals have directions that are 180° from each other.

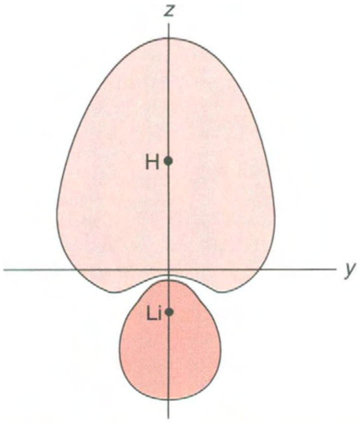

Figure 18.16. Cross Section of the Orbital Region of the Bonding LiH Orbital Made with a Hybrid Lithium Orbital (Schematic). This diagram shows that the LCAO-MO has the typical bonding-orbital properties: it has an appreciable magnitude between the nuclei, and it can be seen by inspection that it is made up from atomic orbitals that have the same symmetry about the bond axis.

approximately the same relative weights of the atomic orbitals as in the Hartree–Fock–Roothaan orbital. Figure 18.16 shows schematically the orbital region of the 2σ LCAO-MO and shows that it is a bonding orbital. Occupying the nonbonding 1σ space orbital with two electrons and the bonding 2σ space orbital with two electrons gives a bond order of 1 for lithium hydride.

The 3σ molecular orbital has roughly equal coefficients for the 2*s* and 2*p* atomic orbitals and can be approximated as a linear combination of the 2*sp*,2 hybrid orbital and the hydrogen 1*s* orbital. The 4σ orbital can also be represented in this way. 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.

*Exercise 18.16

a. Estimate the coefficients to represent approximately the 3σ molecular orbital as a linear combination of the 2*sp*,2Li hybrid orbital and the 1*s*H orbital. Is this 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 2*sp*,1Li hybrid orbital and the 1*s*H orbital. Is this molecular orbital a bonding, an antibonding, or a nonbonding orbital?

Dipole Moments

In the 2σ LCAO-MO 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 lithium nucleus if it occupies this space orbital. The shared electrons are not equally shared and we call this kind of chemical bond a **polar covalent bond**. The ends of the molecule possess net charges, giving the molecule a **dipole moment**. The dipole moment of a collection of n charges at fixed positions is a vector defined by

$$\boldsymbol{\mu} = \sum_{i=1}^{n} Q_i \mathbf{r}_i \tag{18.4-9}$$

where Q_i is the value of charge number i and $\mathbf{r}_i$ is its position vector. This definition applies only if the sum of the charges equals zero. The dipole moment of a molecule is a measure of the charge separation in the molecule. If a molecule contains only two electric charges $+Q$ and $-Q$ separated by a distance r, the magnitude of its dipole moment is

$$|\boldsymbol{\mu}| = \mu = Qr \tag{18.4-10}$$

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 or to larger charges or both.

Exercise 18.17

For two charges of equal magnitude and opposite signs at arbitrary locations, show that the magnitude of the vector in Eq. (18.4-9) is the same as that given by Eq. (18.4-10).

Exercise 18.18

A **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 vanishes.

The classical expression for the dipole moment in Eq. (18.4-9) contains no momentum components, so its quantum-mechanical operator is just the multiplication operator:

$$\hat{\mu} = \mu = \sum_{i=1}^{n} Q_i \mathbf{r}_i \tag{18.4-11}$$

The expectation value of the electric dipole of a molecule in a state Ψ is

$$\langle \mu \rangle = \int \Psi^* \mu \Psi \, dq = \int \mu |\Psi|^2 dq \tag{18.4-12}$$

where q stands for all of the coordinates of all particles in the molecule. 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 sum their contributions algebraically.

With a one-term orbital wave function in which the orbitals are orthogonal to each other, each electron makes its contribution to the probability density independently (see Eq. (16.3-24), 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. (16.3-26). The integral in Eq. (18.4-12) is equal to a sum of one-electron integrals:

$$\langle \boldsymbol{\mu} \rangle = \boldsymbol{\mu}_{\text{nuc}} - e \sum_{i=1}^{n_e} \int \psi_i(i)^* \mathbf{r}_i \psi_i(i)\, d^3\mathbf{r}_i \tag{18.4-13}$$

where ψ_i is the ith occupied space orbital and where n_e is the number of electrons. For most molecules each space orbital is occupied by two electrons and occurs twice in this equation. The contribution of the nuclei is computed with the nuclei at fixed positions:

$$\boldsymbol{\mu}_{\text{nuc}} = \sum_{A=1}^{n_n} eZ_A \mathbf{r}_A \tag{18.4-14}$$

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.

The formula shown in Eq. (18.4-13) is the same as if the ith electron were a classical "smeared-out" charge with a density distribution equal to $\psi_i{}^*\psi_i$. 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. Therefore 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 LCAO-MOs 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 bond length in the LiH is experimentally measured to be 1.596×10^{-10} m, so that if the bond were purely ionic with an undistorted Li$^+$ ion and an undistorted H$^-$ ion,

$$\mu_{\text{ionic}} = (1.6022 \times 10^{-19}\,\text{C})(1.595 \times 10^{-10}\,\text{m}) = 2.56 \times 10^{-29}\,\text{C m}$$

There is a common unit named the **debye**, which is defined by

$$1\ \text{debye} = 3.335641 \times 10^{-30}\,\text{C m} \tag{18.4-15}$$

The debye unit is named for Peter Debye, of the Debye–Hückel theory, whose 1936 Nobel Prize was for his work on dipole moments.

The debye unit was 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 1 to 10 debye. The ionic dipole moment of the LiH molecule corresponds to 7.675 debye.

EXAMPLE 18.5

Estimate the dipole moment of the LiH molecule from the orbitals of Eq. (18.4-8.)

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

$$|\psi_{2\sigma}|^2 = (0.47)^2|\psi_{2sp,1\text{Li}}|^2 + (0.47)(0.88)\psi^*_{2sp,1\text{Li}}\psi_{1s\text{H}} + (0.88)^2|\psi_{1s\text{H}}|^2$$

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. (18.4-13) 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 $1.595 \times 10^{-10}\,\mathrm{m}$,

$$\mu = (8.9 \times 10^{-20}\,\mathrm{C})(1.595 \times 10^{-10}\,\mathrm{m}) = 1.42 \times 10^{-29}\,\mathrm{C\,m} = 4.3\,\mathrm{debye}$$

This 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. Because of the crudity of our analysis, our value of 4.3 debye agrees only roughly with the experimental value of the LiH dipole moment, 5.88 debye.

Qualitative Description of Bonding in Molecules

The properties of the LCAO-MOs from the Hartree–Fock–Roothaan treatment of lithium hydride conform to a general pattern of results that can be summarized in the following rules:

1. *Two atomic orbitals on different nuclei must have roughly equal orbital energies to form a good bonding LCAO-MO.* If the energies are different, the lower-energy (bonding) LCAO-MO constructed from them will have a coefficient of larger magnitude for the atomic orbital of lower energy, and the higher-energy (antibonding) LCAO-MO will have a coefficient of larger magnitude for the higher-energy atomic orbital. For greatly different energies the lower-energy LCAO-MO will be almost the same as the lower-energy atomic orbital, making it nearly a nonbonding orbital.
2. *Two atomic orbitals on different nuclei must have a fairly large overlap region to form a good bonding LCAO-MO.*
3. *If two atomic orbitals on different nuclei do not have the same symmetry around the bond axis, they will not form a good bonding LCAO-MO.* Two such orbitals cannot form an eigenfunction of the proper symmetry operators for a diatomic molecules and are similarly unsuitable for polyatomic molecules.

These three rules are generalizations that we will use as a means of predicting qualitatively (without calculation) what would probably result if a calculation were carried out. We can relate the results of the lithium hydride calculation to these rules. The $1s$ lithium orbital and the $1s$ hydrogen orbital do not form a good bonding LCAO-MO because of the large difference in energies and because the overlap region of these two orbitals is small (the orbital region of the $1s$ orbital does not extend to the outer part of the atom). The result is that the lowest-energy σ orbital is essentially identical with the lithium $1s$ atomic orbital. The $2sp,1$ hybrids orbital has better overlap with the $1s$ hydrogen orbital than either the $2s$ or $2p_z$ orbital, since it is directional and its orbital region extends farther from the nucleus than either the $2s$ or $2p$ orbital so it is a good choice to include in a bonding orbital. The $2p_x$ and $2p_y$ orbitals do not have the same symmetry around the bond axis as the other orbitals, so they are included in our

LCAO-MOs. If they were included in the basis set, they would not end up in linear combinations with the other orbitals (they would not "mix" with the other orbitals). These orbitals have an overlap region with a 1*s* hydrogen orbital that is composed of two parts, with the product of the two orbital functions having a positive sign in one part and a negative sign in the other part. This produces a zero value of the overlap integral.

EXAMPLE 18.6

Describe the bonding in hydrogen fluoride. Include a statement about the polarity of the molecule.

Solution

The fluorine 1*s* orbital will act 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 1*s* orbital, so they also act as nonbonding orbitals. We make two hybrid orbitals with the fluorine 2*s* and $2p_z$ orbitals, denoted by 2*sp*,1 and 2*sp*,2. The 2*sp*,1 orbital forms a bonding orbital called the 1σ orbital with the hydrogen 1*s* orbital. There is also an antibonding orbital, which we denote by $2\sigma^*$ (it remains vacant in the ground state). The 2*sp*,2 orbital acts as a nonbonding orbital. The energy of the fluorine 2*sp*,1 hybrid is presumably lower than that of the hydrogen 1*s* orbital so this bonding orbital will have a coefficient of larger magnitude for the fluorine atomic orbital than for the hydrogen orbital (the bonding orbital is "heavy" on the fluorine end). The vacant antibonding orbital $2\sigma^*$ orbital is "heavy" on the hydrogen end.

The energies of the LCAO-MOs and hybrid orbitals are shown schematically in the correlation diagram of Figure 18.17. The line segment for the bonding orbital is closer to the fluorine side to indicate that this orbital is heavy on the fluorine end. From the Aufbau principle, the ground-state electron configuration is

$$(1s\mathrm{F})^2(2sp2\,\mathrm{F})^2(2p_x\mathrm{F})^2(2p_y\mathrm{F})^2(1\sigma)^2$$

The bond is polar, with the fluorine end negative.

Example 18.6 is the kind of discussion that our crude level of analysis permits. To begin such a discussion you need a rough energy level diagram for all of the atomic orbitals. The relative energies of atomic orbitals on different atoms can be estimated from the effective nuclear charges or from the electronegativities of the atoms. For example, the fluorine 2*sp* hybrids lie lower than the hydrogen 1*s* orbitals, and fluorine is known to be more electronegative than hydrogen.

Exercise 18.19

Describe the bonding in LiF. How much ionic character do you think there will be in the bond?

Carbon monoxide is an interesting molecule. A qualitative description of the chemical bonding is obtained by constructing LCAO-MOs similar to those of N_2, which is isoelectronic with CO. Oxygen's effective nuclear charge is greater than that of carbon so the bonding LCAO-MOs will have somewhat larger coefficients for the oxygen orbitals than for the carbon orbitals, and the antibonding LCAO-MOs will have somewhat larger coefficients for carbon than for oxygen. The electron configuration of the molecule is

$$(\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\pi 2p_x)^2(\pi 2p_y)^2(\sigma 2p_z)^2$$

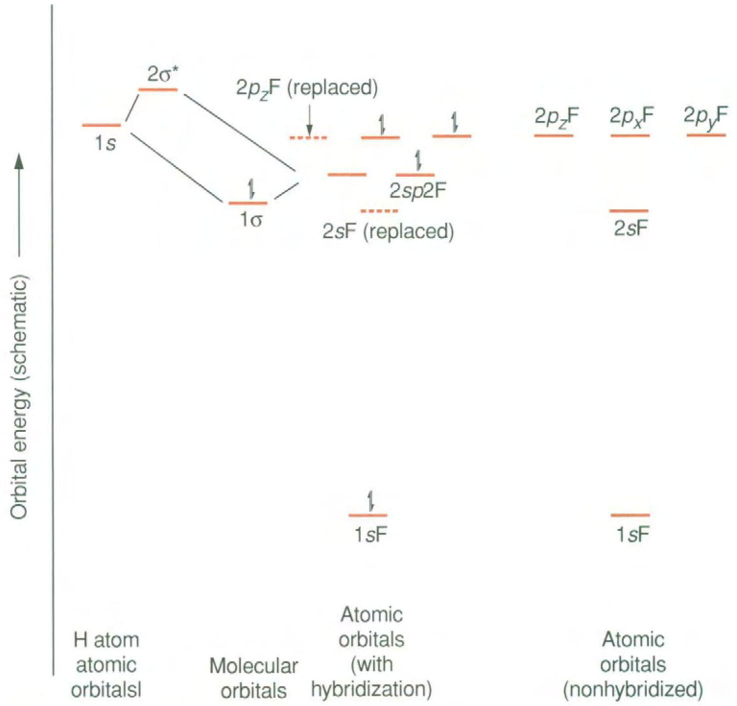

Figure 18.17. Correlation Diagram for Hydrogen Fluoride. This correlation diagram shows that in the simple approximation used, the bonding orbital is made as a linear combination of the 1*s* hydrogen orbital and one of the 2*sp* hybrid fluorine orbitals. The antibonding orbital is made from the same two atomic orbitals. The other orbitals used in the description are nonbonding fluorine orbitals.

The designations g and u are not used since the orbitals are not eigenfunctions of the inversion operator, but we keep the * 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 also 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 dipole moment of the CO molecule is rather small, about 0.1 debye. The fact that the coefficients of the oxygen orbitals are greater in the bonding orbitals causes the bonding electrons to contribute a net negative charge at the oxygen end of the molecule. However, the oxygen nucleus is more positive than the carbon nucleus by two protons, and this contributes a positive charge at the oxygen end, which slightly more than cancels the charge due to the electrons. The carbon end is negative and it is this end that coordinates to transition metal atoms in various complexes, including the binding of a CO molecule to an iron atom in hemoglobin in cases of CO poisoning.

*Exercise 18.20

Assuming the alternate electron configuration with eight electrons occupying nonbonding 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.

Exercise 18.21

Give a qualitative description of the bonding of the BN molecule using molecular orbitals. Compare it with diatomic carbon.

The Valence Bond Method for Heteronuclear Diatomic Molecules

A valence bond wave function such as that of Eq. (18.3-8) or Eq. (18.3-16) corresponds to equally shared electrons in completely covalent bonds. The two ionic terms in Eq. (18.3-11) do not correspond to ionic bonding, since one ionic term corresponds to bond polarity in one direction and the other to bond polarity in the opposite direction. In the lithium hydride molecule, the hydrogen end of the molecule is negative, and an approximate description of the bonding can be obtained in the valence bond method by including only one ionic term. We write the modified valence bond function for LiH:

$$\Psi_{\mathrm{MVB}} = c_{\mathrm{VB}}\Psi_{\mathrm{VB}} + c_{\mathrm{I}}\Psi_{\mathrm{I}} \qquad (18.4\text{-}16)$$

where

$$\begin{aligned}\Psi_{\mathrm{VB}} = {} & \psi_{1s\mathrm{Li}}(1)\alpha(1)\psi_{1s\mathrm{Li}}(2)\beta(2)[\psi_{2sp1\mathrm{Li}}(3)\psi_{1s\mathrm{H}}(4) + \psi_{1s\mathrm{H}}(3)\psi_{2sp1\mathrm{Li}}(4)] \\ & \times [\alpha(3)\beta(4) - \beta(3)\alpha(4)] \end{aligned} \qquad (18.4\text{-}17)$$

and

$$\Psi_{\mathrm{I}} = \psi_{1s\mathrm{Li}}(1)\alpha(1)\psi_{1s\mathrm{Li}}(2)\beta(2)\psi_{1s\mathrm{H}}(3)\psi_{1s\mathrm{H}}(4)[\alpha(3)\beta(4) - \beta(3)\alpha(4)] \qquad (18.4\text{-}18)$$

Only the ionic term is added that corresponds to both electrons being on the hydrogen atom. This term represents purely ionic bonding with a positive lithium ion and a negative hydride ion. The wave function Ψ_{VB} represents purely covalent bonding, with equally shared electrons. If $|c_{\mathrm{VB}}|$ is larger than $|c_{\mathrm{I}}|$ this corresponds to a bond that is primarily ionic and if $|c_{\mathrm{VB}}|$ is smaller than $|c_{\mathrm{I}}|$ this corresponds to a bond that is primarily covalent.

***Exercise 18.22**

Calculate the values of c_{VB} and c_{I} that make the wave function Ψ_{MVB} equivalent to the LCAO-MO wave function in Eq. (18.4-5) if the orbitals of Eq. (18.4-8) are used. Find the percent ionic character, defined as $[c_{\mathrm{I}}^2/(c_{\mathrm{VB}}^2 + c_{\mathrm{I}}^2)] \times 100\%$.

Electronegativity

The **electronegativity** is an empirical parameter than 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 are generally stronger (have larger bond dissociation energies) than purely covalent bonds and used this as a measure of the bond polarity. If the electronegativity of element A is denoted by X_{A} and that of element B is denoted by X_{B}, Pauling defined

$$|X_{\mathrm{A}} - X_{\mathrm{B}}| = (0.102\,\mathrm{mol}^{1/2}\,\mathrm{kJ}^{-1/2})(\Delta E_{\mathrm{AB}})^{1/2} \qquad (18.4\text{-}19)$$

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.

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:

$$\Delta E_{\mathrm{AB}} = E_{\mathrm{AB}} - \tfrac{1}{2}[E_{\mathrm{AA}} + E_{\mathrm{BB}}] \tag{18.4-20}$$

There are other definitions that are used to obtain values of the electronegativity, but we do not discuss them. Since only the difference in electronegativity is defined, the value for one element is chosen arbitrarily and the other values are relative to it. Choosing a value of 4.0 for fluorine makes all electronegativities positive, ranging in value from 0.7 to 4.0. Table A.21 in Appendix A gives the values of the electronegativity for several elements. Fluorine is the most electronegative element, followed by oxygen and chlorine. The alkali metals are the least electronegative. In any row of the periodic chart the electronegativity increases from left to right, and in any column it decreases from top to bottom. 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 pure covalent bond requires a difference of zero.

We can understand the trends in electronegativity on the basis of the observed fact that when a bonding molecular orbital is constructed from atomic orbitals of different energy, optimizing the values of the coefficients gives a coefficient of larger magnitude for the lower-energy atomic orbital than for the other atomic orbital. With atomic orbitals in the same shell, a larger apparent nuclear charge must correspond to a larger electronegativity, since a larger apparent nuclear charge corresponds to a lower atomic orbital energy, as indicated in Eq. (16.2-12). As one moves from left to right across a row of the periodic chart, the nuclear charge and the effective nuclear charge increase, corresponding to the observed increase in the electronegativity.

***Exercise 18.23**

Using average bond energies from Table A.9 in Appendix A, calculate the differences in electronegativity between (a) H and F, (b) C and O, and (c) C and Cl. Compare with the values in Table A.21.

***Exercise 18.24**

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, and (d) H and F, (e) Li and F, and (f) F and F.

18.5 Symmetry in Polyatomic Molecules. Groups of Symmetry Operators

In many molecules, the equilibrium nuclear conformation has important symmetry properties. In Section 18.1 we introduced several symmetry operators: the identity operator, the inversion operator, reflection operators, and rotation operators. For polyatomic molecules another set of operators is needed: **improper rotations**, which are equivalent to ordinary rotations followed by a reflection through a plane perpendicular to the axis of rotation. We consider only point symmetry operators, so the axis and the plane of an improper rotation both pass through the origin. An operator for an improper rotation of 360°/n is denoted by $\hat{S}_n$. For example, an $\hat{S}_4$ operator with the z axis as its symmetry element will have the effect on a point at (x, y, z):

$$\hat{S}_{4z}(x, y, z) = (x', y', z') = (-y, x, -z) \tag{18.5-1}$$

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. If $\hat{S}_4$ operates twice, the effect is the same as $\hat{C}_2$, since the two reflections cancel each other. If the axis of symmetry is the z axis,

$$\hat{S}_4^2(x, y, z) = \hat{C}_2(x, y, z) = (-x, -y, z) \tag{18.5-2}$$

Some improper rotations are equivalent to other operations. The $\hat{S}_1$ operation has the same effect as a reflection operation, and the $\hat{S}_2$ operation is equivalent to the inversion operator (the $\hat{i}$ notation is preferred). The lowest-order improper rotation that is not equivalent to another operator is $\hat{S}_3$. If n is an even integer, n applications of $\hat{S}_n$ restore the molecule to its original conformation:

$$\hat{S}_n^n = \hat{E} \qquad (n\,\text{even}) \tag{18.5-3}$$

If n is an odd integer, n applications of $\hat{S}_n^n$ are equivalent to a reflection through the plane perpendicular to the axis of rotation:

$$\hat{S}_n^n = \hat{\sigma} \qquad (n\,\text{odd}) \tag{18.5-4}$$

EXAMPLE 18.7

Consider the $\hat{S}_4$ operator with the y axis as its symmetry element. Find the location to which the point (x, y, z) is moved by this operator.

Solution

The rotation moves the point from (x, y, z) to $(z, y, -x)$. The reflection through the x–z plane moves the point to $(z, -y, -x)$.

*Exercise 18.25

Consider the $\hat{S}_3$ operator whose symmetry element is the x axis. Find the coordinates of the point to which the point $(1, 2, 3)$ is moved by this operator.

Groups of Symmetry Operations

We now apply the symmetry operators to the equilibrium nuclear locations in a polyatomic molecule, allowing the operators to move all nuclei simultaneously. 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 type (same isotope of the same element). It is not necessary to think of symmetry operators as mathematical operators. We will think of symmetry operations as physically moving the nuclei in space instead of applying a mathematical operator to the coordinates of the nuclei. The effect is the same. A symmetry operation will be denoted by the same symbol as a symmetry operator without the caret (ˆ). There are three different but related things: symmetry operators, symmetry operations, and symmetry elements. We use the same symbol for the symmetry operation and symmetry element.

EXAMPLE 18.8

List the symmetry operations that belong to the water molecule.

Solution

In its equilibrium conformation the molecule is angular (bent), with two equal bond lengths and a bond angle of 104.5°. We place the center of mass of the molecule at the origin of coordinates. 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.

In this example, we have used the standard scheme for orienting a molecule. The center of mass goes on the origin, the rotation axis of highest order (largest n) goes on the z axis, and as many other symmetry elements as possible are oriented on the x and y axes. The rotation axis of highest order is called the **principal rotation axis**.

*Exercise 18.26

List the symmetry operations that belong to the ammonia molecule, NH_3.

The symmetry operations that belong to any specific molecule (or other symmetrical object) are an example of a mathematical **group**. A mathematical group is a set of objects that are called **members** of the group. There must be a single method for combining two members of the group to produce another member of the group, and other conditions must be met, which we describe below. In our application of group theory, the members of the groups are symmetry operators or symmetry operations and the method for combining two members of the group is operator multiplication as defined in Eq. (15.2-3). This is equivalent to successive application of the two symmetry operations with the operation on the right applied first. In mathematical group theory, the members of a group are usually called "elements" and the method of combining two elements is called an "operation". To avoid confusion with symmetry elements, we use the name "member". The members of our groups are operations, and calling the method of combination the "operation" would be confusing, so we refer to the operator multiplication as a "method" or refer to multiplication.

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 **C** is the product **AB** such that **C** = **AB**, then **C** must be a member of the group.
2. It is not necessary that the members of the group commute with each other. That is, it is possible that

$$\mathbf{AB} \neq \mathbf{BA} \qquad \text{(possible, but not necessary)} \tag{18.5-5}$$

If **A** and **B** are operators or operations, **AB** means that **B** operates first and **A** operates second, while **BA** means that **A** operates first and **B** operates second. If all the members of the group commute with each other, the group is called **abelian**.

Abelian groups are named after Niels Henrik Abel, 1802–1829, a great Norwegian mathematician who was the first to show that a fifth-degree algebraic equation does not necessarily have a radical expression as a solution.

3. The group must contain the identity, **E**, such that

$$\mathbf{AE} = \mathbf{EA} = \mathbf{A} \tag{18.5-6}$$

4. The inverse of every member of the group must be a member of the group. If $\mathbf{A}^{-1}$ is the inverse of **A**, then $\mathbf{A}^{-1}$ must be a member of the group if **A** is a member. The inverse is defined such that

$$\mathbf{AA}^{-1} = \mathbf{A}^{-1}\mathbf{A} = \mathbf{E} \tag{18.5-7}$$

5. The associative law must hold:

$$\mathbf{A}(\mathbf{BC}) = (\mathbf{AB})\mathbf{C} \tag{18.5-8}$$

We have asserted that the set of symmetry operations that belong to a molecule (or other symmetrical object) form a group if we define successive operation to be the group method of combining two members. This fact is not obvious, but we can show it to apply in every specific case.

EXAMPLE 18.9

Show that the symmetry operations belonging to the H_2O molecule form a group.

Solution

Figure 18.18a shows the nuclear framework oriented as in Example 18.8. The hydrogen atoms are arbitrarily labeled H_a and H_b. The symmetry elements of the H_2O molecule are shown in the figure. They are E, C_2, and σ_{yz}, the vertical reflection plane passing through the positions of the hydrogen atoms, and σ_{xz}, the vertical reflection plane at right angles to the first 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 18.4. The operations listed in the first column of the table are to be used as the left factor and the operations listed in the first row of the table are to be used as the right factor in a product. The right factor operates first. 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 18.18b. 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 that there is a second coordinate system that moves with the nuclei. A reflection turns a right-handed coordinate system into a left-handed coordinate system in which the positive end of the y axis points to the left if the x and z axes are in their usual positions. Since the two operations reverse the handedness of the coordinate system as would σ_{xz}, then

$$\sigma_{yz}C_2 = \sigma_{xz} \tag{18.5-9}$$

The action of the σ_{xz} operation is shown in Figure 18.18c.

Condition 2. The group does contain the identity operation, E.

Condition 3. It is not required that the members commute, but this group is abelian.

Condition 4. The inverse of every member is in the group because each member of this group is its own inverse.

Condition 5. The group operation is associative, because operator multiplication is associative.

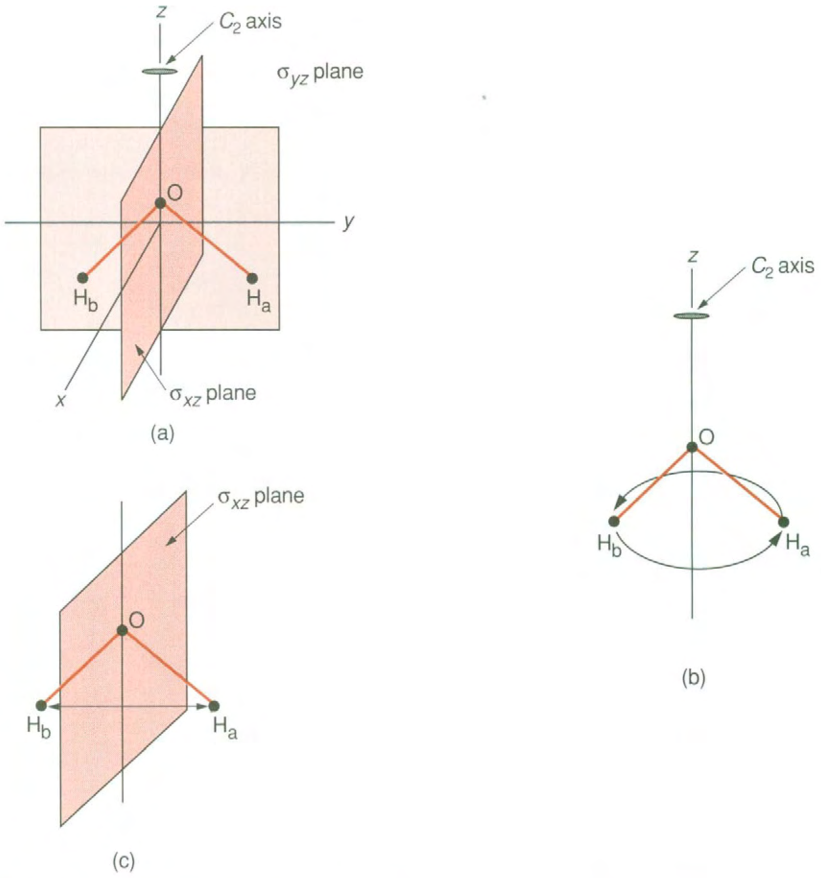

Figure 18.18. The H_2O molecule. (a) The molecule in the standard location in the coordinate system. The symmetry elements C_2, σ_{xz}, and σ_{yz} are shown. (b) The action of the C_2 operation on the nuclei. (c) The action of the σ_{xz} operation on the nuclei.

Exercise 18.27

Verify several of the entries in Table 18.4, the multiplication table for this group.

Exercise 18.28

Show that the group of operations belonging to the water molecule is abelian (all operations commute with each other).

Table 18.4. 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

Schoenflies Symbols for Point Groups

A group that consists of point symmetry operations is called a **point group**. Each point group is assigned a unique symbol called a **Schoenflies symbol**. 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 vertical mirror planes. You can specify the symmetry properties of a molecule like H_2O or SO_2 quickly to a knowledgeable person 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.

Exercise 18.29

a. Obtain the multiplication table for the C_{3v} point group.
b. Show that it satisfies the conditions to be a group.
c. Show that C_3^2 must be included in the group.
d. Show that the group is not abelian.

There are many different point groups. Table 18.5 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 the group. In the list of operations, it is customary to list these two operations as $2C_3$. Benzene has a six-fold axis so that in order to include all the operations and their inverses for this axis, we would have 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 C_2 indicates C_6^3, which is equivalent to a rotation of 180°.

The main part of the Schoenflies symbol 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

Table 18.5. Examples of Some Point Groups

Schoenflies Symbol	Symmetry Operations	Example Molecule
C_1	E	ClBrClF
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_∞, σ_v	HF
D_{3h}	$E, 3C_3, 3C_2, 3\sigma_v, \sigma_h$	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
$D_{\infty h}$	$E, C_\infty, C_2, \sigma_h, \sigma_v$	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

highest-order rotation axis. A subscript v indicates the presence of vertical mirror plans, and a subscript h denotes the presence of a horizontal mirror plane. For example, the group C_{4v} has a C_4 axis and four vertical mirror planes as well as 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, and the O_h group is the group of octahedral molecules.

Figure 18.19 presents a scheme for assigning a molecule to a point group. This diagram can be called a **decision tree** or a **flow chart**. One starts at the top of the diagram with knowledge of the equilibrium nuclear conformation. It is assumed that the user can recognize linear molecules, tetrahedral molecules, and octahedral molecules immediately. After this, at each branching point one answers yes or no to whether a particular symmetry element is present and 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.

EXAMPLE 18.10

Assign the benzene molecule to a point group.

Solution

The molecule is in the shape of a regular hexagon of six carbon atoms, with a hydrogen atom bonded to each carbon atom, forming a second regular 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, it 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 have to 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. If neither the σ_h plane nor the six σ_v planes had been present, corresponding to the dash on the third choice, the group would have been the D_6 group.

Exercise 18.30

Using the decision tree of Figure 18.19, assign the following molecules to point groups:

a. 1,1-Dichloroethene
b. *trans*-1,2-Dichloroethene
c. *cis*-1,2-Dichloroethene
d. Ethane (staggered)
e. Ethane (eclipsed)
f. Cyclohexane (boat conformation)

Some Elementary Applications of Group Theory

Once a molecule has been assigned to a point group we can draw some conclusions about it. The first conclusion relates to a molecular dipole moment, which is a vector pointing from a negative region of the molecule to a positive region, as defined in Eq. (18.4-9). 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

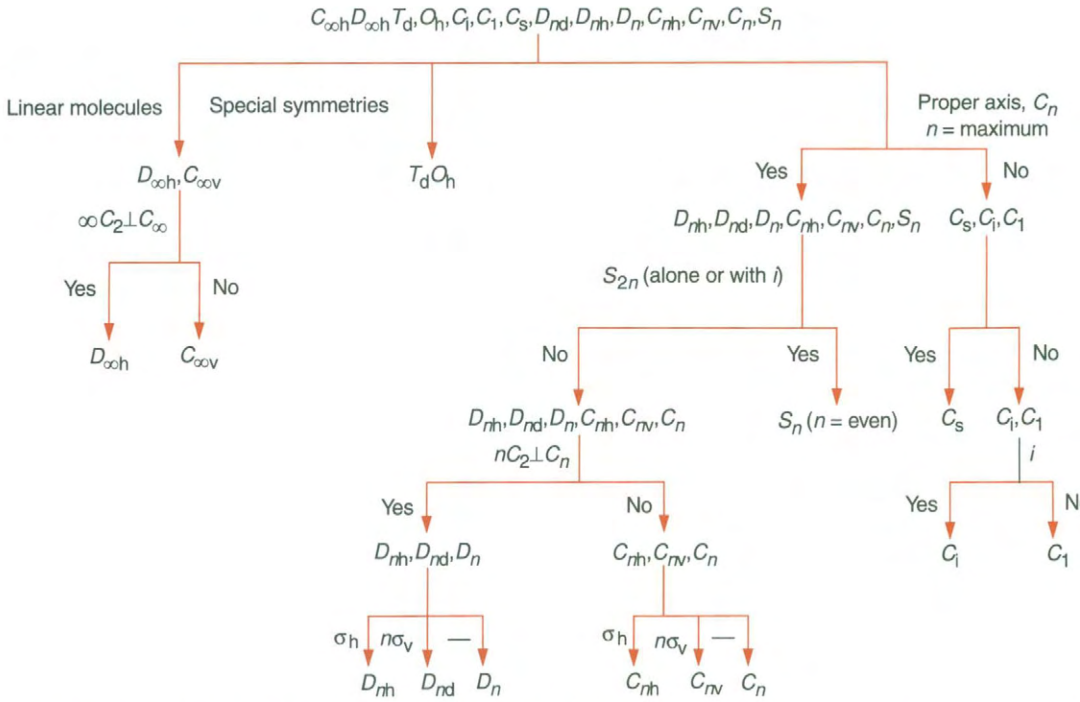

Figure 18.19. Flow Chart (Decision Tree) for the Assignment of a Molecule to a Point Group. To use this chart start at the top and follow the path that corresponds to the answer to each question.

of the same type. A symmetry operation does not move a point if it lies in the symmetry element of the operation so any vector lying in a symmetry element will not be changed by the symmetry operation. Only if the dipole moment vector is contained in all of the symmetry elements can there be a dipole moment. Any molecule with a dipole moment must belong to one of the groups C_n, C_s, or C_{nv}. A molecule with a center of symmetry cannot have a dipole moment since the symmetry element of the inversion operator is a single point.

The other 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. The two enantiomorphs will rotate the plane of 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. 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, etc. These applications require the use of representations of groups, which are briefly introduced in Appendix I.

18.6 Electronic Structure of Polyatomic Molecules

As with diatomic molecules, we base our treatment of the electronic structure of polyatomic molecules on the Born–Oppenheimer approximation, assuming stationary nuclei that are in their equilibrium conformation. The zero-order Born–Oppenheimer Hamiltonian operator consists of one-electron operators plus internuclear repulsion terms, which are treated as constants. Interelectron repulsion terms are neglected. In this approximation the wave function is a product of orbitals. In order for the wave function to survive antisymmetrization, the Pauli exclusion principle must be applied, with no more than two electrons occupying each space orbital. For the ground state, the wave function is constructed according to the Aufbau principle.

We will now use simple LCAO molecular orbitals constructed according to the same policies that we applied to diatomic molecules in Section 18.4: each bonding LCAO-MO 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 a bond axis. As a simple example, we consider the H_2O molecule. The equilibrium nuclear conformation is known from experiment to have a bond angle of 104.5° and a bond length of 95.8 pm. The molecule has a dipole moment of magnitude 1.85 debye bisecting the bond angle, with the oxygen end negative. Figure 18.20 is a correlation diagram showing schematically the energies of the seven lowest-energy atomic space orbitals of one oxygen atom and two hydrogen atoms. For our first approximate description, we use these unmodified atomic orbitals as our basis set. The 1*s* oxygen orbital is far lower in energy than the other orbitals, so we use it as a nonbonding orbital.

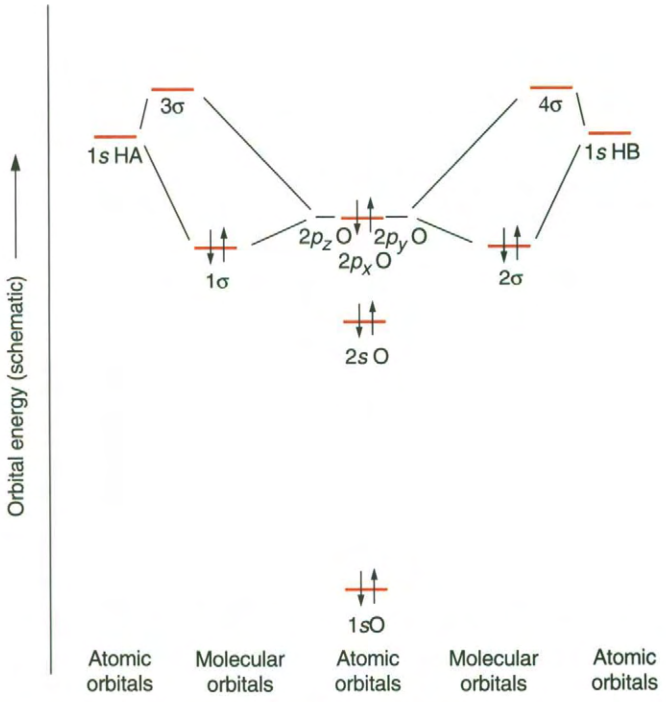

Figure 18.20. Correlation Diagram for the Water Molecule. Here we see two bonding LCAO-MOs, each made from a hydrogen 1*s* orbital and one of the 2*p* oxygen orbitals. This description is unsatisfactory, because the bond angle is predicted to be 90° in order to satisfy the criteria for bonding LCAO-MOs. The actual bond angle is around 105°.

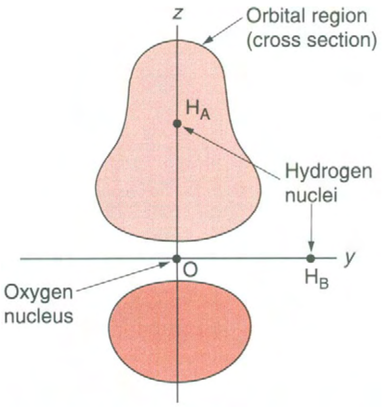

Figure 18.21. The Nuclear Framework of the Water Molecule Using the Molecular Orbitals of Equations (18.5-1) and (18.5-2). The figure shows the positions of the nuclei, as well as the cross section of the orbital region of the 1σ orbital. Again we see the unsatisfactory description with a bond angle of 90°.

We first try to use the $2p$ orbitals in constructing bonding LCAO-MOs. The atomic orbitals in an LCAO-MO must have the same symmetry about the bond axis. Since the $2p_z$ orbital is cylindrically symmetric about the z axis, we place a hydrogen nucleus denoted by A on the z axis and construct the bonding molecular orbital

$$\psi_{1\sigma} = c_{\mathrm{O}}\psi_{2p_z\mathrm{O}} + c_{\mathrm{H}}\psi_{1s\mathrm{A}} \tag{18.6-1}$$

where $\psi_{1s\mathrm{A}}$ is the $1s$ hydrogen orbital centered on hydrogen nucleus A. The 1σ orbital is a σ orbital because its bond axis is the z axis and because it is a linear combination of two atomic orbitals corresponding to $m = 0$. Figure 18.21 shows the nuclear framework in the required position, as well as the orbital region of the 1σ orbital. This orbital region is cylindrically symmetrical. It is an eigenfunction of every $\hat{C}_n$ operator with the bond axis as its symmetry element as well as being an eigenfunction of every reflection operator whose symmetry plane includes the bond axis. Orbitals that are cylindrically symmetrical about a bond axis are σ orbitals, which allows us to recognize σ orbitals by inspection of the orbital regions.

We place a hydrogen atom denoted by B on the y axis and construct the LCAO-MO:

$$\psi_{2\sigma} = c_{\mathrm{O}}\psi_{2p_y\mathrm{O}} + c_{\mathrm{H}}\psi_{1s\mathrm{B}} \tag{18.6-2}$$

Because of the similarity of the $2p_y$ and $2p_z$ orbitals, the coefficients in Eq. (18.6-2) will be equal to those in Eq. (18.6-1). The 2σ orbital bears the same relationship to the y axis as the 1σ orbital does to the z axis, so by analogy the projection of the orbital angular moment on the y axis for this orbital also vanishes, and it is also a σ orbital. We predict that optimization of the coefficients will give

$$|c_{\mathrm{O}}| > |c_{\mathrm{H}}| \tag{18.6-3}$$

because oxygen is more electronegative than hydrogen. Of the ten electrons, two can occupy the nonbonding oxygen $1s$ space orbital, 4 can occupy the $2s$ and $2p_x$ oxygen orbitals, and 4 can occupy the bonding LCAO-MOs. The ground-state electron configuration is thus $(1s\mathrm{O})^2(2s\mathrm{O})^2(2p_x\mathrm{O})^2(1\sigma)^2(2\sigma)^2$. There are two single bonds, with a bond angle of 90°. The molecule is polar with the oxygen end negative.

This description needs to be improved, even with our limited goals. The bond angle of 90° is in poor agreement with the experimental value of 104.5°. One of the unshared pairs in the oxygen valence shell is in a $2s$ orbital, and the other is in a $2p$ orbital. This disagrees with the predictions of the valence shell electron pair repulsion (VSEPR) theory. According to this elementary theory, the shared and unshared electron pairs in the valence shell of an atom should arrange themselves so that they are as far from each other as possible. The two bonding electron pairs and the two nonbonding electron pairs around the oxygen atom should arrange themselves in a tetrahedral shape, with a bond angle near 109°.

A better wave function for the water molecule is obtained by creating a set of hybrid orbitals that are linear combinations of the $2s$ space orbital and all three of the $2p$ space orbitals. These orbitals are called the $2sp^3$ **hybrid orbitals**:

$$\psi_{2sp^3,1} = \tfrac{1}{2}[-\psi_{2s} + \psi_{2p_x} + \psi_{2p_y} + \psi_{2p_z}] \tag{18.6-4a}$$

$$\psi_{2sp^3,2} = \tfrac{1}{2}[-\psi_{2s} + \psi_{2p_x} - \psi_{2p_y} - \psi_{2p_z}] \tag{18.6-4b}$$

$$\psi_{2sp^3,3} = \tfrac{1}{2}[-\psi_{2s} - \psi_{2p_x} + \psi_{2p_y} - \psi_{2p_z}] \tag{18.6-4c}$$

$$\psi_{2sp^3,4} = \tfrac{1}{2}[-\psi_{2s} - \psi_{2p_x} - \psi_{2p_y} + \psi_{2p_z}] \tag{18.6-4d}$$

Exercise 18.31

Using the fact that the $2s$, $2p_x$, $2p_y$, and $2p_z$ atomic orbitals are all normalized and all orthogonal to each other, choose one of the hybrid orbitals in Eq. (18.6-4) and show that it is normalized. Choose a pair of orbitals in Eq. (18.6-4) and show that they are orthogonal to each other.

The orbital regions of the $2sp^3$ hybrid orbitals are directional, as were the $2sp$ hybrids. Figure 18.22a shows schematically how the three $2p$ orbitals combine in the $2sp^3,1$ hybrid orbital. The figure includes a cube centered at the origin and parallel to the coordinate planes. In the figure, dots are drawn along the positive coordinate axes (the directions of the largest positive values of the $2p$ orbitals). Since the $2s$ orbital is negative in the outer part of its orbital region, it is included in the linear combinations with a negative coefficient so that it will make a positive contribution in this region. The four orbitals combine to form 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. This direction is an axis of cylindrical symmetry of the hybrid orbital. The symmetry axes of the other three hybrid orbitals are shown in the figure, pointing toward alternate corners of the cube.

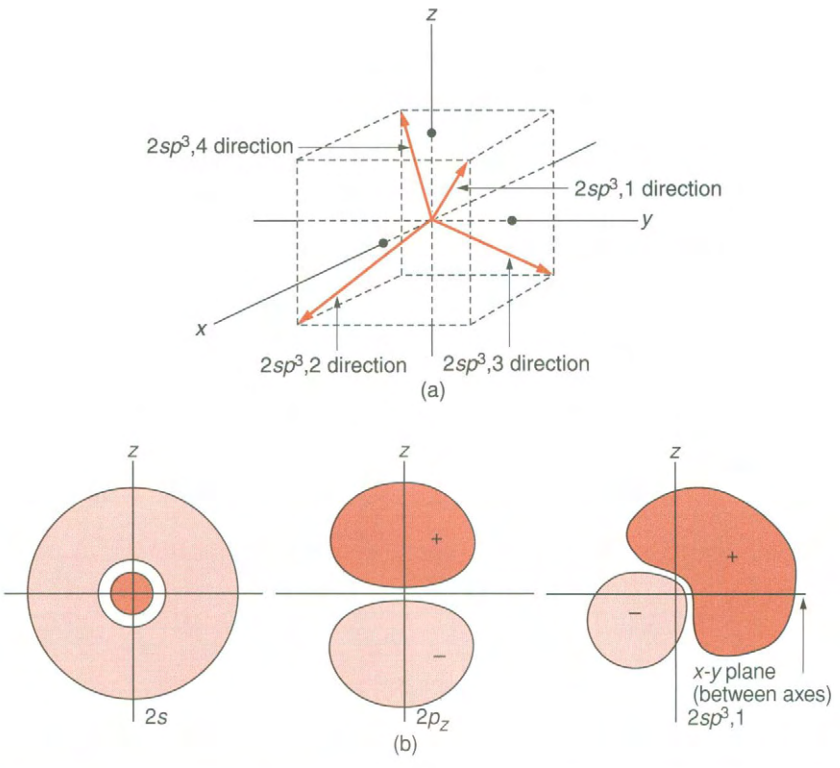

Figure 18.22 The sp^3 Hybrid Orbitals. (a) **The addition of s and p atomic orbitals to form sp^3 hybrid orbitals (represented by vectors in the directions of positive contributions).** This figure shows the directions of maximum extension of the four sp^3 hybrid orbitals, which point to alternate corners of a cube entered at the origin. (b) **The orbital regions of $2s$, $2p$, and $2sp^3$ orbitals.** The orbital region of the sp^3 hybrid orbital resembles that of the sp hybrids, except for the direction of maximum extension.

Exercise 18.32

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 18.22a.

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 18.22a is called the **tetrahedral angle**, equal to 109 degrees, 28 minutes, 16.39... seconds.

Exercise 18.33

Using the theorem of Pythagoras and values of trigonometric functions, show that the angle between alternate diagonals of a cube is 109 degrees, 28 minutes, 16.39... 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 18.22b. 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 more strongly bonding LCAO-MO using a $2sp^3$ orbital than using a $2p$ orbital.

We can now construct an approximate wave function for the water molecule using the $2sp^3$ hybrid orbitals, as shown in the correlation diagram of Figure 18.23. In this diagram the energies of the unhybridized atomic orbitals are shown with broken lines.

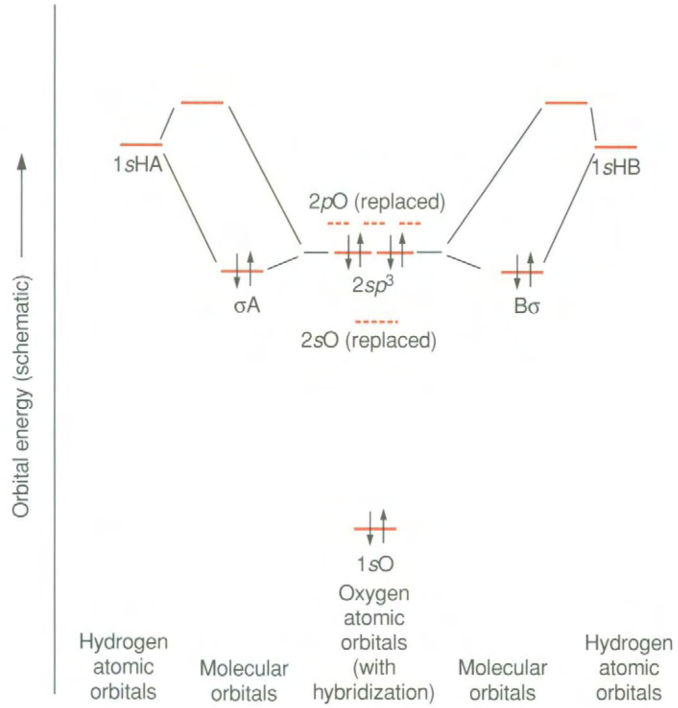

Figure 18.23. Correlation Diagram for the Water Molecule Using $2sp^3$ Hybrid Orbitals. This description is the most nearly satisfactory description that can be obtained with the hybrid orbitals that we have defined and with the policy that no more than two atomic orbitals be used in one LCAO-MO. The bond angle is 109.5°, the angle between two of the directions shown in Figure 18.22a.

We place the two hydrogens on the symmetry axes for two $2sp^3$ hybrid orbitals in order to satisfy our criteria for making good LCAO bonding molecular orbitals. Hydrogen A is placed on the axis of the $2sp^3,2$ orbital and hydrogen B is placed on the axis of the $2sp^3,3$ hybrid orbital. We form two bonding LCAO molecular orbitals:

$$\psi\sigma_{\mathrm{A}} = c_{\mathrm{O}}\psi_{2sp^3,2} + c_{\mathrm{H}}\psi_{1s\mathrm{A}} \tag{18.6-5a}$$

$$\psi\sigma_{\mathrm{B}} = c_{\mathrm{O}}\psi_{2sp^3,3} + c_{\mathrm{H}}\psi_{1s\mathrm{B}} \tag{18.6-5b}$$

From the fact that oxygen is more electronegative than hydrogen we assume that

$$|c_{\mathrm{O}}| > |c_{\mathrm{H}}| \tag{18.6-6}$$

This indicates that the oxygen $2sp^3$ hybrid orbitals are lower in energy than the hydrogen $1s$ orbitals. Along with the bonding orbitals σA and σB, there are antibonding orbitals σ^*A and σ^*B, which are heavy on the hydrogen end. These antibonding orbitals remain vacant in the ground state.

By the Aufbau principle, the electron configuration of the ground state is $(1s\mathrm{O})^2(2sp^3,1)^2(2sp^3,4)^2(\sigma\mathrm{A})^2(\sigma\mathrm{B})^2$. The electron configuration is also denoted in the energy level diagram of Figure 18.23 by arrows pointing up and down to represent electrons occupying a space orbital with spin up and spin down. As with the earlier approximate wave function, there are two single bonds and two pairs of valence-shell nonbonding electrons, which occupy nonbonding sp^3 hybrid orbitals. The bond angle is equal to the tetrahedral angle, 109.5°, in fairly good agreement with the experimental bond angle of 104.5°, and the nonbonding electrons ("lone pairs") are in similar orbitals, as expected. Figure 18.24 shows the water molecule structure according to our description. Better descriptions of the water molecule can be constructed by using LCAO-MOs that are linear combinations of all atomic orbitals in the basis set. Hybrid orbitals are then not needed and their use would only restrict the flexibility needed in finding the optimum orbitals.[8] Improvements can also be obtained by using a larger basis set.

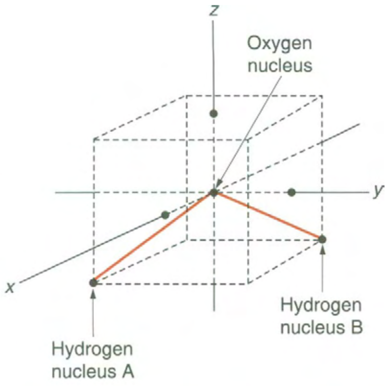

Figure 18.24. The Positions of the Nuclei in the Description of the Water Molecule Using sp^3 Hybrid orbitals. This figure shows the placement of the nuclei to obtain proper bonds using only two atomic orbitals in the LCAO molecular orbitals.

We can now understand the **octet rule** of G. N. Lewis. According to this elementary rule, atoms 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 molecular structure of many substances. For the water molecule and other molecules made from elements of the second row of the periodic chart, the valence shell is the second shell, in which eight spin orbitals (four space orbitals) occur. When linear combinations of functions are made, the number of independent linear combinations is the same as the number of basis functions used. Two linear combinations can be made from two atomic orbitals, and so on. From two atomic orbitals on different atoms, one bonding LCAO-MO and one antibonding LCAO-MO will result. If the antibonding orbitals remain vacant, the total number of occupied spin orbitals around a given nucleus of a second-row element equals eight, including nonbonding atomic orbitals and bonding molecular orbitals. This corresponds to the octet rule of Lewis.

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[8] Levine, *op. cit.*, pp. 424ff (Note 4).

EXAMPLE 18.11

Give a qualitative description of the bonding in methane, CH_4. Does the molecule have a nonzero dipole moment?

Solution

Place each hydrogen nucleus on a symmetry axis of one of the $2sp^3$ hybrid orbitals. Form four bonding LCAO molecular orbitals, each one from a $2sp^3$ hybrid and the corresponding hydrogen $1s$ orbital. Occupy the $1s$ carbon space orbital with two nonbonding electrons and occupy each bonding molecular space orbital with two electrons, making four single bonds, each at the tetrahedral angle with the other three bonds. The dipole contributions from the four bonds cancel each other because of the symmetry of the molecule, and the molecule has zero dipole moment.

Exercise 18.34

Give a qualitative description of the bonding in ammonia, NH_3, including a statement about the dipole moment of the molecule.

Molecules with Double and Triple Bonds

In Section 18.2, we discussed several diatomic molecules with double or triple bonds. In our approximate wave functions for these molecules, some of the shared electrons occupied π LCAO-MOs that were constructed from $2p$ atomic orbitals. We can construct similar π LCAO-MOs for polyatomic molecules. The Lewis electron dot formula for ethyne (acetylene), C_2H_2, is

$$\mathrm{H : C ::: C : H}$$

The VSEPR theory predicts a linear shape around each carbon atom. The acetylene molecule is isoelectronic with N_2, which also has a triple bond. In the simple LCAO-MO (description of N_2, two of the bonding electrons occupy the $\sigma_g 2p_z$ orbital, two occupy the $\pi_u 2p_x$ orbital, and two occupy the $\pi_u 2p_y$ orbital. The other eight electrons occupy $\sigma_g 1s$, $\sigma_u^* 1s$, $\sigma_g 2s$, and $\sigma_u^* 2s$ orbitals. In the description of N_2 with nonbonding atomic orbitals, the other eight electrons occupy the two $1s$ and two $2s$ orbitals.

Let us make a wave function for acetylene similar to the second description of N_2. Instead of occupying the $2s$ carbon orbitals with nonbonding electrons, we make a bonding LCAO-MO from each $2s$ carbon orbital and the ls hydrogen orbital on the adjacent hydrogen. Call one of these σA and the other one σB. Assuming the C–C bond axis to be the z axis, the electron configuration of the molecule is

$$(1s\mathrm{A})^2(1s\mathrm{B})^2(\sigma\mathrm{A})^2(\sigma\mathrm{B})^2(\sigma_g 2p_z)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2$$

There are two C–H single bonds and a C–C triple bond, consisting of a σ bond and two π bonds. The carbon–carbon σ bonding orbital is constructed from $2p_z$ orbitals, while the two carbon–hydrogen σ bonding orbitals are constructed from carbon $2s$ orbitals and hydrogen $1s$ orbitals. The C–H bonds can point in any direction because the $2s$ orbitals are not directional.

A better description is obtained by constructing two 2*sp* hybrids on each carbon from the 2*s* and $2p_z$ orbitals. The orbital regions of the two 2*sp* hybrids on the same atom point in opposite directions. We construct a carbon–carbon σ bonding orbital from the two 2*sp* hybrid orbitals that overlap between the carbon atoms. Call this the 1σ bonding orbital. On each carbon atom, this leaves a 2*sp* hybrid orbital with an orbital region that is directed away from the C–C bond. From each of these and a hydrogen 1*s* orbital we form a carbon–hydrogen σ bonding orbital, placing the hydrogens on the same axis as the C–C bond (the *z* axis). Call these two bonding orbitals $\sigma A'$ and $\sigma B'$. The π bonds are constructed from the unhybridized $2p_x$ and $2p_y$ orbitals, as before. The electron configuration is now

$$(1sA)^2(1sB)^2(\sigma A')2(\sigma B')^2(1\sigma)^2(\pi_u 2p_x)^2(\pi_u 2p_y)^2$$

This electron configuration is similar to the earlier configuration, but the wave function corresponding to it provides a lower energy (greater bonding energy) due to the greater overlap of the 2*sp* hybrid orbitals, and it correctly predicts that the molecule is linear. The triple bond still consists of a σ bond and two π bonds. The σ bond is made from two 2*sp* hybrid orbitals the π bonds are made from unhybridized *p* orbitals. This is the general pattern that will occur with our simple policy of making LCAO molecular orbitals from no more than two atomic orbitals.

Exercise 18.35

Describe the bonding in N_2 using orbitals similar to those in the second description of acetylene.

In addition to the *sp* and sp^3 hybrid orbitals, there are hybrid orbitals constructed from one *s* orbital and two *p* orbitals. From the 2*s*, $2p_x$, and $2p_y$ orbitals, three $2sp^2$ hybrid orbitals can be constructed:

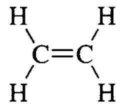
$$\psi_{2sp^2,1} = -\sqrt{\frac{1}{3}}\,\psi_{2s} + \sqrt{\frac{2}{3}}\,\psi_{2p_x} \qquad (18.6\text{-}7a)$$

$$\psi_{2sp^2,2} = -\sqrt{\frac{1}{2}}\,\psi_{2s} - \sqrt{\frac{1}{6}}\,\psi_{2p_x} + \sqrt{\frac{1}{2}}\,\psi_{2p_y} \qquad (18.6\text{-}7b)$$

$$\psi_{2sp^2,3} = -\sqrt{\frac{1}{2}}\,\psi_{2s} - \sqrt{\frac{1}{6}}\,\psi_{2p_x} + \sqrt{\frac{1}{2}}\,\psi_{2p_y} \qquad (18.6\text{-}7c)$$

The orbital regions of these $2sp^2$ hybrids are directional and lie 120° apart from each other in the *x*–*y* plane. Figure 18.25a shows the direction of the symmetry axes for the three $2sp^2$ orbitals and Figure 18.25b shows a cross section of the orbital region for one of them.

The $2sp^2$ hybrid orbitals can be used to construct approximate wave functions for molecules containing double bonds. For example, ethene (ethylene) has the following structural formula



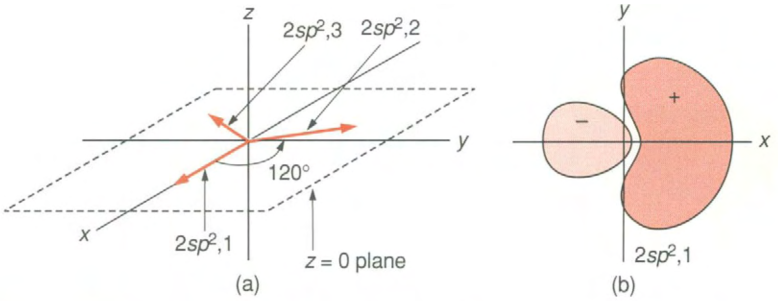


Figure 18.25. The sp^2 Hybrid Orbitals. (a) **Directions of the symmetry axes of the Orbital Regions of the 2*sp*,2 hybrid orbitals.** (b) **A cross section of an orbital region.** Since only the $2p_x$ and $2p_y$ atomic orbitals are used in these hybrid orbitals, the directions of maximum extension lie in the x–y plane, 120° apart. Again, the orbital region resembles those of the other hybrid orbitals except for direction.

The molecule is planar with a C–C–H bond angle of 122°. To describe the bonding in this molecule we construct three σ bonding orbitals around each carbon from the $2sp^2$ hybrids. Let the plane of the molecule be the x–y plane and orient the x axis through the double bond. The hybrids in Eq. (18.6-7) are appropriate for both carbons if we reverse the direction of the x axis for one carbon to make the larger lobes of the two $2sp^2$ orbital regions point toward each other. We construct a C–C σ bonding orbital from the $2sp^2$ hybrid orbitals with orbital regions that overlap between the carbon atoms. Denote this molecular orbital by 1σ. The C–C π bonding orbital is a linear combination of the two unhybridized $2p_z$ orbitals. Denote this orbital by 1π. Construct each of four C–H bonding orbitals from a $2sp^2$ hybrid and a hydrogen $1s$ orbital. Denote them by 2σ, 3σ, 4σ, and 5σ. The electron configuration of the molecule in the ground state is

$$(1sA)^2(1sB)^2(1\sigma)^2(1\pi)^2(2\sigma)^2(3\sigma)^2(4\sigma)^2(5\sigma)^2$$

Since the nuclei must be placed on the symmetry axes of the hybrid orbitals to have good σ bonds, the C–C–H bond angles equal 120°, in fairly good agreement with the experimental value of 122°.

Exercise 18.36

Describe the bonding in diatomic carbon using orbitals such as those used in ethylene. Do you think this description would be superior to that in Section 18.2?

The Valence Bond Description of Polyatomic Molecules

In the examples that we have considered so far, no antibonding orbitals were needed. In such cases we can obtain a valence bond wave function by replacing each pair of bonding molecular spin orbitals with a bond factor such as that of Eq. (18.3-8). The same types of hybrid orbitals can be used, and hybrid orbitals were first used in the valence bond method. 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. The nuclei are placed to maximize the overlap of the atomic orbitals as in our simple molecular orbital treatment. In early applications of the valence bond theory, the strength of a bond was assumed to be proportional to the overlap integral.

For the water molecule a partially antisymmetrized (but unnormalized) valence bond wave function is

$$\begin{aligned}\Psi_{\mathrm{VB}} = {} & \psi_{1s\mathrm{O}}(1)\alpha(1)\psi_{1s\mathrm{O}}(2)\beta(2)\psi_{2sp^3,1}(3)\alpha(3)\psi_{2sp^3,1}(4)\beta(4) \\ & \times \psi_{2sp^3,4}(5)\alpha(5)\psi_{2sp^3,4}(6)\beta(6) \\ & \times [\psi_{2sp^3,2}(7)\psi_{1s\mathrm{A}}(8) + \psi_{1s\mathrm{A}}(7)\psi_{2sp^3,2}(8)][\alpha(7)\beta(8) - \beta(7)\alpha(8)] \\ & \times [\psi_{2sp^3,3}(9)\psi_{1s\mathrm{B}}(10) + \psi_{1s\mathrm{B}}(9)\psi_{2sp^3,3}(10)][\alpha(9)\beta(10) - \beta(9)\alpha(10)]\end{aligned} \tag{18.6-8}$$

where 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. The hydrogen atoms are placed on the symmetry axes of the oxygen hybrid orbitals. This wave function corresponds to nonpolar covalent bonds. 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. An ionic term could be added as in Eq. (18.4-16), writing

$$\Psi_{\mathrm{MVB}} = c_{\mathrm{VB}}\Psi_{\mathrm{VB}} + c_{\mathrm{I}}\Psi_{\mathrm{I}} \tag{18.6-9}$$

where Ψ_{I} is the completely ionic wave function, containing only the ionic terms with both electrons on the oxygen, and where the value of the coefficients c_{VB} and c_{I} would be determined by minimizing the variational energy.

*Exercise 18.37

Write the expression for Ψ_{I} in Eq. (18.6-9).

The ionic character of the bond can also be represented by placing an ionic term in each bonding factor. The space factor of the first bonding factor would become

$$[\psi_{2sp^3,2}(7)_{1s\mathrm{A}}(8) + \psi_{1s\mathrm{A}}(7)\psi_{2sp^3,2}(8) + c\psi_{2sp^3,2}(7)\psi_{2sp^3,2}(8)] \tag{18.6-10}$$

with a similar factor for the other bond. Only one ionic term is included, with both electrons placed on the more electronegative oxygen atom. The value of the coefficient c could be optimized by minimizing the variational energy of the molecule.

Exercise 18.38

Using the valence bond method, give a description of the bonding in

a. Ammonia
b. Methane
c. Hydrogen fluoride

Valence bond descriptions of multiple bonds are also similar to the LCAO-MO description, with a double bond consisting of a σ bond and a π bond and a triple bond consisting of a σ bond and two π bonds. Each bonding factor replaces a pair of LCAO spin orbitals, but nonbonding orbitals are the same in both methods. There are no analogues to antibonding orbitals in the simple valence bond method, so molecules that require antibonding orbitals cannot be well described in this method. Molecules with unpaired electrons such as O_2 also cannot be well described in this method.

EXAMPLE 18.12

Describe the bonding in the ethyne (acetylene) molecule, using the valence bond method.

Solution

Four electrons occupy the two carbon $1s$ space orbitals. Two electrons occupy a carbon–carbon σ bonding factor made from a $2sp$ hybrid on each carbon, and four electrons occupy two carbon–hydrogen σ bonding factors made from a $2sp$ hybrid orbital on a carbon atom and a $1s$ orbital on a hydrogen atom. The last four electrons occupy two carbon–carbon π 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 18.39

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 three common types of 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, which are called dsp^3 hybrids if the d orbital is from the next lower shell or sp^3d hybrids if the d orbital is from the same 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. The sp^3d orbitals can be used to construct σ LCAO molecular orbitals or valence bonding factors for molecules such as IF_3, PF_5, SF_4, etc., that have five pairs of electrons in the valence shell of a central atom.

Exercise 18.40

Write the LCAO-MO electron configuration of the iodine trifluoride molecule. Choose arbitrary subscripts for the five sp^3d hybrids and the σ bonding orbitals, but specify the direction of the orbital region of each. 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.

Hybrid orbitals can also be formed from two d orbitals, one s orbital, and three p orbitals. These orbitals are called d^2sp^3 if the d subshell is from the shell below that of the s and p orbitals, and sp^3d^2 if the d subshell is from the same shell. These six orbitals have symmetry axes pointing along the positive and negative Cartesian coordinate axes, pointing toward the apices of a regular octahedron. When these hybrids are used in a molecule wave function, all of the bond angles are equal to 90°. Examples of molecules with this electronic geometry are SF_6, XeF_4, and various complexes of transition metals. The five types of hybrid orbitals we have defined suffice to give all of the electronic geometries predicted by the VSEPR theory for up to six pairs of valence shell electrons. In addition, the dsp^2 or sp^2d hybrids give a square planar electronic geometry.

Exercise 18.41

Using either the LCAO-MO method or the valence bond method, describe the bonding in the following molecules, including a specification of the molecular geometry.

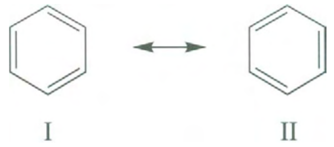
a. Sulfur hexafluoride, SF_6
b. Xenon difluoride, XeF_2
c. Phosphorus trichloride, PCl_3

Delocalized Bonding

In all of the cases considered thus far, we have used LCAO molecular orbitals constructed from no more than two atomic orbitals or have used valence bond factors containing two atomic orbitals. In some molecules this kind of description is unsatisfactory. The deficiency is usually that the approximate wave function has different kinds of bonds in two locations where the actual molecule has two equivalent bonds. In the molecular orbital method this deficiency can be remedied by using delocalized LCAO-MOs, which are linear combinations of atomic orbitals centered on three or more nuclei. In the valence bond method, it can be remedied by the use of a technique called *resonance*.

The Valence-Bond Treatment of Delocalized Bonding

We assume that the benzene (C_6H_6) molecule is hexagonal with six equivalent carbon–carbon bonds. In the valence bond treatment any bond is either a single bond, a double bond, or a triple bond, and each bond consists of electrons shared by two atoms. To represent benzene, we draw two structural formulas corresponding to different valence bond wave functions:



These structures are called **resonance structures**. It is customary to write a double-headed arrow between resonance structures. Let the valence bond wave functions corresponding to the two structures be called Ψ_{I} and Ψ_{II}. The unhybridized $2p_z$ orbitals are used to form the three π bonding factors, and the only difference between the two structures is the location of the three π bonds.

The wave function of the molecule is a linear combination:

$$\Psi = c_{\mathrm{I}}\Psi_{\mathrm{I}} + c_{\mathrm{I}}\Psi_{\mathrm{II}} \tag{18.6-11}$$

where c_{I} and c_{II} are coefficients whose values can be found by minimizing the variational energy. This is the mathematical expression of resonance. Neither formula alone represents the structure of the molecule, and the linear combination corresponds to "blending" of the two structural formulas. Since the resonance structures differ only by the double bond locations, the two coefficients in this case will be equal to each other. 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 presumably have smaller coefficients, so they are usually omitted.

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**, but this same term 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. The value of this estimate is $150\,\mathrm{kJ\,mol^{-1}}$.

***Exercise 18.42**

Verify the estimate of the resonance energy by calculating the enthalpy changes of hydrogenation of benzene and of ethylene.

LCAO-MO Treatment of Delocalized Bonding

In the LCAO-MO method the concept of resonance is not needed to describe delocalized bonding. Instead, delocalized LCAO-MOs are constructed that are linear combinations of atomic orbitals centered on more than two nuclei. In the case of benzene we proceed as follows: We first construct ordinary (localized) σ bonding orbitals for the carbon–carbon bonds and carbon–hydrogen bonds. Since the molecule is hexagonal, all bond angles are equal to 120°. We choose the x–y plane for the plane of the molecule, so that $2sp^2$ carbon hybrid orbitals are the appropriate atomic orbitals for the σ LCAO-MOs, turning the x and y axes or changing the coefficients of the $2p$ orbitals in the hybrids as necessary. The $2p_z$ orbitals remain unhybridized.

The molecule has 42 electrons. Twelve of these will occupy the six nonbonding carbon $1s$ space orbitals. Twelve electrons will occupy the six carbon–carbon σ bonding space orbitals, and 12 will occupy the six carbon–hydrogen σ bonding space orbitals. This leaves six electrons and six unhybridized $2p_z$ carbon space orbitals with orbital regions lying above and below the plane of the molecule. We construct delocalized LCAO-MOs from these six $2p_z$ orbitals:

$$\varphi_i = c_1^{(i)}\psi_1 + c_2^{(i)}\psi_2 + c_3^{(i)}\psi_3 + c_4^{(i)}\psi_4 + c_5^{(i)}\psi_5 + c_6^{(i)}\psi_6 \tag{18.6-12}$$

where i is an index used to specify which of the delocalized LCAO-MOs is meant, and where the six unhybridized $2p_z$ orbitals are denoted by $\psi_1, \psi_2, \ldots, \psi_6$. Since there are six atomic orbitals, six independent delocalized molecular orbitals can be constructed. All six atomic orbitals are included in each LCAO-MO, so an electron occupying such an orbital moves around the entire ring of carbon atoms. These LCAO-MOs are called π orbitals, although we cannot specify an angular momentum projection on a single bond axis.

The Hückel Method

The coefficients in Eq. (18.6-12) can be determined by applying the variational method or by the self-consistent field method. However, in most calculations one does not begin with the Born–Oppenheimer Hamiltonian operator and carry out the full calculation, but uses approximate Hamiltonians and makes other approximations, ultimately using empirical data to assign numerical values. Such a procedure is called a **semiempirical** method. The Hückel method was the first semiempirical molecular orbital method, and was developed in the 1930s. It is applied only to planar molecules with delocalized π bonding and treats only the electrons in these bonds.

The Hückel method is named for Erich Hückel, 1896–1980, a German chemist who was also the co-inventor of the Debye–Hückel theory of electrolyte solutions.

The Hückel method begins with the assumption that the σ bond framework has already been treated. The Hamiltonian for the π electrons is assumed to be separate from that for the σ framework, and is assumed to be a sum of "effective" one-electron Hamiltonian operators that include electron–electron repulsions in some kind of unspecified average way. No specific expression for these one-electron operators is given, and no integrals are explicitly calculated. The wave function of the π electrons is a product of one-electron functions (delocalized orbitals) and the energy of these electrons is a sum of orbital energies.

The variational method is applied to minimize the energy of the π electrons, which is the sum of orbital energies. The energy of the molecule can be minimized by separately minimizing the orbital energies. The variational energy for the ith delocalized orbital is

$$W_i = \frac{\int \varphi_i^* \hat{H}_1^{\text{eff}} \varphi_i d^3\mathbf{r}}{\int \varphi_i^* \varphi_i d^3\mathbf{r}} \tag{18.6-13}$$

where $\hat{\mathrm{H}}_1^{\text{eff}}$ is the effective one-electron Hamiltonian operator for one electron, and where $d^3\mathbf{r}$ stands for the volume element of this electron.

When the expression of Eq. (18.6-12) is substituted into Eq. (18.6-13), W is given as a function of the coefficients $c_1^{(i)}, c_2^{(i)}$, etc., and the minimum in W is found by differentiating W with respect to each of the c coefficients and setting these derivatives equal to zero. This procedure gives a set of simultaneous equations that can be solved for the coefficients. The simultaneous equations are linear homogeneous equations, which must obey a certain condition in order to have a nontrivial solution.[9] This condition is an equation that equates a certain determinant to zero, and is called a **secular equation**. It can be solved to find the permissible values of W, the orbital energy. The number of values of the orbital energy W is equal to the number of orbitals in the linear combinations, although some of the values may be equal to each other. A different set of $c_j^{(i)}$ coefficients is obtained by solving the simultaneous equations for each value of W. Each set gives a different delocalized molecular orbital, so there are as many delocalized orbitals as there are basis functions. The procedure, which involves a further set of assumptions, is discussed in Appendix H.

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[9] Levine, *op. cit.*, pp. 202ff (Note 4).

We present without derivation some of the results for benzene. The lowest orbital energy is

$$W = \alpha + 2\beta \tag{18.6-14}$$

since β turns out to be negative. When this value of W is substituted into the simultaneous equations, we obtain equal values for all six c's, so that the normalized lowest-energy LCAO-MO is

$$\varphi_1 = \sqrt{\frac{1}{6}}[\psi_1 + \psi_2 + \psi_3 + \psi_4 + \psi_5 + \psi_6] \tag{18.6-15}$$

Figure 18.26a shows the orbital energies of this space orbital and the other five π LCAO-MOs.[10] Three of the orbital energies are relative minima in the energy, and three are relative maxima. Note the interesting fact that 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. Figure 18.26b shows a view of the orbital regions of the six LCAO-MOs, looking perpendicular to the plane of the molecule. The broken lines show the nodal planes.

The general relation between energy and number of nodes is followed. There are no nodal surfaces in the lowest-energy orbital, one nodal plane in 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 could perhaps have guessed the number of energy levels and the number of states in each from the facts: (1) no more than three nodal planes can be drawn between the atoms in the six-membered ring, (2) there is only one way to have no nodes, (2) there are two perpendicular directions in which a single nodal plane can be drawn, (3) there are two simple ways to draw two nodal planes between the atoms, and (4) there is only one way to draw three nodal planes between the atoms.

There are six electrons that occupy the π orbitals, so that in the ground state each of the lowest three space orbitals is occupied by two electrons, as shown by arrows in Figure 18.26a. In the first excited state, an electron in one of the highest occupied molecular orbitals will be promoted to one of the lowest unoccupied molecular orbitals, increasing the energy of the molecule by $2|\beta|$. This transition can be observed spectroscopically, and the value of β is ordinarily determined from these observations.

Exercise 18.43

From the fact that benzene absorbs strongly at wavelengths near 180 nm, estimate the value of β.

EXAMPLE 18.13

Describe the delocalized π molecular orbitals for *trans*-1,3-butadiene.

Solution

The molecule is planar, with bond angles near 120°. We choose the x–y plane for the plane of the molecule, and construct $2sp^2$ hybrids for the σ bonds. After the nonbonding electrons and σ bonding electrons are assigned, there are four electrons and four unhybridized $2p_z$ carbon orbitals left. The delocalized orbitals are linear combinations of all four of these orbitals.

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[10] Levine, *op. cit.*, pp. 555ff (Note 4).

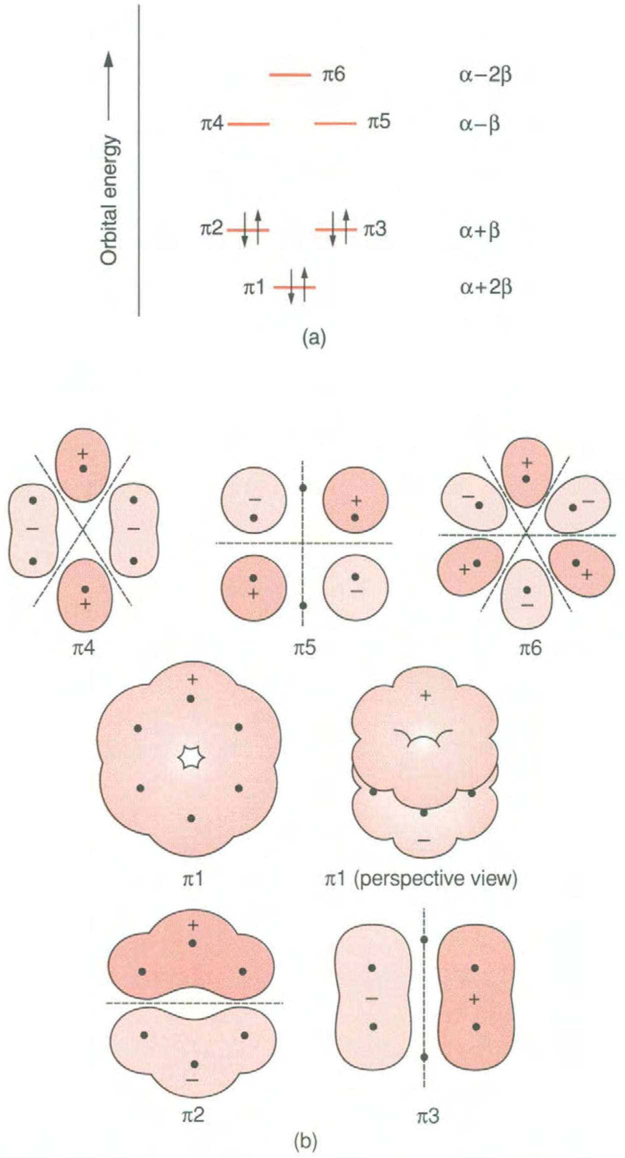


Figure 18.26. Results of the Hückel Molecular Orbital Calculation for Benzene. (a) **Orbital energies.** It is interesting that if a diagram of the hexagonal shape of the six carbons is placed over the orbital energy diagram, each corner corresponds to one of the orbital energies. (b) **The orbital regions.** Each orbital region is shown from above (from the direction of the positive end of the *z* axis), except that the orbital region of the $\pi 1$ orbital is shown twice, once from above and once from an oblique angle. Each of the orbital regions has a region below the plane of the nuclei and one above the plane of the nuclei. The sign shown applies to the region above the plane. The region directly below has the opposite sign, because there is a nodal plane in the plane of the nuclei. Note that the energies correlate with the numbers of nodes in the same way as with other systems: the more nodes, the higher the energy.

Without doing any calculations, we can see that there are four possible numbers of nodes between the atoms: no nodes, one node, two nodes, and three nodes. There is only one symmetrical way to have each number of nodes. Therefore, the orbital regions of the four delocalized orbitals must be as shown in Figure 18.27a, looking perpendicularly to the plane of the molecule. Since each orbital has a different number of nodes from the others, the orbitals are nondegenerate. Figure 18.27b gives the energies from the Hückel calculation. Each of the two lowest-energy orbitals is occupied by two electrons in the ground state.

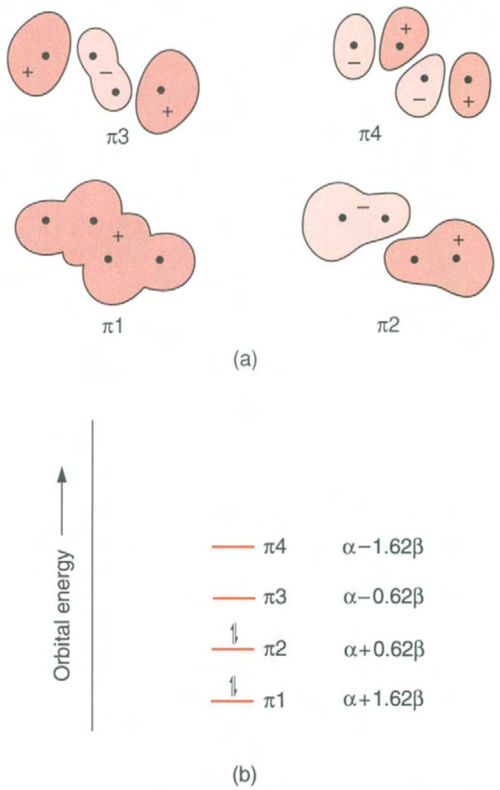
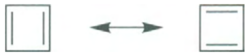


Figure 18.27 Results of the Hückel Molecular Orbital Calculation for 1,3-Butadiene. (a) **The orbital regions for the 1,3-butadiene Hückel molecular orbitals.** These orbital regions are shown in much the same way as those for the benzene molecule shown in Figure 18.26. (b) **The orbital energies.** Once again, we see the correlation between number of nodes and energy: the more nodes, the higher the energy.

Exercise 18.44

a. Describe the π LCAO-MOs in the cyclobutadiene molecule, assuming a square structure. Use $2sp^2$ hybrid orbitals for the σ bonds, although they do not quite fit. There are two ways to make a single node in an LCAO-MO (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 (this is the correct structure; the molecule is not aromatic).[11]

The Free-Electron Molecular Orbital Method

The free-electron molecular orbital (FEMO) method is a way of representing delocalized molecular orbitals that is even simpler than the Hückel method. The electrons that move over several bonds are assumed to move in a one-dimensional box with an appropriate length. Repulsions between the electrons are neglected, so that the wavefunction for the delocalized electrons contains a product of single-electron functions. We discuss 1,3-butadiene, assuming that the σ-bond framework has been separately treated. The experimental carbon–carbon bond lengths are 146 pm for the center bond and 134 pm for the others.[12] From Figure 18.27a, we see that the orbital regions extend beyond the end carbon nuclei, so we assign the length of the box in which the π electrons move to be the sum of the three bond lengths plus one additional bond length at each end with a length equal to the average of the two bond lengths, giving a total box length of 694 pm.

The energy eigenfunctions and energy levels of a particle in a box are given by Eqs. (14.5-10) and (14.5-11):

$$\psi = \psi_n = \sqrt{\frac{2}{a}}\sin\left(\frac{n\pi x}{a}\right), \qquad E = E_n = \frac{h^2n^2}{8ma^2} \tag{18.6-16}$$

where a is the length of the box and n is a quantum number (a positive integer). Since we have four electrons, the Aufbau principle gives the ground state wave function (including only the π electrons) as

$$\Psi_{\mathrm{gs}} = \psi_1(1)\alpha(1)\psi_1(2)\beta(2)\psi_2(3)\alpha(3)\psi_2(4)\beta(4) \tag{18.6-17}$$

The ground-state π-electron energy is

$$E_{gs} = \frac{h^2}{8ma^2}(1+1+4+4) = \frac{10h^2}{8ma^2} \tag{18.6-18}$$

EXAMPLE 18.14

Calculate the wavelength of the light absorbed when 1,3-butadiene makes the transition from the ground state to the first excited state.

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[11] Levine, *op. cit.*, p. 559 (Note 4); T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, 3d ed., Harper and Row, New York, 1987, pp. 43–44.

[12] K. Kuchitsu, F. Tsutomu, and Y. Morino, *J. Mol. Struct.*, **37**, 2074 (1962).

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 only fair agreement with the experimental value of 217 nm. Better agreement could be attained by adding less than a full bond length at each end of the carbon–carbon chain.

***Exercise 18.45**

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. Compare with the experimental value, $24{,}000\,\mathrm{cm^{-1}}$.

Applications of Symmetry to Molecular Orbitals

The way in which we have treated the electronic structure of polyatomic molecules thus far has not exploited the symmetry properties of the molecules. The reason for this is that we have restricted our descriptions of chemical bonding largely to orbitals made from no more than two atomic orbitals, and have included hybrid orbitals in our basis sets to achieve this goal. The molecular orbitals that we have created are not necessarily eigenfunctions of the symmetry operators belonging to the molecule.

Better LCAO-MOs can be constructed by making linear combinations of all atomic orbitals in our basis set. Hybrid orbitals are not needed in the basis set, and the LCAO-MOs are linear combinations of all atomic orbitals in the basis set and have orbital regions that extend over the entire molecule. These delocalized orbitals can be eigenfunctions of the symmetry operators belonging to the molecule.

Consider the H_2O molecule again. We now assume that each molecular orbital is a linear combinations of all of the basis orbitals. The minimal basis set contains the oxygen $1s$, $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals and the $1s$ orbitals of the two hydrogen atoms. In Section 18.5 we listed the symmetry operators that belong to the H_2O molecule: a $\hat{C}_2$ operator with its symmetry element bisecting the bond angle and coinciding with the z axis, a $\hat{\sigma}_{\mathrm{v}}$ reflection with its symmetry element in the plane of the molecule (the y–z plane) and a $\hat{\sigma}_{\mathrm{v}}$ operator with its symmetry element perpendicular to the plane of the molecule. The oxygen orbitals are eigenfunctions of these operators, but the two hydrogen $1s$ orbitals are not eigenfunctions of these operators. We replace these $1s$ orbitals by linear combinations that are eigenfunctions of the symmetry operators:

$$\psi_{\mathrm{a}_1} = \Psi_{1s\mathrm{Ha}} + \psi_{1s\mathrm{Hb}} \tag{18.6-19}$$

$$\psi_{\mathrm{b}_2} = \Psi_{1s\mathrm{Ha}} - \psi_{1s\mathrm{Hb}} \tag{18.6-20}$$

The labels on these linear combinations are explained in Appendix I. The basis set now consists of the oxygen $1s$, $2s$, $2p_x$, $2p_y$, and $2p_z$ orbitals, and ψ_{a_1} and ψ_{b_2}.

***Exercise 18.46**

Find the eigenvalues of each of the basis orbitals for each of the operators that belong to the H_2O molecule.

The LCAO molecular orbitals are written in the form

$$\begin{aligned}\psi = {} & c_{1sO}\psi_{1sO} + c_{2sO}\psi_{2sO} + c_{2p_zO}\psi_{2p_zO} + c_{2p_yO}\psi_{2p_yO} + c_{2p_xO}\psi_{2p_xO} \\ & + c_{a_1}\psi_{a_1} + c_{b_2}\psi_{b_2} \qquad (18.6\text{-}21)\end{aligned}$$

Only basis orbitals of the same symmetry enter in any one molecular orbital in order for the molecular orbital 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. There is no need to constrain the bond angle to be equal to 109° or any other value, and an optimum bond angle and bond lengths can be found by solving the problem for various bond lengths and angles and then choosing the conformation of minimum energy. Table 18.6 contains the value of coefficients determined by the Hartree–Fock–Roothaan method for a number of orbitals. The orbital designations are explained in Appendix I.

It is possible to take certain linear combinations of the Hartree–Fock–Roothaan delocalized LCAO-MOs that have orbital regions concentrated between pairs of atoms. These molecular orbitals are constructed such that the energy of repulsion of the electrons in one orbital with those in another orbital is minimized. They are called **energy-localized orbitals**. Formation of energy-localized orbitals for the ethylene molecule represents a double bond as two equivalent bonds[13] and represents a triple bond as three equivalent orbitals. These three orbitals 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.[14] Since the energy-localized orbitals are linear combinations of the original LCAO-MOs, it turns out that using them does not change the calculated energy.[15]

Table 18.6. SCF Orbitals for H_2O

MO	c_{1sO}	c_{2sO}	c_{2p_zO}	c_{2p_yO}	c_{2p_xO}	c_{a_1}	c_{b_2}
1_{a_1}	1.000	0.015	0.003	0	0	−0.004	0
2_{a_1}	−0.027	0.820	0.132	0	0	0.152	0
1_{b_2}	0	0	0	0.624	0	0	0.424
3_{a_1}	−0.026	−0.502	0.787	0	0	0.264	0
1_{b_1}	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).

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[13] Levine, *op. cit.*, pp. 450ff (Note 4).

[14] Levine, *op. cit.*, p. 453 (Note 4).

[15] Levine, *op. cit.*, pp. 481ff (Note 4).

18.7

More Advanced Treatments of Molecular Electronic Structure

Our discussion of molecular electronic structure has been extremely crude compared with current quantum chemistry research. The qualitative description of bonding using LCAO-MOs made from only two atomic orbitals is useful for only the most elementary applications, even with hybrid orbitals. The Hückel method and the free-electron method were both designed for hand calculation. In the past several decades, modern digital computers have made calculations possible that previously could only be dreamed of, and a great deal of research effort has been expended in quantum-chemical calculations with the goal of calculating wave functions, molecular geometries, and molecular energies accurately enough for chemical purposes.

There are now a number of easily usable software packages that carry out some of the established methods. Software packages such as CAChe (an acronym for Computer Assisted Chemistry) and Spartan not only deliver numerical results but also graphically exhibit orbital regions, total electron density regions, and other results, and also exhibit vibrational modes and calculated vibrational frequencies as well as electronic spectra.

There are two approaches that are commonly used in these calculations, and in both approaches the molecular orbitals are represented as linear combinations of basis functions (LCAO-MOs).

1. The **semiempirical** approach is somewhat similar to the Hückel method. It begins with assumed effective one-electron Hamiltonian operators as in the Hückel method, but generally adds interelectron repulsion terms. Hartree–Fock–Roothaan calculations are carried out, but since the one-electron operators are generally not explicitly expressed, some integrals are approximated by zero and empirical data are used to assign values to other integrals.
2. The **ab initio** ("from the beginning") approach begins with the correct nonrelativistic Hamiltonian, and requires no inputs of empirical information, although nuclei are often placed according to experimental data on bond lengths and angles.

Dewar and Storch have written a review article comparing the results of different semiempirical and ab initio methods in calculating enthalpy changes of reactions.[16] At the time this article was published, no method had given accuracy that is adequate for quantitative chemical purposes for anything but a few small molecules. However, some progress has been made since that time.

Semiempirical Methods

There are a number of semiempirical methods, each with its own set of approximations. The typical calculation uses the Hartree–Fock–Roothaan self-consistent field method, although the extended Hückel method uses the variational method in the same way as the simple Hückel method. The molecular orbitals are represented as linear combinations of a set of basis functions. There are numerous integrals to be calculated, including matrix elements of one-electron Hamiltonians (see Appendix H), overlap integrals, and integrals representing expectation values of interelectron repulsions. Two types of approximations are invoked: the first is the assumption that certain integrals

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[16] M. J. S. Dewar and D. M. Storch, *J. Am. Chem. Soc.*, **107**, 3898 (1985).

can be approximated by zero, and the second is a scheme to assign values to other integrals such that results agree with experimental data.

The Extended Hückel Method. This method was pioneered by Wolfsberg and Helmholz[17] It is not restricted to the electrons in π orbitals and can treat molecules that are not planar and that do not necessarily have conjugated systems of bonds. All valence shell electrons are included in the treatment. It starts with the same set of equations as the simple Hückel method, representing each orbital with a linear combination like that of Eq. (18.6-12)

$$\psi = \sum_{i=1}^{n} c_i f_i \tag{18.7-1}$$

where $f_1, f_2, \ldots$ are a set of basis functions that includes atomic orbitals from all atoms in the molecule. Slater-type orbitals (STOs), introduced in Section 17.3, are usually chosen because the computations require less computer time when these functions are used. For the extended Hückel method, a **minimal set of basis functions** is used that includes all atomic orbitals in the valence shell of every atom. In more sophisticated methods the basis set also includes the inner-shell atomic orbitals.

The Hamiltonian for the valence electrons is assumed to be a sum of effective one-particle Hamiltonians. No explicit formula is used for the effective Hamiltonians. The approximations employed differ somewhat from the simple Hückel method. The interelectron repulsive energy is neglected, but the overlap integrals are explicitly calculated. The matrix elements of the effective Hamiltonian, Eq. (H-3) of Appendix H, are approximated using formulas that are chosen to give agreement with experiment. 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 an electron from the valence shell of the atom. For a hydrogen atom the valence orbital is the $1s$ orbital, and the VSIP is 13.6 eV. Wolfsberg and Helmholtz approximated the off-diagonal elements by the mean of the VSIP of each orbital times a fixed constant times the overlap integral:

$$H_{\mathrm{ab}} = \tfrac{1}{2}K(H_{\mathrm{aa}}^{\mathrm{eff}} + H_{\mathrm{bb}}^{\mathrm{eff}})S_{\mathrm{ab}} \tag{18.7-2}$$

The constant K has been assigned various values from 1 to 3. A value of 1.75 is common. Ballhausen and Gray use the geometric mean instead of the arithmetic mean.[18]

The extended Hückel method is sometimes used to calculate the molecular energy for various conformations and to find the conformation of lowest energy. Even though electron–electron and nuclear repulsions are omitted, reasonable results are obtained, and the results are sometimes used for starting points of more sophisticated calculations.

Exercise 18.47

Use a software package such as CAChe 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)

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[17] M. Wolfsberg and L. Helmholz, *J. Chem. Phys.*, **20**, 837 (1952).

[18] C. J. Ballhausen and H. B. Gray, *Molecular Orbital Theory*, W. A. Benjamin, New York, 1964, p. 118.

The Pariser–Pople–Parr method. This is the simplest implementation of the self-consistent field method. Like the Hückel method, it treats only the electrons in delocalized π orbitals in planar molecules and represents these orbitals as linear combinations of basis set of orbitals including only the unhybridized p orbitals perpendicular to the plane of the molecule. All overlap integrals are assumed to vanish, as in the Hückel method, but some of the integrals representing interelectron repulsions are included in the method. Two notations are used for these integrals:

$$(rs|tu) = \left\langle rt\left|\frac{1}{r_{12}}\right|su\right\rangle = \int\int f_r^*(1)f_t^*(2)\frac{1}{r_{12}}f_s(1)f_u(2)\,dq_1\,dq_2 \tag{18.7-3}$$

These integrals are multiplied by the square of the electronic charge to give the repulsion energy. An approximation called **zero differential overlap** is invoked to set many of these integrals equal to zero. This name is somewhat confusing because the approximation is not applied to overlap integrals but to these electron-repulsion integrals. The approximation sets integrals like that of Eq. (18.7-3) equal to zero unless $r = t$ and $s = u$.

When the LCAO-MOs are substituted into the Hartree–Fock equations and the above approximations are applied, a set of equations called the Roothaan equations is obtained.[19] The Roothaan equations are solved by iteration and the results are the orbital energies and the values of the c coefficients for each of the LCAO-MOs.

Other Semiempirical Methods. There are a number of other 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[20] and PM3[21] methods, which are included in a package of programs called MOPAC.[22] 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 18.7 summarizes some characteristics of different semiempirical methods.

Exercise 18.48

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 18.47. Construct and view the orbital regions and compare your results with the results using the extended Hückel method.

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[19] Levine, *op. cit.*, pp. 405ff (Note 4).

[20] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.*, **107**, 3902 (1985).

[21] J. J. P. Stewart, *J. Comput. Chem.*, **10**, 209 (1989); **10** 221 (1998).

[22] 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 18.7. 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 seif-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? (y = yes, n = no)
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)

Ab Initio Methods

The principal differences between ab initio and semiempirical calculations is that ab initio calculations use the correct Hamiltonian operator and calculate all of the integrals instead of relying on experimental information to assign values to integrals. The principal ab initio methods are based on the Hartree–Fock–Roothaan self-consistent field procedure, which uses LCAO-MOs constructed from some basis set as in Eq. (18.6-1). 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 hydrogenlike orbitals. These orbitals contain the same spherical harmonic functions as the hydrogenlike 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.[23]

In addition to Slater-type orbitals, **gaussian orbitals** have been widely used. In these functions, the radial factor is

$$R(r) = e^{-br^2} \tag{18.7-4}$$

where b is a constant. The correct spherical harmonic functions are used for the angular factors. 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.

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[23] Levine, *op. cit.*, p. 544 (Note 4).

Some basis sets contain multiple gaussian functions chosen to 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 is used to improve the energies. This means that the wave function, instead of being a Slater determinant corresponding to a particular electronic configuration, is a linear combination of Slater determinants, each corresponding to a different configuration. Up to a million configurations have been used, but present-day computers still require a very long time to do a calculation with this many configurations.

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 approximate the energy change of a reaction. The energy change in a reaction is typically near $500\,\mathrm{kJ\,mol^{-1}}$ (about $5\,\mathrm{eV}$ molecule^{-1}), while the total energies of the molecules might be several thousand eV (several hundred thousand $\mathrm{kJ\,mol^{-1}}$). 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.

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 might be a source of such information.

Molecular Mechanics

Molecular mechanics is a branch of calculational chemistry that has achieved some degree of success in predicting geometries of molecules and intermediates without direct study of the electronic wave functions of a molecule. In this method, approximations to Born–Oppenheimer energies as functions of bond lengths and bond angles are calculated, using various formulas for the interaction of different atoms and groups of atoms in molecules. Such potential energy functions are built into a computer program, which then carries out the process of finding the conformations of minimum potential energy. With many atoms in a molecule, this minimization can be a difficult problem, and various techniques exist for its solution.[24]

Summary of the Chapter

In this chapter, we have discussed the quantum mechanics of electrons in molecules using the Born–Oppenheimer approximation, which is the assumption that the nuclei are stationary as the electrons move. In this approximation the time-independent Schrödinger equation for the hydrogen molecule ion, H_2^+, can be solved exactly to give energy eigenvalues and orbitals dependent on the internuclear distance R.

Linear combinations of atomic orbitals, called LCAO-MOs, provide an approximate representation of molecular orbitals for H_2^+. The ground-state LCAO-MO, called the $\sigma_g 1s$ function, is a sum of the $1s$ atomic orbitals for each nucleus, and is called a

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[24] U. Burkert and N. L. Allinger, *Molecular Mechanics.* ACS Monograph 177, American Chemical Society, Washington, D.C., 1982.

bonding orbital. The first excited-state LCAO-MO, called the $\sigma_u^* 1s$ function, is an antibonding orbital.

An approximate wave function for a diatomic molecule is a product of two LCAO molecular orbitals similar to those of H_2^+. The ground state of the H_2 molecule corresponds to the electron configuration $(\sigma_g 1s)^2$. A wave function with a single configuration can be improved upon by adding terms corresponding to different electron configurations. Most of the information about an LCAO-MO 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, a bonding factor is included in the wave function. This 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, which are a linear combination of atomic orbitals on the same nucleus. A bonding molecular orbital made from a $2sp$ hybrid on the Li nucleus and a $1s$ orbital on the H nucleus provides an adequate description of the bonding in LiH.

The criteria for a good bonding LCAO-MO were presented: A good bonding LCAO-MO is formed from a pair of atomic orbitals with nearly equal energies, atomic orbitals with considerable overlap, and atomic orbitals with the same symmetry about the bond axis.

LCAO-MOs for polyatomic molecules were constructed as linear combinations of only two atomic orbitals, conforming to the three general criteria that predict good bonding molecular orbitals. 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°. The sp^2 hybrid orbitals were useful in constructing LCAO-MOs for molecules with double bonds, such as ethene. The sp hybrid orbitals were used in molecules with triple bonds, such as ethyne.

Delocalized bonding was described in the valence bond method by use of the concept of resonance. In the molecular orbital description, delocalized LCAO-MOs are used. For example, in the benzene molecule, six of the electrons occupy delocalized orbitals.

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.

PROBLEMS

Problems for Section 18.1

***18.49** What is the symmetry operation that is equivalent to the product $\hat{i}\hat{\sigma}_h$? Is this the same as the product $\hat{\sigma}_h\hat{i}$?

18.50. What is the symmetry operation that is equivalent to the product $\hat{C}_2\hat{i}$? Is it the same as the product $\hat{i}\hat{C}_2$?

***18.51.** Write the function that is equal to $\hat{C}_{4z}\psi_{2p_x}$.

18.52. Write the function that is equal to $\hat{C}_{2z}\psi_{2p_x}$.

Problems for Section 18.2

18.53. Predict what will be formed if a hydrogen molecule ion in the state corresponding to the $\sigma_g^*2p_x$ LCAO-MO dissociates.

18.54. Sketch the orbital region of the $\sigma_g 3s$ LCAO-MO for a homonuclear diatomic molecule.

18.55. For a homonuclear diatomic molecule, sketch the orbital regions for the six LCAO molecular orbitals that can be formed from the $3p$ atomic orbitals.

18.56. For a heteronuclear diatomic molecule, sketch the orbital region for the LCAO-MO

$$\psi = c_1\psi_{2sA} + c_2\psi_{2p_zA} + c_1\psi_{2sB} - c_2\psi_{2p_zB}$$

where c_1 and c_2 are roughly but not exactly the same size and are both positive. Take the z axis as the bond axis. Determine whether this orbital will be an eigenfunction of $\hat{i}$ and of $\hat{\sigma}_h$. Give the eigenvalues if it is an eigenfunction.

18.57. Sketch the orbital region of the (unusable) LCAO-MO for a diatomic molecule

$$\psi = c(\psi_{1sA} + \psi_{2p_yB})$$

The z axis is the bond axis. Explain why it is unusable.

18.58. By inspection of the orbital regions, predict which united-atom orbital will result from each of the following LCAO-MOs of the hydrogen molecule ion:

a. $\pi_u 2p_x$
b. $\pi_u 2p_y$
c. $\sigma_g 2p_z$

Problems for Section 18.3

***18.59.** 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. $(\pi_u 2p1)(\sigma_g^* 2p, -1)$

18.60. Give the term symbol or symbols for each of the excited electron configurations of the hydrogen molecule:

a. $(\sigma_g 2p0)^2$
b. $(\sigma_g 1s)(\sigma_g 2p0)$

18.61. Give the term symbol for the ground-state electron configuration of each of the second-row homonuclear diatomic molecules (lithium through fluorine).

18.62. 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.

***18.63.** For each of the following ions or molecules, give the bond order and the number of unpaired electrons in the ground state:

a. O_2^-
b. N_2^+
c. F_2^+

18.64. 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. F_2^+
c. Be_2^+

Problems for Section 18.4

18.65. Describe the bonding in the possible molecule LiB. Do you think the molecule could exist?

18.66. Describe the bonding in the possible molecule BeC. So you think the molecule could exist?

18.67. Using the modified valence bond method, describe the bonding of the 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.

18.68. 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.

18.69. By analogy with the $2sp$ hybrid orbitals, sketch the orbital region of the two $3sp$ hybrid orbitals.

18.70. By analogy with the $2sp^3$ hybrid orbitals, sketch the orbital region of one of the $3sp^3$ hybrid orbitals.

18.71. Using the molecular orbital method, describe the bonding of the NaCl molecule. Consider an isolated molecule in the gas phase, not the crystal. Predict what the bonding molecular orbitals will look like if optimized.

18.72. Describe the bonding in the carbon monoxide molecule using the valence bond method. Include ionic terms.

18.73. Describe the bonding in the boron nitride (BN) molecule using the valence bond method. Compare it with diatomic carbon.

18.74. 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.

***18.75.** 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.

18.76. Using average bond energies from Table A.9 in Appendix A, calculate the electronegativity differences for H and C and for H and N. Compare with the values in Table A.21.

***18.77.** Using average bond energies from Table A.9 in Appendix A, calculate the electronegativity differences for C and N and for C and Cl. Compare with the values in Table A.21.

Problems for Section 18.5

18.78. List all of the symmetry operations that belong to the BH_3 molecule. Assign it to a point group, using Figure 18.19.

***18.79.** List all of the symmetry operators that belong to the formaldehyde (CH_2O) molecule. Assign it to a point group, using Figure 18.19.

18.80. Construct the multiplication table for the C_{4v} point group.

18.81. Construct the multiplication table for the $D_{\infty h}$ point group.

18.82. Assign the following molecules to point groups:

a. Dichlorodibromomethane
b. Toluene
c. Naphthalene

***18.83.** Assign the following molecules to point groups:

a. 1,4-Dichlorobenzene
b. 1,2-Dichlorobenzene
c. Tetrachloroethene

Problems for Section 18.6

18.84. Show that the $2sp^2$ hybrid orbitals of Eq. (18.6-7) are normalized and orthogonal to each other.

18.85. Show that the $2sp^3$ hybrid orbitals of Eq. (18.6-4) are normalized and are orthogonal to each other.

18.86. Using the valence bond method with resonance, describe the bonding in CO_3^{2-}.

***18.87.** Say 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.

18.88. Say which of the following molecules will have nonzero dipole moments:

a. $H_2C{=}C{=}CH_2$
b. NO_2
c. CO_2

Explain your answers.

18.89. Show geometrically that the dipole moment of a molecule such as carbon tetrachloride vanishes. Hint: There are four polar bonds of equal magnitude directed along the four tetrahedral directions. Place the bonds on alternate diagonals of a cube and use cartesian components.

18.90. Using hybrid orbitals and LCAO-MOs, describe the bonding and molecular shape of each of the molecules or ions in Problem 18.87.

18.91. Using hybrid orbitals and LCAO-MOs, describe the bonding and molecular shape of each of the molecules in Problem 18.88.

18.92. 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)

18.93. Using the valence bond method, with resonance where appropriate, describe the bonding in the molecules:

a. H_2CO
b. HNO_3
c. SO_2

18.94. The methylene radical, CH_2, is thought to be linear, while 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?

18.95. Describe the bonding of the carbonate ion using LCAO molecular orbitals. 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.

18.96. 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.

***18.97.** 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 $-2.71\,\mathrm{eV}$[25] and explain why the values do not agree.

18.98. The motion of the π 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, etc. Find the energy and wavelength of the photons absorbed in the longest-wavelength ultraviolet absorption and compare with the value given in Problem 18.97.

***18.99.** 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.

18.100. Find the correct fraction of a bond length to add to each end of the carbon–carbon chain in 1,3-butadiene to give agreement with the observed wavelength of light absorbed in the longest-wavelength absorption.

18.101. Write an approximate LCAO-MO wave function without antisymmetrization for the formaldehyde molecule, using no more than two atomic orbitals in an LCAO-MO. Place the C–O bond on the z axis and the H atoms in the y–z plane. Use hybrid orbitals where appropriate. Specify which atomic orbitals make up each LCAO-MO and identify each with an index and the designation σ or π. Give the shape of the molecule.

18.102. Calculations[26] indicate that the C–H bond in methane has 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 carbon positive. If each σ C–H bond is represented by

$$C(\psi_{2sp^3\mathrm{C}} + c_\mathrm{H}\psi_{1s\mathrm{H}})$$

estimate the value of the coefficient c_H. Neglect the overlap integral in the calculation.

***18.103.** 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. State any assumptions.

18.104. 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.

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[25] Donald J. Royer, *Bonding Theory*, McGraw-Hill, New York, 1968, p. 162.

[26] A. E. Reed and F. Weinhold, *J. Chem. Phys.*, **84**, 2428 (1986).

Problems for Section 18.7

18.105. Use a computer program such as CAChe or Spartan to find the semi-empirical approximations to the SCF orbitals for benzene, using several methods, such as AM1, PM3, extended Hückel, etc. Calculate the wavelength of the lowest-energy transition (from the highest occupied MO to the lowest unoccupied MO). Compare the values with the experimental value 180 nm and with each other.

18.106. Use a computer program such as CAChe or Spartan to find the conformation of minimum energy for 1,3-butadiene, using a semi-empirical 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.

18.107. Use a computer program such as Spartan that will carry out ab initio calculations to find the conformation of minimum energy for 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 whether the orbitals are eigenfunctions of any symmetry operators. Compare your results with those of Problem 18.106 if you did that problem.

General Problems

18.108. Describe the bonding in the HF molecule using sp^3 hybrids for the fluorine instead of the sp hybrids used in Example 18.6. Which description fits better with the VSEPR theory? To which point group does the molecule belong? What does group theory say about the dipole moment of this molecule?

18.109. Consider the two molecules, BH_3 and NH_3.

a. Describe the bonding in each, using the simple LCAO-MO approach of using two atomic orbitals in each LCAO-MO. 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 LCAO-MO 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?

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

a. The total electronic angular momentum of a diatomic molecular is a good quantum number.

b. The orbital angular momentum of the electrons of a diatomic molecule is a good quantum number.

c. The component on the bond axis of the orbital angular momentum of an electron in a diatomic molecule is a good quantum number.

d. Hybrid orbitals are used to allow reasonable approximate molecular orbitals to be written as linear combinations of only two atomic orbitals.

e. Every orbital must be an eigenfunction of every operator that belongs to the molecule.

f. In the self consistent field treatment, if the method were carried out to exact consistency, a correct energy eigenvalue would be obtained.

g. Configuration interaction is one way to reduce the correlation error.

h. In a variation wave function, introducing explicit dependence on interelectron distances is one way to reduce the correlation error.

Problems for Appendix I

18.111. Show by matrix multiplication that each of the matrices is the inverse of the other:

$$\mathrm{A} = \begin{bmatrix} 2 & 1 & 0 \\ 1 & 2 & 1 \\ 0 & 1 & 2 \end{bmatrix} \quad \text{and} \quad \mathrm{A}^{-1} \begin{bmatrix} 3/4 & -1/2 & 1/4 \\ -1/2 & 1 & -1/2 \\ 1/4 & -1/2 & 3/4 \end{bmatrix}$$

18.112 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

$$R(\hat{\sigma}_{yz})R(\hat{C}_2) = R(\hat{\sigma}_{xz})$$

18.113. a. Verify the entire multiplication table for the one-dimensional representation of Eqs. (I-7) to (I-9).

b. Generate the other two one-dimensional representations and show that they obey the same multiplication table.

18.114. 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.

18.115. **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.

18.116. 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.

18.117. **a.** Verify the representation of Eqs. (I-20)–(I-22) using the formulas for the real 3*d* orbitals from Table 16.3.

b. Obtain five one-dimensional representations from the matrices of Eqs. (I-20)–(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.

18.118. **a.** Show that the overlap integral of the oxygen 2*s* orbital and symmetry-adapted orbital in Eq. (18.6-19) does not vanish.

b. Show that the overlap integral of the two symmetry-adapted orbitals in Eqs. (18.6-19) and (18.6-20) vanishes.

18.119. **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.

18.120. Find the matrix product

$$\begin{bmatrix} 1 & 2 & 3 \\ 0 & 1 & 2 \\ 0 & 0 & 1 \end{bmatrix}\begin{bmatrix} 4 & 5 & 6 \\ 4 & 5 & 0 \\ 4 & 0 & 0 \end{bmatrix}$$

18.121. Construct the multiplication table for the matrices in Eqs. (I-3)–(I-6) and show that it is identical to the multiplication table for the point group C_{2v}.

18.122. 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}.

18.123. 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 18.26. If the orbital is not an eigenfunction, state that fact.

a. $\hat{C}_6$ (axis perpendicular to the plane of the molecule)
b. $\hat{C}_6^2$ (axis perpendicular to the plane of the molecule)
c. $\hat{C}_6^3$ (axis perpendicular to the plane of the molecule)
d. $\hat{\sigma}_h$ (reflection plane in the plane of the molecule)

18.124. Determine whether the oxygen 2*s* orbital and a hydrogen 1*s* orbital in the H_2O molecule in its equilibrium conformation will have zero overlap.

19

Translational, Rotational, and Vibrational States of Atoms and Molecules

OBJECTIVES

After studying this chapter, the student should:

1. understand the separation of the translational and electronic energy of atomic substances and be able to solve problems related to the translational energy;
2. understand the translational, rotational, and vibrational energy levels of diatomic molecules and be able to solve problems related to these energy levels;
3. understand the equilibrium populations of diatomic energy levels and be able to solve problems related to these populations;
4. understand the effects of nuclear spin symmetry or antisymmetry;
5. understand the rotational and vibrational energy levels of polyatomic molecules and be able to solve problems related to these energy levels.

PRINCIPAL FACTS AND IDEAS

1. Atoms have only translational and electronic energy.
2. The translational energy of an atom is like that of a structureless particle.
3. Molecules have rotational and vibrational energy in addition to translational and electronic energy.
4. The Born–Oppenheimer approximation is used to separate the electronic motion from the rotational and vibrational motion of molecules.
5. Translation, rotation, and vibration of diatomic molecules can be discussed separately from the electronic structure.
6. In homonuclear diatomic molecules, only half of the values of J, the rotational quantum number, are permitted.
7. The equilibrium populations of the energy levels of molecules are governed by the Boltzmann probability distribution.
8. The rotational and vibrational energies of polyatomic molecules can be discussed in the Born–Oppenheimer approximation.

19.1 Translational Motions of Atoms

Chapter 16 focused on solution of the Schrödinger equation for atoms, beginning with the hydrogen atom. The wave function (energy eigenfunction) of a hydrogen atom is given by Eq. (16.1-14) as a product of the center-of-mass factor ψ_c and the relative factor ψ_r:

$$\Psi = \psi_c(X, Y, Z)\psi_r(x, y, z)$$

The factor ψ_c is the same as the wave function of a moving particle with mass equal to the total mass of the atom. We now denote this factor by ψ_{tr} and call it the **translational factor**. The factor ψ_r corresponds to the relative motion of the electron and the nucleus around the center of mass. Since the nucleus is much more massive than the electron, the center of mass is close to the nucleus, and the relative motion is almost the same as electronic motion about the nucleus. We now denote the relative factor by ψ_{el} and call it the **electronic factor**.

$$\Psi = \psi_{tr}(X, Y, Z)\psi_{el}(x, y, z) \tag{19.1-1}$$

The total energy of a hydrogen atom is given by Eq. (16.1-14)

$$E_{total} = E_c + E_r = E_{tr} + E_{el} \tag{19.1-2}$$

where E_{tr} is the translational energy (previously called E_c, the center-of-mass energy), and E_{el} is the electronic energy (previously called the relative energy E_r). For multielectron atoms, we have 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 the electrons follow the nucleus, adapting to each new position of the nucleus almost as though the nucleus had always been there. Equations (19.1-1) and (19.1-2) can be used as a good approximation for all atoms.

If the atom is not confined in a container, its center of mass obeys the time-independent Schrödinger equation of a free particle, Eq. (14.5-32). The solution of this Schrödinger equation for the center-of-mass motion is given by Eq. (14.5-33). The translational energy is given by Eq. (14.5-35), and is not quantized. Now assume that an atom is confined in a rectangular box like that of Section 14.5, located in the first octant of a cartesian coordinate system with its lower left rear corner at the origin. Its length in the x direction is a, its length in the y direction is b, and its length in the z direction is c. If the atom were a mass point confined in this box, the potential energy would be represented by

$$\mathcal{V}_{ext} = \mathcal{V}_{ext}(x, y, z) = \begin{cases} 0 & \text{if } 0 < x < a,\, 0 < y < b, \text{ and } 0 < z < c \\ \infty & \text{otherwise} \end{cases} \tag{19.1-3}$$

This potential function does not exactly apply to an atom. The center of the atom cannot move completely up to the wall because of the presence of the electrons in the atom. However, if the box is much larger than the size of an atom Eq. (19.1-3) will be a good approximation.

With this approximation, the solution of the time-independent Schrödinger equation for the translation of the center of mass of an atom in a box is the same as that of a mass point in a rectangular box, Eq. (14.5-17):

$$\psi_{tr} = \sqrt{\frac{8}{abc}}\sin\left(\frac{n_x \pi x}{a}\right)\sin\left(\frac{n_y \pi y}{b}\right)\sin\left(\frac{n_z \pi z}{c}\right) \tag{19.1-4}$$

where n_x, n_y, and n_z are three positive integral quantum numbers, the **translational quantum numbers**. The translational energy is given by Eq. (14.5-18):

$$E_{\mathrm{tr}} = \frac{h^2}{8M}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \tag{19.1-5}$$

where M is the total mass of the atom. The translational energy levels lie very close together for a box of macroscopic size, and in the limit that the box becomes infinitely large, adjacent energy levels approach each other, like those of a free particle.

EXAMPLE 19.1

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 (112), (121), and (211), so the energy difference is

$$\begin{aligned}\Delta E = E_{112} - E_{111} &= \frac{h^2}{8ma^2}(6-3)\\ &= \frac{(6.6261\times10^{-34}\ \mathrm{J\ s})^2}{8(1.674\times10^{-27}\ \mathrm{kg})(0.100\ \mathrm{m})^2}(3)\left(\frac{1\ \mathrm{eV}}{1.6022\times10^{-19}\ \mathrm{J}}\right)\\ &= 6.14\times10^{-20}\ \mathrm{eV}\end{aligned}$$

which is smaller than the electronic excitation energy by a factor of 10^{-20}.

*Exercise 19.1

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 electronvolts. Compare it with the corresponding value for a hydrogen atom in Example 19.1, 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 close together, the translational quantum numbers of an atom can be very large. In Chapter 10, we found that in a macroscopic system of point mass molecules the average translational energy is equal to

$$\langle E_{\mathrm{tr}}\rangle = \frac{3k_{\mathrm{B}}T}{2} \tag{19.1-6}$$

where k_{B} is Boltzmann's constant, equal to $1.3807\times10^{-23}\ \mathrm{J\ K^{-1}}$, and where T is the absolute temperature. We now change notation and denote a molecular energy by a capital E instead of a lower-case ε. This formula for the energy was obtained classically, but it is an accurate value for atoms.

EXAMPLE 19.2

a. For a hydrogen atom in the box of Example 19.1 with translational energy equal to $3k_{\mathrm{B}}T/2$ at 300 K, find the value of the 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.

Solution

a.

$$\frac{3k_BT}{2} = \frac{3}{2}(1.3807 \times 10^{-23}\ \mathrm{J\,K^{-1}})(300\ \mathrm{K}) = 6.21 \times 10^{-21}\ \mathrm{J} = \frac{h^2}{8Ma^2}(3n_x^2)$$

$$n_x = \left(\frac{8(1.674 \times 10^{-27}\ \mathrm{kg})(0.100\ \mathrm{m})^2(6.21 \times 10^{-21}\ \mathrm{J})}{3(6.6261 \times 10^{-34}\ \mathrm{J\,s})^2}\right)^{1/2}$$

$$= [6.32 \times 10^{17}]^{1/2} = 7.95 \times 10^8$$

b.

$$\Delta E = \frac{h^2}{8Ma^2}[(n_x+1)^2 - n_x^2]$$

$$= \frac{(6.6261 \times 10^{-34}\ \mathrm{J\,s})^2}{8(1.674 \times 10^{-27}\ \mathrm{kg})(0.100\ \mathrm{m})^2}(2n_x + 1)$$

$$= (3.278 \times 10^{-39}\ \mathrm{J})(2(7.95 \times 10^8) + 1)$$

$$= 5.213 \times 10^{-30}\ \mathrm{J}$$

$$\text{Ratio} = \frac{5.213 \times 10^{-30}\ \mathrm{J}}{6.21 \times 10^{-21}\ \mathrm{J}} = 8.39 \times 10^{-10}$$

***Exercise 19.2**

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 300 K. Compare your values with those of Example 19.2.

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 19.2.

19.2 The Nonelectronic States of Diatomic Molecules

In addition to translation, molecules have rotational and vibrational motion. This section focuses on diatomic molecules, but we first write some equations that apply to all molecules.

Equations for All Molecules

In the Born–Oppenheimer approximation, the Schrödinger equation for the electronic motion is constructed with the nuclei assumed to be stationary. We now assume that the Schrödinger equation for the electrons has been solved in the Born–Oppenheimer approximation, giving the energy for a given electronic state as the electronic energy eigenvalue plus the energy of internuclear repulsions, as in Eq. (18.1-6):

$$E_{\mathrm{BO}} = E_{\mathrm{el}} + \mathcal{V}_{\mathrm{nn}} \tag{19.2-1}$$

The nuclear repulsion energy $\mathcal{V}_{\mathrm{nn}}$ is given by

$$\mathcal{V}_{\mathrm{nn}} = \frac{e^2}{4\pi\varepsilon_0}\sum_{A=2}^{n}\sum_{B=1}^{A-1}\frac{Z_AZ_B}{r_{AB}} \tag{19.2-2}$$

where Z_A is the number of protons in nucleus A, Z_B is the number of protons in nucleus B, r_{AB} is the distance between these two nuclei, and n is the total number of nuclei. The limits of the sums are chosen so that the indexes A and B are never equal to each other and each pair of nuclei is included only once.

The Born–Oppenheimer energy, E_{BO}, is independent of the location of the molecule's center of mass, and depends only on the relative coordinates of the nuclei. It acts like a potential energy for nuclear motion. We denote it now as $\mathcal{V}$:

$$\mathcal{V}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) = E_{BO} \tag{19.2-3}$$

where $\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n$ are the nuclear position vectors. The Hamiltonian operator for nuclear motion is now

$$\hat{H}_{nuc} = -\hbar^2 \sum_{A=1}^{n} \frac{1}{2m_A} \nabla_A^2 + \mathcal{V}(\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_n) + \mathcal{V}_{ext} \tag{19.2-4}$$

where $\nabla_1^2, \nabla_2^2, \ldots, \nabla_n^2$ are the Laplacian operators for the nuclear positions. For a molecule that can move anywhere in space, $\mathcal{V}_{ext}$ can be set equal to zero. If the molecule is confined in a rectangular box, $\mathcal{V}_{ext}$ is the potential function that confines it, shown in Eq. (19.1-3). As with atoms, this use is in approximation, since the closeness of approach of the center of mass of molecule to the wall of a box will depend on the electronic, rotational and vibrational state of the molecule. For a box of macroscopic size, Eq. (19.1-3) will be a good approximation.

Diatomic Molecules

The Born–Oppenheimer energy of a diatomic molecule with nuclei A and B depends only on the internuclear distance r_{AB}, which we now denote by r since there are only two nuclei. The nuclear Hamiltonian operator for a diatomic molecule is

$$\hat{H}_{nuc} = -\hbar^2 \left[\frac{1}{2m_A} \nabla_A^2 + \frac{1}{2m_B} \nabla_B^2 \right] + \mathcal{V}(r) + \mathcal{V}_{ext} \tag{19.2-5}$$

where m_A and m_B are the nuclear masses and where we now denote the internuclear distance by r instead of by R as in Chapter 18. Since $\mathcal{V}_{ext}$ does not depend on the relative coordinates, $\hat{H}_{nuc}$ is the Hamiltonian operator for a central-force system, and can be transformed into the same form as Eq. (16.1-10):

$$\hat{H}_{nuc} = -\frac{\hbar^2}{2M} \nabla_c^2 + \mathcal{V}_{ext} - \frac{\hbar^2}{2\mu} \nabla_r^2 + \mathcal{V}(r) = \hat{H}_c + \hat{H}_r \tag{19.2-6}$$

The difference between this Hamiltonian and that for the hydrogen atom is that here the two particles are both nuclei and that the potential energy is the Born–Oppenheimer energy instead of the Coulomb energy. The center-of-mass (translational) Hamiltonian is

$$\hat{H}_c = \hat{H}_{tr} = \frac{\hbar^2}{2M} \nabla_c^2 + \mathcal{V}_{ext} \tag{19.2-7}$$

The relative Hamiltonian is given by Eq. (16.1-12):

$$\hat{H}_r = -\frac{\hbar^2}{2\mu} \nabla_r^2 + \mathcal{V}(r) \tag{19.2-8}$$

Here ∇_c^2 is the Laplacian operator for the center of mass of the two nuclei and ∇_r^2 is the Laplacian operator for the relative coordinates. M is the sum of the masses of the two nuclei, and μ is their reduced mass:

$$M = m_A + m_B; \qquad \mu = \frac{m_A m_B}{m_A + m_B} \tag{19.2-9}$$

All of the analysis of the central-force problem in Section 16.1 applies to the Hamiltonian operator of Eq. (19.2-6) until we get to the part that depends on the form of $\mathcal{V}$. The variables separate to give two separate Schrödinger equations:

$$\hat{H}_{tr}\psi_{tr} = E_{tr}\psi_{tr} \tag{19.2-10}$$

and

$$\hat{H}_r\psi_r = E_r\psi_r \tag{19.2-11}$$

The translational Schrödinger equation, Eq. (19.2-10) is the same as for atoms or for a structureless particle. The translational wave function for a diatomic molecule in a rectangular box will be given by Eq. (19.1-4) and the translational energy levels will be given by Eq. (19.1-5). The relative Schrödinger equation for a diatomic molecule is given in spherical polar coordinates by Eq. (16.1-18). This equation is solved by the trial function of Eq. (16.1-20):

$$\psi_r(r, \theta, \phi) = R(r)Y(\theta, \phi) = R(r)\Theta(\theta)\Phi(\phi) \tag{19.2-12}$$

The Θ and Φ factors are the same as in Chapter 16. The equation for the radial factor R is Eq. (16.1-21):

$$-\frac{\hbar^2}{2\mu}\left[Y\frac{1}{r^2}\frac{d}{dr}\left(r^2\frac{dR}{dr}\right) + R\hat{L}^2Y\right] + (\mathcal{V} - E_r)RY = 0 \tag{19.2-13}$$

The Rigid Rotor

The rigid rotor is a model system that approximately represents the rotation of a diatomic molecule. It is a central-force system consisting of two masses with fixed interparticle distance (no vibration is possible). Since r is fixed and $\mathcal{V}$ depends only on r, the potential energy has a constant value that can be chosen to equal zero:

$$r = r_e \text{ (fixed)}, \qquad \mathcal{V} = 0 \text{ (fixed)} \tag{19.2-14}$$

Since r is constant, the derivatives with respect to r are omitted, and Eq. (19.1-13) becomes

$$R\frac{1}{2\mu r^2}\hat{L}^2 Y = E_r RY \tag{19.2-15}$$

The radial factor R can be canceled. The equation is now the same as the angular momentum eigenvalue equation except for the constant factor $1/(2\mu r^2)$, so that the energy eigenfunction is the same as the spherical harmonic function that is the eigenfunction of $\hat{L}^2$ in Eq. (16.1-39):

$$\psi_{rot} = Y_{JM}(\theta, \phi) = \Theta_{JM}(\theta)\Phi_M(\phi) \tag{19.2-16}$$

where we call the eigenfunction ψ_{rot}. We use different letters for the quantum numbers, but they are the same as l and m and obey the same relations as l and m. The use of the

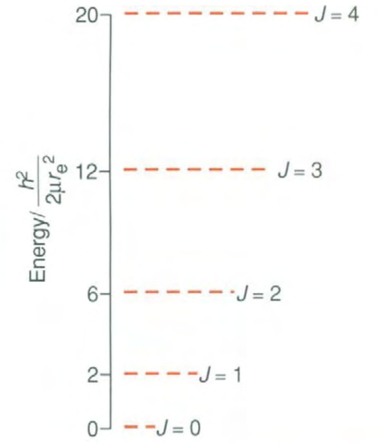

Figure 19.1. Energy Levels of the Rigid Rotor. Degeneracies are shown by placing a line segment for each state of the energy level.

letters J and M instead of l and m is the customary usage for rotational states. The energy eigenvalue is $1/(2\mu r^2)$ times the eigenvalue of $\hat{L}^2$. From Equation (16.1-39),

$$E = E_J = \frac{\hbar^2}{2\mu r_e^2}J(J+1) \quad \text{(rigid rotor)} \tag{19.2-17}$$

There is one energy eigenfunction for each set of values of J and M, but the energy eigenvalue does not depend on M. The degeneracy of the energy level (the number of states in the energy level) for a given value of J is

$$g_J = (2J+1) \tag{19.2-18}$$

Figure 19.1 shows the first few energy levels with their degeneracies. The degeneracy of the rotational energy level is obtained by counting up the number of values that M can take on: a number of positive values equal to J, a number of negative values equal to J, plus the zero value, for a total of $2J+1$ values.

*Exercise 19.3

a. The internuclear distance of the carbon monoxide molecule is 1.128×10^{-10} m. Assume that it rotates like a rigid rotor and find the value of the rotational energy in the $J = 0$ and $J = 1$ energy levels.

b. 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.

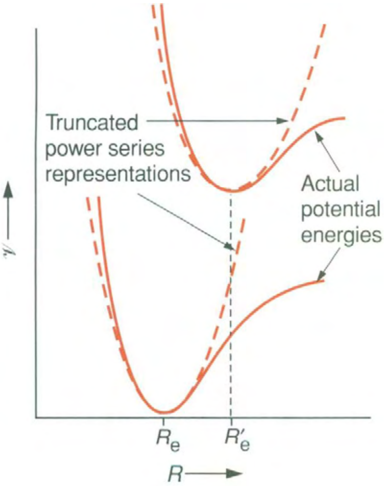

Figure 19.2. Vibrational Potential Energy for a Typical Diatomic Molecule in Two Electronic States. This figure shows not only the realistic curve representing the Born–Oppenheimer energy (which acts as the vibrational potential energy), but also the parabolic curve representing the quadratic truncated power series representation. The equilibrium internuclear distances for the two electronic states are not equal to each other, and show the general pattern that the excited state has the longer equilibrium internuclear distance.

Rotating and Vibrating Diatomic Molecules

In order to discuss vibration as well as rotation, we now return to Eq. (19.2-13) without assuming a fixed internuclear distance. Equation (16.2-2) is the equation for the radial factor R obtained by separation of variables:

$$-\frac{d}{dr}r^2\frac{dR}{dr} + \frac{2\mu r^2}{\hbar^2}(\mathcal{V} - E)R + J(J+1)R = 0 \tag{19.2-19}$$

where we drop the subscript on the relative energy E_r and where we replace l by J.

For a typical diatomic molecule, the function $\mathcal{V}(r)$ is a function such as the one depicted in Figure 19.2. We express $\mathcal{V}(r)$ as a Taylor series in the variable $x = r - r_e$, where r_e is the value of r at the minimum in $\mathcal{V}$:

$$\mathcal{V}(r) = \mathcal{V}(r_e) + \left(\frac{d\mathcal{V}}{dr}\right)_{r_e} x + \frac{1}{2!}\left(\frac{d^2\mathcal{V}}{dr^2}\right)_{r_e} x^2 + \cdots \tag{19.2-20}$$

where the subscript r_e means that the derivative is evaluated at $r = r_e$. The function $\mathcal{V}$ is at a minimum at $r = r_e$, so the first derivative vanishes. To a fairly good approximation, we truncate the series at the quadratic term and write

$$\mathcal{V}(r) = \mathcal{V}_e + \frac{1}{2!}\left(\frac{d^2\mathcal{V}}{dr^2}\right)_{r_e} x^2 = \mathcal{V}_e + \frac{1}{2}kx^2 \tag{19.2-21}$$

where $\mathcal{V}_e = \mathcal{V}(r_e)$ and where we denote the second derivative evaluated at $r = r_e$ by k, which is the same kind of force constant as was introduced for the harmonic oscillator in Eq. (14.1-13) and Eq. (14.6-1). The potential function of Eq. (19.2-21) is called a

harmonic potential. It will lead to vibrational energy levels identical to those of a harmonic oscillator. There will be different values of k, of $\mathcal{V}_e$, and of r_e for different molecules, and even for different bound electronic states of the same molecule. A double or triple chemical bond will generally have a greater dissociation energy and a larger value of k than a single bond. Figure 19.2 shows schematically the function $\mathcal{V}$ and the truncated power series representations for two electronic states of a typical diatomic molecule.

The radial Schrödinger equation is now

$$\frac{d}{dr} r^2 \frac{dR}{dr} - J(J+1)R + \frac{2\mu r^2}{\hbar^2}\left(E - \mathcal{V}_e - \frac{kx^2}{2}\right)R = 0 \tag{19.2-22}$$

We define a new dependent variable

$$S(r) = rR(r) \tag{19.2-23}$$

When this variable is substituted into Eq. (19.2-22), the result is

$$\frac{\hbar^2}{2\mu}\left(\frac{d^2S}{dr^2} - \frac{J(J+1)S}{r^2}\right) + \left(E - \mathcal{V}_e - \frac{kx^2}{2}\right)S = 0 \tag{19.2-24}$$

To express this equation in terms of x, we write

$$\frac{1}{r^2} = \frac{1}{(r_e + x)^2} = \frac{1}{r_e^2}\left(1 - \frac{2x}{r_e} + \frac{3x^2}{r_e^2} + \cdots\right) \tag{19.2-25}$$

If x is quite small, it is a fairly good approximation to keep only the first term of this series:

$$\frac{1}{r^2} \approx \frac{1}{r_e^2} \tag{19.2-26}$$

Equation (19.2-24) becomes

$$-\frac{\hbar^2}{2\mu}\frac{d^2S}{dx^2} + \frac{kx^2}{2}S = \left(E - \mathcal{V}_e - \frac{\hbar^2}{2\mu r_e^2}J(J+1)\right)S \tag{19.2-27}$$

Exercise 19.4

Carry out the mathematical steps to obtain Eq. (19.2-27) from Eq. (19.2-22).

Equation (19.2-27) is the same as the harmonic oscillator Schrödinger equation of Eq. (14.6-1) except for the presence of the two constant terms subtracted from the energy eigenvalue. The function S is therefore the same as the harmonic oscillator energy eigenfunction, given by Eqs. (14.6-4), etc., and the energy eigenvalue E is the harmonic oscillator energy eigenvalue of Eq. (14.6-6) plus the two constant terms. (See Exercise 14.22) for the effect of adding a constant to a potential energy function.)

$$E = E_{vJ} = h\nu_e\left(v + \frac{1}{2}\right) + \frac{\hbar^2}{2I_e}J(J+1) + \mathcal{V}_e \tag{19.2-28}$$

where ν_e is the oscillator frequency predicted by classical mechanics in Eq. (14.1-10):

$$\nu_e = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \tag{19.2-29}$$

We have introduced the symbol I_e for the equilibrium **moment of inertia** of the diatomic molecule:

$$I_e = \mu r_e^2 \tag{19.2-30}$$

The subscript e denotes the equilibrium value. The quantum number v can equal $0, 1, 2, \ldots$, and the quantum number J can also equal $0, 1, 2, \ldots$. The energy eigenvalue is now that of a harmonic oscillator plus that of a rigid rotor plus a constant, $\mathscr{V}_e$.

We have now completed our solution of the Schrödinger equation for the motion of nuclei in a diatomic molecule. The wave function for the relative motion of the nuclei is

$$\psi_r = \Theta_{JM}(\theta)\Phi_M(\phi)\frac{S_v(r - r_e)}{r} = \psi_{\text{rot},JM}\psi_{\text{vib},v} \tag{19.2-31}$$

The rotational wave function

$$\psi_{\text{rot}} = \Theta_{JM}(\theta)\Phi_M(\phi) = Y_{JM} \tag{19.2-32}$$

is the same as the spherical harmonic function of Section 16.1, and has the same two quantum numbers, which we now call J and M instead of l and m. The radical factor R is the vibrational wave function, equal to a harmonic oscillator (HO) wave function divided by r, the internuclear distance.

$$\psi_{\text{vib}} = R(r) = \frac{S_v}{r} = \frac{\psi_{\text{HO}}}{r} \tag{19.2-33}$$

We sometimes sketch vibrational wave functions as though they were harmonic oscillator functions. This practice is acceptable if r remains nearly equal to r_e.

The total 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:

$$\psi_{\text{tot}} = \psi_{\text{tr}}\psi_r = \psi_{\text{tr}}\psi_{\text{rot}}\psi_{\text{vib}}\psi_{\text{el}} \tag{19.2-34}$$

For a diatomic molecule, the total energy is the translational energy plus the relative energy in Eq. (19.2-28). The second term in the right-hand side of Eq. (19.2-28) is the same as the energy of a rigid rotor, Eq. (19.2-17), and we call it the rotational energy:

$$E_{\text{rot}} = \frac{\hbar^2}{2I_e}J(J+1) \qquad (J = 0, 1, 2, \ldots) \tag{19.2-35}$$

The degeneracy is also the same as that of the rigid rotor, Eq. (19.2-18):

$$g_J = 2J + 1 \tag{19.2-36}$$

The $J = 0$ energy level consists of one state, the $J = 1$ level consists of three states, etc.

The first term in the right-hand side of Eq. (19.2-28) is the energy of a harmonic oscillator, and we call it the vibrational energy:

$$E_{\text{vib}} = h\nu_e\left(v + \frac{1}{2}\right) \qquad (v = 0, 1, 2, 3, \ldots) \tag{19.2-37}$$

The energy levels of a harmonic oscillator are nondegenerate, so that there is only one vibrational state for each value of v.

The final term is the value of the Born–Oppenheimer (electronic) energy at the minimum, and we call it the electronic energy:

$$E_{\text{el}} = \mathscr{V}_e = \mathscr{V}(r_e) \tag{19.2-38}$$

This electronic energy is a different constant for each electronic state. It is equal to the Born–Oppenheimer energy at $r = r_e$. The rest of the Born–Oppenheimer energy depended on r, and was taken as the potential energy of vibration. Sometimes the zero-point vibrational energy is included in the electronic energy, so that

$$E_{el} = \mathcal{V}_e + \frac{h\nu_e}{2} \quad \text{(alternate version)} \tag{19.2-39}$$

and

$$E_{vib} = h\nu_e v \quad \text{(alternate version)} \tag{19.2-40}$$

The total energy is unchanged by this choice. The center-of-mass (translational) energy is given by Eq. (19.1-5):

$$E_{tr} = E_{n_x n_y n_z} = \frac{h^2}{8M}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right) \tag{19.2-41}$$

We can write the total energy as a sum of translational, vibrational, rotational, and electronic contributions:

$$\mathrm{E}_{tot} = \mathrm{E}_{tr} + \mathrm{E}_{vib} + \mathrm{E}_{rot} + \mathrm{E}_{el} \tag{19.2-42}$$

The translational energy is independent of the rotational, vibrational, and electronic states. The electronic energy E_{el} is a different constant for each electronic state, and the quantities ν_e, I_e are different for each electronic state. The electronic energy E_{el} is often chosen to equal zero for the electronic ground state, which makes E_{el} equal to a different positive constant for each excited level. The spacings between the different quantized values of the energy contributions are widely different.

EXAMPLE 19.3

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 $6.505 \times 10^{13}\ \mathrm{s}^{-1}$ for the ground electronic state. The excitation energy to the minimum in the first excited electronic state is 6.036 eV.

Solution

We assume the most common isotopes, ^{12}C and ^{16}O. For translation,

$$E_{211} - E_{111} = \frac{h^2}{8Ma^2}(6-3) = \frac{(6.6261 \times 10^{-34}\ \mathrm{J\ s})(3)}{8(4.469 \times 10^{-26}\ \mathrm{kg})(0.100\ \mathrm{m})^2}$$
$$= 3.68 \times 10^{-40}\ \mathrm{J} = 2.30 \times 10^{-21}\ \mathrm{eV}$$

For rotation,

$$E_1 - E_0 = \frac{\hbar^2}{2I_e}(2-0) = \frac{h^2}{8\pi^2 \mu r_e^2}(2-0)$$
$$= \frac{(6.6261 \times 10^{-34}\ \mathrm{J\ s})^2(2)}{8\pi^2(1.138 \times 10^{-26}\ \mathrm{kg})(1.128 \times 10^{-10}\ \mathrm{m})^2}$$
$$= 7.68 \times 10^{-23}\ \mathrm{J} = 4.79 \times 10^{-4}\ \mathrm{eV}$$

For vibration,

$$E_1 - E_0 = h\nu_e\left(\frac{3}{2} - \frac{1}{2}\right) = h\nu_e$$

$$= (6.6261 \times 10^{-34}\ \mathrm{J\ s})(6.505 \times 10^{13}\ \mathrm{s^{-1}}) = 4.310 \times 10^{-20}\ \mathrm{J} = 0.269\ \mathrm{eV}$$

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 19.3 are typical. For most molecules, the translational levels are much closer together than the rotational levels, which are quite a bit close together than the vibrational levels, which are in turn quite a bit closer together than the electronic levels.

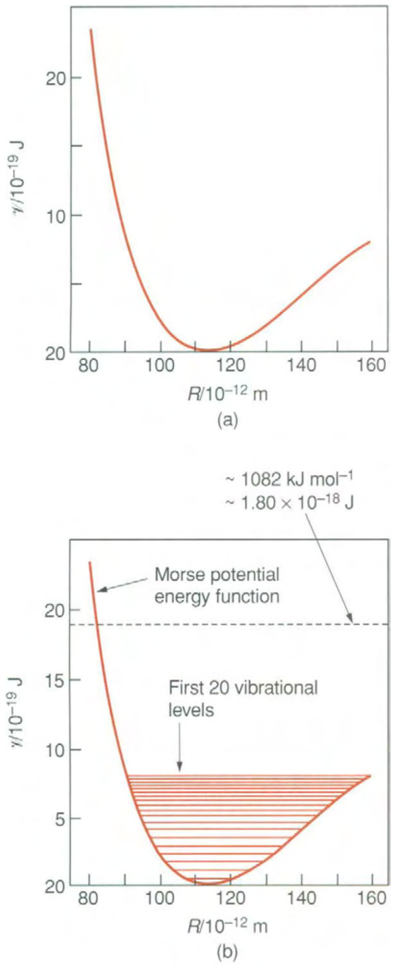

Figure 19.3. The Vibrational Potential Energy and Energy Levels of the CO Molecule. (a) **The vibrational potential energy represented by the Morse function.** (b) **The first 20 vibrational energy levels for the harmonic potential.** The Morse potential parameters for CO are $D_e = 11.2\ \mathrm{eV} = 1.80 \times 10^{-18}$ J and $a = 2.2994 \times 10^{10}\ \mathrm{m^{-1}}$. The force constant for the harmonic potential is $k = 1900\ \mathrm{N\ m^{-1}}$.

*Exercise 19.5

Compare the energy level spacings for a Cl_2 molecule in a cubical box 0.200 m on a side. Its vibration frequency is $1.694 \times 10^{13}\ \mathrm{s^{-1}}$ and its equilibrium 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 2.208 eV above that of the ground electronic state.

The energy level expression of Eq. (19.2-28) is only a first approximation. The power series expression for the vibrational potential function $\mathcal{V}$ was truncated at the quadratic term. One additional term of this expansion can be kept[1] or an alternate representation of the potential energy can be used. The most commonly used representation is the **Morse function**

$$\mathcal{V}(r) = \mathcal{V}(r_e) + D_e(1 - e^{-a(r-r_e)})^2 \qquad (19.2\text{-}43)$$

where D_e is the **dissociation energy**, or the energy required to dissociate the molecule from the state of minimum $\mathcal{V}$. 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 molecule. Figure 19.3a depicts the Morse potential function for the CO molecule. The Schrödinger equation for the Morse potential has been solved.[2] It also provides an instructive application of second-order perturbation theory.[3]

Exercise 19.6

***a.** Using the general relation between potential energy and force, Eq. (D-6) of Appendix D, 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 $r = r_e$.

---

[1] Jeff 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).

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

$$\begin{aligned} E_{vJ} &= h\nu_e\left(v+\frac{1}{2}\right) - h\nu_e x_e\left(v+\frac{1}{2}\right)^2 + hB_e J(J+1) \\ &\quad - h\mathfrak{D}J^2(J+1)^2 - h\alpha\left(v+\frac{1}{2}\right)J(J+1) \end{aligned} \tag{19.2-44}$$

The constant parameters in this expression are given for the Morse potential by[4]

$$\alpha = \frac{3h^2\nu_e}{16\pi^2\mu r_e^2 D_e}\left(\frac{1}{ar_e} - \frac{1}{a^2 r_e^2}\right) \tag{19.2-45}$$

$$x_e = \frac{h\nu_e}{4D_e} \tag{19.2-46}$$

$$B_e = \frac{\hbar}{4\pi I_e} = \frac{h}{8\pi^2 I_e} \tag{19.2-47}$$

$$\mathfrak{D} = \frac{4B_e^3}{\nu_e^2} \tag*{(19.2-48))}$$

The term containing the parameter $\mathfrak{D}$ causes the corrected levels to be more closely spaced for larger values of J than are the uncorrected levels, and corresponds to centrifugal stretching of the molecule, which increases the value of the moment of inertia. (Do not confuse the parameter $\mathfrak{D}$ with the dissociation energy D_e). This effect is typically small, and the term in $\mathfrak{D}$ 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 and is a correction for the anharmonicity of the potential energy function. Figure 19.3b shows the vibrational energy levels of the CO molecule, including the anharmonicity correction. The dissociation energy D_e is sometimes related to ν_e and x_e by determining the energy at which the energy difference between two successive levels shrinks to zero (see Problem 19.25). The term containing the parameter α contains both the vibrational and rotational quantum numbers, and expresses the interaction of vibration and rotation. The physical origin of this interaction can be seen in Figure 19.3, which shows that 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 level expression.

EXAMPLE 19.4

Calculate the energy of the $v = 2$, $J = 2$ level of the CO molecule using the values of the parameters: $\nu_e = 6.5049 \times 10^{13}\ \mathrm{s^{-1}}$, $x_e = 6.124 \times 10^{-3}$, $B_e = 5.7898 \times 10^{10}\ \mathrm{s^{-1}}$, $\mathfrak{D} = 1.83516 \times 10^{5}\ \mathrm{s^{-1}}$, $\alpha = 5.24765 \times 10^{8}\ \mathrm{s^{-1}}$.

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[4] Davis, *op. cit.*, p. 351 (Note 1).

Solution

$$\begin{aligned}
E/h &= \nu_e(5/2) - \nu_e x_e(5/2)^2 + B_e(2)(3) - \mathfrak{D}(36) - \alpha(5/2)(6) \\
&= (6.5049 \times 10^{13}\ \mathrm{s}^{-1})(5/2) - (3.9836 \times 10^{11}\ \mathrm{s}^{-1})(5/2)^2 \\
&\quad + (5.7898 \times 10^{10}\ \mathrm{s}^{-1})(6) - (1.83516 \times 10^{5}\ \mathrm{s}^{-1})(36) \\
&\quad - (5.24765 \times 10^{8}\ \mathrm{s}^{-1})(5/2)(6) \\
&= 1.6262 \times 10^{14}\ \mathrm{s}^{-1} - 2.4897 \times 10^{12}\ \mathrm{s}^{-1} + 3.4739 \times 10^{11}\ \mathrm{s}^{-1} \\
&\quad - 6.6066 \times 10^{6}\ \mathrm{s}^{-1} - 7.8715 \times 10^{9}\ \mathrm{s}^{-1} \\
&= 1.6047 \times 10^{14}\ \mathrm{s}^{-1} \\
E &= (6.6261 \times 10^{-34}\ \mathrm{J\ s})(1.6047 \times 10^{14}\ \mathrm{s}^{-1}) = 1.0633 \times 10^{-19}\ \mathrm{J}
\end{aligned}$$

To five significant digits the $\mathfrak{D}$ term is insignificant, and the α term is fairly small. The $\nu_e x_e$ term is large compared with the main rotational term (the J term), but is fairly small compared with the main vibrational term (the ν_e term).

The energy levels are also sometimes given in terms of energies divided by hc, where c is the speed of light. 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 the transition between these levels. It is sometimes called the "term" of the level, and denoted by T. The terms are commonly given in reciprocal centimeters, sometimes called "wave numbers."

$$\begin{aligned}
T_{vJ} = E_{vJ}/hc = \tilde{\nu}_e\left(v + \frac{1}{2}\right) - \tilde{\nu}_e x_e\left(v + \frac{1}{2}\right)^2 + \tilde{B}_e J(J+1) \\
- \tilde{\mathfrak{D}} J^2 (J+1)^2 - \tilde{\alpha}\left(v + \frac{1}{2}\right) J(J+1) \qquad (19.2\text{-}49)
\end{aligned}$$

The parameters in this equation are marked with a tilde (~) to distinguish them from the parameters in Eq. (19.2-44). 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 for several diatomic molecules. Some reference books use the same letters without a tilde to represent the parameters in Eq. (19.2-49).

***Exercise 19.7**

a. Using the expression of Eq. (19.2-49), 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 $\tilde{\alpha}$ and $\tilde{\mathfrak{D}}$.

c. Find the wavelength for the same transition, neglecting the terms in x_e, $\tilde{\alpha}$, and $\tilde{\mathfrak{D}}$.

Nuclear Spins and Wave Function Symmetry

For the special case of homonuclear diatomic molecules (molecules with two nuclei of the same kind), we return to the wave function of Eq. (19.2-34) and determine the consequence of complying with the requirement that the wave function must not pretend to distinguish between two identical nuclei, which are just as indistinguishable from each other as are two electrons. As is the case with electrons as discussed in

Section 16.3, the interchange of two identical nuclei must not change the probability density, which is the square of the magnitude of the wave function.

For our purposes, a nucleus can be considered to be made up of protons and neutrons, collectively called **nucleons**. Protons and neutrons have a spin quantum number of 1/2, as do electrons, and therefore are fermions. If a nucleus contains an odd number of nucleons, the nucleus is a fermion, since 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, since exchanging two such nuclei changes the sign of the wave function an even number of times, leaving the original sign.

The wave function for nuclear motion in Eq. (19.2-21) must be multiplied by a nuclear spin wave function to be a complete wave function. The nuclear spin angular momentum **I** has the same general properties as any angular momentum. Its magnitude takes on the values

$$|\mathbf{I}| = \hbar\sqrt{I(I+1)} \tag{19.2-50}$$

The projection of the spin angular momentum on the z axis takes on the values

$$I_z = \hbar M_I \tag{19.2-51}$$

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 vector **I** is the vector sum of the spin angular momenta of all of the nucleons in the nucleus. The nuclear spin quantum number I is an integer if the nucleus contains an even number of nucleons, and is a half-integer if the nucleus contains an odd number of nucleons. Its value depends on how the nucleon angular momenta add vectorially in the particular nuclear state. A given nucleus can have different spin states, just as an 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. Table A.23 in Appendix A lists the spin quantum numbers for the nuclear ground states of several common nuclei.

If $I = 0$, there is a single symmetric spin function. The total wave function of a homonuclear diatomic molecule with $I = 0$ must be symmetric with respect to exchange of the nuclei, since they must contain an even number of nucleons and therefore are bosons. The space factor must be symmetric. If $I = 1/2$, as with H_2, the nuclear spin wave functions are like those of two electrons, with singlet and triplet states. The triplet nuclear spin functions for such a diatomic molecule are symmetric,

$$\alpha(1)\alpha(2), \quad \beta(1)\beta(2), \quad \sqrt{\tfrac{1}{2}}[\alpha(1)\beta(2) + \beta(1)\alpha(2)]$$

and the singlet spin function is antisymmetric,

$$\sqrt{\tfrac{1}{2}}[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

The space part of the total wave function must be antisymmetric if it is combined with a triplet nuclear spin function and must be symmetric if it is combined with the singlet spin function. For values of I greater than 1/2, the spin functions are more complicated than those of two hydrogen nuclei, and we will not discuss them. The total wave function must be symmetric if I is an integer or antisymmetric if I is a half-integer.

The space factor of the total wave function of a homonuclear diatomic molecule could be symmetrized or antisymmetrized by constructing a two-term wave function, as we did with a two-electron wave function. However, the wave functions we have constructed are generally eigenfunctions of spatial symmetry operators, and this fact makes them either symmetric or antisymmetric with respect to exchange of the nuclei.

If the entire wave function is operated on by the inversion operator and then the electronic factor is operated on again by the inversion operator, the effect is to exchange the nuclei but not the electrons. If the entire molecule rotates by 180° around an axis perpendicular to the internuclear axis and if the electrons are then reflected through a plane perpendicular to the axis of rotation and finally inverted, the nuclei are exchanged and the electrons are back where they started. We can determine the effect of such operations on each factor of the total wave function.

Exercise 19.8

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 electron back at its original location.

As described in Chapter 18, 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**. A superscript $+$ is used to denote eigenfunctions of $\hat{\sigma}_{\mathrm{v}}$ with eigenvalue $+1$, and a superscript $-$ is used to denote eigenfunctions of $\hat{\sigma}_{\mathrm{v}}$ with eigenvalue -1. The rotational factor of the wave function of a diatomic molecule is a spherical harmonic function. The spherical harmonic functions for even value of J are eigenfunctions of the inversion operator with eigenvalue $+1$ (are "gerade"), and for odd values of J are eigenfunctions with eigenvalue -1 (are "ungerade"). The same eigenvalues apply to a rotation of 180° around an axis perpendicular to the bond axis, since this operation has the same effect as inversion.

Exercise 19.9

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 vibrational factor depends only on r, which is a scalar quantity that remains unchanged under inversion. The vibrational factor is an eigenfunction of the inversion operator with eigenvalue $+1$ for all values of the quantum number v. For any diatomic molecule, we must choose wave functions such that the outcome of a set of symmetry operations that exchanges the nuclei changes the sign of the wave function for fermion nuclei, and does not change the sign of the wave function for boson nuclei.

EXAMPLE 19.5

Find the permitted wave functions for H_2 in its electronic ground state.

Solution

The ground electron configuration is $(\sigma_g 1s)^2$. The electronic wave function is a product of two gerade space orbitals, and is gerade. The nuclear factor in the wave function must be antisymmetric. If the nuclear spin function is the antisymmetric singlet function, the rotational wave function must be gerade, which means that J must be an even integer. If the nuclear spin function is one of the triplet functions, which are symmetric, the rotational wave function must be ungerade, which means that J must be an odd integer.

The form of hydrogen with triplet nuclear spin states and odd values of J is called **ortho hydrogen**, and the singlet, even-J form is called **para hydrogen**. 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. The interconversion between the singlet and triplet states is extremely slow in the absence of a magnetic field or a catalyst, so these two forms of hydrogen can be separated from each other.

In Example 19.5, we have seen that for each of the forms of hydrogen, only half of the rotational wave functions occur. This is a general occurrence for homonuclear diatomic molecules, since a given electronic wave function will always demand either a symmetric or antisymmetric nuclear function. Therefore, for a given electronic state and a given nuclear spin state in a homonuclear diatomic molecule, either odd values of J will occur or even values of J will occur, but not both. The restriction that either even J occurs or odd J occurs does not apply to a heteronuclear molecule, since the nuclei are not identical.

***Exercise 19.10**

For ^{200}Hg, $I = 0$ and the electronic ground state is g and +. What values of J can occur with $^{200}Hg_2$?

19.3 Rotation and Vibration in 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 uncorrected energy level expression of Eq. (19.2-28) for diatomic molecules. To study the rotation of a polyatomic molecule, we pretend that the molecule is somehow prevented from vibrating. To study the vibration of a polyatomic molecule we pretend that the molecule is prevented from rotating. We could have obtained Eq. (19.2-28) for the energy of a diatomic molecule by adopting this policy, since the result was that the energy was that of a nonrotating harmonic oscillator plus that of a nonvibrating rigid rotor.

Rotation of Polyatomic Molecules

We assume that all bond lengths and bond angles of a polyatomic molecule are locked at their equilibrium values, so that the molecule rotates as a rigid body. For example, we assume that a methane molecule rotates with all bond angles held at the tetrahedral angle of 109.5° and with all bond lengths held fixed at the equilibrium length of 111 pm. This is a fairly good approximation for small values of the rotational and vibrational energies.

The classical rotation of a rigid body is described in terms of **moments of inertia** taken relative to three mutually perpendicular axes. For an object consisting of n point masses, the moment of inertia about an axis is defined to be

$$I_{\text{axis}} = \sum_{i=1}^{n} m_i r_{i(\text{axis})}^2 \tag{19.3-1}$$

where m_i is the mass of the ith point mass and $r_{i(\text{axis})}$ is the perpendicular distance from this point mass to the specified axis. For example, the moment of inertia about the z axis is

$$I_z = \sum_{i=1}^{n} m_i(x_i^2 + y_i^2) \tag{19.3-2}$$

The moments of inertia about the x and y axes are defined similarly. There are six additional quantities, which are called **products of inertia**:

$$I_{xy} = I_{yx} = \sum_{i=1}^{n} m_i x_i y_i \tag{19.3-3}$$

The other two distinct products of inertia, $I_{yz} = I_{zy}$ and $I_{xz} = I_{zx}$, are defined analogously. For both the moments of inertia and the products of inertia, we neglect the masses of the electrons and include only the nuclei in the sums.

There is a theorem that states for any rigid object it is possible to choose a set of perpendicular axes with the origin at the center of mass of the molecule 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. One first decides on the symmetry operators that belong to the molecule. Principal axes are then obtained by placing 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, a set of principal axes is obtained simply by choosing this rotation axis as one of the axes. If there is a two-fold rotation axis, as with a molecule that has $C_{2\text{v}}$ symmetry, a set of principal axes is obtained by choosing this axis as one of the principal axes and placing the other two axes in planes of symmetry.

Since 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

$$I_A \leq I_B \leq I_C \tag{19.3-4}$$

If all three of its principal moments are equal, an object is called a **spherical top**. The name "top" is apparently chosen because of the rotating toys by that name. Any kind of a smooth spherical ball such as a billiard cue ball is a spherical top, and a tetrahedral molecule such as methane or an octahedral molecule such as sulfur hexafluoride is also a spherical top. Any mutually perpendicular axes passing through the center of mass are principal axes. If two of the principal moments 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 a symmetric top or a spherical top. If all three principal moments of inertia are unequal, the object is called an **asymmetric top**. A boomerang is an asymmetric top, as is a bent triatomic molecule such as sulfur dioxide or water.

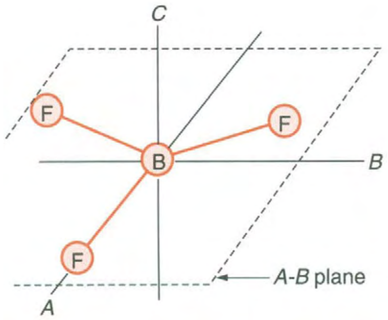

Figure 19.4. The Boron Trifluoride Molecule and Its Principal Axes. These principal axes are identified by inspection. All must pass through the center of mass, and one must coincide with the three-fold rotational axis. The *A* and *B* axes could be placed anywhere in the horizontal plane with no change in the moments of inertia.

EXAMPLE 19.6

Show that BF_3, a trigonal planar molecule, is an oblate symmetric top.

Solution

Orient the molecule as in Figure 19.4, with one BF 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 19.11

Show that methane is a spherical top.

The total angular momentum **L** of any object is the vector sum of the angular momenta of all the particles making up the object. The classical rotation energy of a rigid object is given in terms of its angular momentum and its principal moments of inertia by

$$E_{\text{classical}} = \frac{L_A^2}{2I_A} + \frac{L_B^2}{2I_B} + \frac{L_C^2}{2I_C} \tag{19.3-5}$$

where L_A, L_B, and L_C are the instantaneous components of the vector **L** on the *A*, *B*, and *C* axes. We can write the quantum-mechanical expression for the rotational energy from Eq. (19.3-5) by replacing the classical variables by their quantum-mechanical eigenvalues. Consider first the case of a diatomic molecule or linear polyatomic molecule, for which I_A vanishes and for which the other two moments are equal. There can be no component of angular momentum on the *A* axis, because there are no nuclei that are not on this axis (the contributions of the electrons are very small and we neglect them). Equation (19.3-5) becomes

$$E_{\text{classical}} = \frac{1}{2I_B}(L_B^2 + L_C^2) = \frac{L^2}{2I_B} \tag{19.3-6}$$

From Eq. (16.1-40) we have the values that a general angular momentum can assume in quantum mechanics. Substitution of this formula into Eq. (19.3-6) gives

$$E_{\text{qm}} = E_J = \frac{\hbar^2}{2I_B}J(J+1) \tag{19.3-7}$$

which agrees with Eq. (19.2-17) for a diatomic molecule, but also applies to a linear polyatomic molecule such as C_2H_2. The possible values of L_z are given by Eq. (16.1-43).

$$L_z = \hbar M \qquad (M = 0, \pm 1, \pm 2, \ldots, \pm J) \tag{19.3-8}$$

The energy does not depend on the quantum number *M*, so the energy level for a particular value of *J* has a degeneracy of $2J + 1$ (one state for each value of *M*).

Consider next a spherical top, for which $I_A = I_B = I_C$. For this case

$$E_{\text{classical}} = \frac{1}{2I_A}(L_A^2 + L_B^2 + L_C^2) = \frac{1}{2I_A}L^2 \tag{19.3-9}$$

The quantum-mechanical energy is

$$E_{\text{qm}} = E_J = \frac{\hbar^2}{2I_A}J(J+1) \tag{19.3-10}$$

This formula is the same as that for the energy of the linear molecule, with the energy depending only on the quantum number J. The degeneracy is not the same as for a linear molecule. In both cases, there is a quantum number M that specifies the projection of the angular momentum on one of the coordinate axes, which we choose as the z axis. 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

$$L_A = \hbar K \qquad (K = 0, \pm 1, \pm 2, \ldots, \pm J) \tag{19.3-11}$$

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

$$g_J = (2J+1)^2 \qquad \text{(spherical top)} \tag{19.3-12}$$

The energy levels of symmetric tops and asymmetric tops are quite complicated, and we do not discuss them.[5] In all cases, the three quantum numbers J, M, and K occur. The energy levels can depend on the values of all three quantum numbers.

In Section 19.3, we found that only half of the values of the rotational quantum number J occurred for a homonuclear diatomic molecule. In the case of polyatomic molecules, the situation 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. It is defined as the number of equivalent orientations of the molecule, which means the number of rotational positions in which a model of the nonvibrating molecule can be placed and have each nuclear location occupied by a nucleus of the same kind as in the first orientation. No inversion or reflection operations are used in determining a symmetry number.

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 in these cases. The symmetry number of boron trifluoride is 6 (three positions with one side of a model 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 positions 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.

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[5] G. Herzberg, *Infrared and Raman Spectra*, Van Nostrand Reinhold, New York, 1945, pp. 42ff.

*Exercise 19.12

Find the symmetry numbers of the molecules:

- **a.** Chloroform, $CHCl_3$
- **b.** Water, H_2O
- **c.** Benzene, C_6H_6
- **d.** Dichloromethane, CH_2Cl_2
- **e.** Toluene, $C_6H_5CH_3$
- **f.** Sulfur hexafluoride, SF_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. An observed vibration consists of concerted motions of all or part of the nuclei. The first problem in analyzing the vibrations is to determine the vibrations that the molecule would undergo if governed by classical mechanics. This is a complicated process, and we will give only a cursory summary of the starting point.[6] Some software packages such as CAChe and Spartan carry out the process automatically. We assume that the molecule is not rotating but that the nuclei can be displaced from their equilibrium positions. 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 let 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.

We assume that the Born–Oppenheimer electronic energy (the vibrational potential energy) depends quadratically on these displacements:

$$\mathscr{V} = \mathscr{V}_e + \sum_{i=1}^{3n}\sum_{j=1}^{i} b_{ij}q_iq_j \qquad (19.3\text{-}13)$$

where the b's are constants and where the limits of the sums are chosen such that there is only one term for a given i and a given j. In addition to terms with $i = j$, "cross terms" can occur in which $i \neq j$. Equation (19.3-13) is analogous to Eq. (19.2-21) and will be a good approximation for small values of the q's. We refer to it as a **harmonic potential energy function**. The presence of the cross terms makes the q coordinates interfere with each other so that they do not vibrate independently.

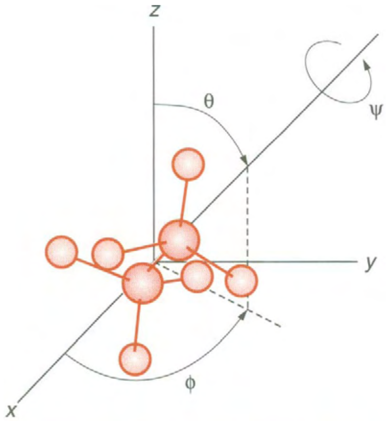

Figure 19.5. Three Angles to Specify the Orientation of a Nonlinear Polyatomic Molecule. Two angles are required to specify the orientation of one molecular axis. The angles θ and ϕ are used for these two angles. The angle ψ is used to specify the angle of rotation about this axis.

We now find a transformation to a new set of coordinates such that each new coordinate can oscillate independently from the other new coordinates. In order to do this, we must find new coordinates such that the potential energy function is given by a formula like that of Eq. (19.3-3) but without cross terms. The number of such coordinates turns out to be smaller than $3n$. 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 19.5. The Born–Oppenheimer energy is independent of the location of the center of mass of the molecule and the orientation of the molecule. This energy, which acts as a potential energy for nuclear motion, therefore depends on

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[6] E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, *Molecular Vibrations*, McGraw-Hill, New York, 1955.

only $3n - 5$ of the new coordinates for a linear molecule, and on $3n - 6$ of them for a nonlinear molecule.

We will not discuss the procedure, but new coordinates can be found that are linear combinations of the q's:

$$w_i = \sum_{j=1}^{3n} c_{ij} q_j \tag{19.3-14}$$

where the c's are constants, such that

$$\mathcal{V} = \mathcal{V}_e + \frac{1}{2} \sum_{i=1}^{3n-5(6)} \kappa_i w_i^2 \tag{19.3-15}$$

These coordinates are called **normal coordinates**. The κ's are constants (effective force constants for the new coordinates). The upper limit of the sum indicates that there are $3n - 5$ terms for a linear molecule and $3n - 6$ terms for a nonlinear molecule, and we will use this notation in the future.

The classical vibrational energy can be written

$$E_{\text{vib}} = \mathcal{K}_{\text{vib}} + \mathcal{V}_{\text{vib}} = \frac{1}{2} \sum_{i=1}^{3n-5(6)} \left[M_i \left(\frac{dw_i}{dt} \right)^2 + \kappa_i w_i^2 \right] + \mathcal{V}_e \tag{19.3-16}$$

where the M's are constants (effective masses for the new coordinates). Equation (19.3-16) is a sum of harmonic oscillator energy expressions. According to classical mechanics, each normal coordinate oscillates independently with a characteristic classical frequency given by

$$\nu_i = \frac{1}{2\pi} \sqrt{\frac{\kappa_i}{M_i}} \tag{19.3-17}$$

The motions of the normal coordinates are called **normal modes** of motion. 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 is written, 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:

$$\psi_{\text{vib}} = \psi_1(w_1)\psi_2(w_2) \cdots = \prod_{i=1}^{3n-5(6)} \psi_i(w_i) \tag{19.3-18}$$

where each factor is a harmonic oscillator wave function. The energy is a sum of harmonic oscillator energy eigenvalues:

$$E_{\text{vib}} = \prod_{i=1}^{3n-5(6)} h\nu_i \left(v_i + \frac{1}{2} \right) \tag{19.3-19}$$

where $v_1, v_2, \ldots$ are vibrational quantum numbers, one for each normal mode, and $\nu_1, \nu_2, \ldots$ are the classical frequencies. The quantum numbers are nonnegative integers, and are not required to be equal to each other. Just as in classical mechanics, each normal mode oscillates independently of the others.

Figure 19.6 shows schematically the motion for 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. These values are generally called

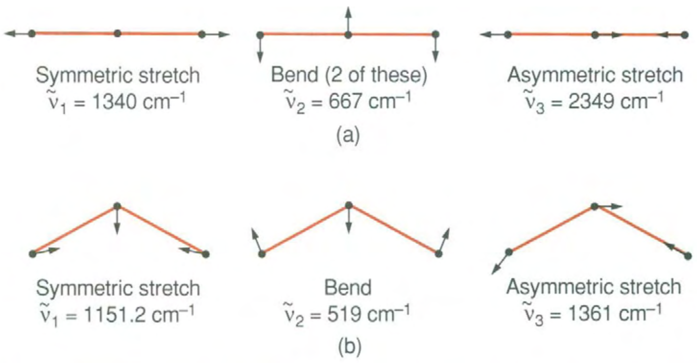

Figure 19.6. Vibrational Normal Modes. (a) **Carbon dioxide**. The linear CO_2 molecule has four normal modes. The two bends have the same frequency and are shown together. (b) **Sulfur dioxide**. The nonlinear SO_2 molecule has three normal modes, as shown. The general pattern is followed by both molecules: the bend has the lowest frequency, the symmetric stretch has an intermediate frequency, and the asymmetric stretch has the highest frequency.

"frequencies." The common unit is cm^{-1}, although the SI unit would be m^{-1}. The arrows in the diagrams show the direction of motion of each nucleus away from its equilibrium position. Each nucleus oscillates, returning to its equilibrium position and passing through it. In each of the triatomic molecules there is a normal mode called a **symmetric stretch** in which both bonds shorten and lengthen together. There is also a mode called an **asymmetric stretch** in which one bond lengthens while the other shortens. There is also a mode called a **bend** in which the bond angle oscillates. A linear triatomic molecule such as carbon dioxide can bend in two perpendicular directions, so there are two bending modes with the same frequency. A nonlinear triatomic molecule 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.

There is a common pattern of frequencies for triatomic molecules, which we see in these examples: *Asymmetric stretches have the highest frequency, symmetric stretches are a little lower in frequency, and bends are considerably lower in frequency.* For a molecule with more than three atoms there are numerous normal modes, and we do not attempt to describe all of them for other molecules. 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. Advanced techniques, including group theory, are used in studying the normal modes of polyatomic molecules.[7]

In some large molecules, a few of the normal modes correspond to fairly large oscillations of one bond length or bond angle while other bond lengths and bond angles remain nearly constant. 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 $2850\,\mathrm{cm}^{-1}$ to $3000\,\mathrm{cm}^{-1}$ range, and compounds with an O–H bond usually exhibit an O–H stretching frequency in the $3600\,\mathrm{cm}^{-1}$ to $3700\,\mathrm{cm}^{-1}$ range. Table A.24 of Appendix A lists a few such characteristic frequencies and organic chemistry textbooks give longer lists.

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[7] Ira N. Levine, *Molecular Spectroscopy*, Wiley, New York, 1975, pp. 427ff.

Exercise 19.13

Using a software package such as Spartan or CAChe, find the normal modes and their predicted frequencies for carbon dioxide, sulfur dioxide, and water. Compare the predicted frequencies with the experimental frequencies. The Spartan software package shows movies of classical normal mode motions. The frequencies for carbon dioxide and sulfur dioxide are in Figure 19.6, and the frequencies (divided by the speed of light) for water are $3657\,\mathrm{cm}^{-1}$, $1595\,\mathrm{cm}^{-1}$, and $3756\,\mathrm{cm}^{-1}$.

19.4 The Equilibrium Populations of Molecular States

We have derived formulas for the energy eigenvalues for vibrational, rotational, and translational energy for molecules. These eigenvalues correspond to the states that are available to molecules in a dilute gas. At thermal equilibrium, the states are occupied by numbers of molecules proportional to the Boltzmann factor of Eqs. (1.5-17) and (10.2-35):

$$(\text{Population of state of energy } E) \propto e^{-E/k_\mathrm{B}T} \tag{19.4-1a}$$

where k_B is Boltzmann's constant, equal to $1.3807 \times 10^{-23}\ \mathrm{J\,K^{-1}}$, and T is the absolute temperature. Each state in an energy level will have the same population, so that if g is the degeneracy of the level,

$$(\text{Population of energy level}) \propto g e^{-E/k_\mathrm{B}T} \tag{19.4-1b}$$

Populations of Rotational Energy Levels of Diatomic Molecules

To the approximation of Eq. (19.2-42), a diatomic molecule has a rotational energy eigenvalue that is independent of the vibrational energy. A rotational level has an energy eigenvalue

$$E_J = hB_\mathrm{e}J(J+1) = hc\tilde{B}_\mathrm{e}J(J+1) \tag{19.4-2}$$

and a degeneracy

$$g_J = 2J + 1 \tag{19.4-3}$$

Therefore, for the vibrational quantum number equal to J,

$$\begin{pmatrix}\text{Population of rotational}\\ \text{energy level } J\end{pmatrix} \propto (2J+1)e^{-E_J/k_\mathrm{B}T} \tag{19.4-4}$$

EXAMPLE 19.7

a. Using the value of B_e for CO in Example 19.4, 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 this temperature.

c. Find the level with the largest population at this temperature.

Solution

a. Let $N(J, M)$ be the number of molecules with quantum numbers equal to J and M. The population of all of the $J = 2$ states is the same. For the $J = 2$, $M = 0$ state:

$$\frac{N(2,0)}{N(0,0)} = e^{-(E_2-E_0)/k_BT} = e^{-6hB_e/k_BT}$$

$$= \exp\left(\frac{-2.302\times 10^{-22}\ \text{J}}{(1.3807\times 10^{-23}\ \text{J K}^{-1})(298\ \text{K})}\right) = e^{-0.055947} = 0.9456$$

b. Let $N(J)$ be the population of level J:

$$N(J) = (2J+1)N(J,M)$$

$$\frac{N(2)}{N(0)} = \frac{5N(2,0)}{N(0,0)} = 5(0.9456) = 4.728$$

c. 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 will give the desired value.

$$\frac{d}{dJ}\{(2J+1)\exp[-hc\tilde{B}_eJ(J+1)/k_BT]\} = \exp\left(\frac{-hc\tilde{B}_eJ(J+1)}{k_BT}\right)\left(2-\frac{hc\tilde{B}_e}{k_BT}(2J+1)^2\right)$$

The exponential factor does not vanish, so this expression vanishes when the second factor vanishes, which occurs when J has the value J_{mp}:

$$(2J_{\text{mp}}+1)^2 = \frac{2k_BT}{hc\tilde{B}_e} = 214.5$$

$$J_{\text{mp}} = 6.82 \approx 7$$

For a typical molecule at room temperature, several of the rotational energy levels are significantly populated. Molecules with smaller reduced masses have fewer occupied rotational levels, and molecules with larger reduced masses have more occupied rotational levels.

*Exercise 19.14

Find the rotational level with the largest population for HF molecules at 500.0 K. The internuclear distance equals 0.9168×10^{-10} m.

Since the vibrational levels of a diatomic molecule are nondegenerate, we have for the population of a vibrational energy level with quantum number v

$$(\text{Population of vibrational level}) \propto e^{-E_v/k_BT} \tag{19.4-5}$$

EXAMPLE 19.8

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 19.4, $\nu_e = 6.5049 \times 10^{13}\ \mathrm{s}^{-1}$:

$$\frac{E_{10} - E_{00}}{k_B T} = \frac{h\nu_e}{k_B T}$$

$$= \frac{(6.6261 \times 10^{-34}\ \mathrm{J\ s})(6.5049 \times 10^{13}\ \mathrm{s}^{-1})}{(1.3807 \times 10^{-23}\ \mathrm{J\ K}^{-1})(298.15\ \mathrm{K})} = 10.47$$

$$\frac{N(1,0)}{N(0,0)} = e^{-10.47} = 2.84 \times 10^{-5}$$

Since the vibrational energy levels are much more widely spaced than the rotational energy levels, the population of the excited vibrational states is very small at room temperature for typical diatomic molecules, as seen in this example. However, the difference is smaller with molecules that have larger reduced masses or smaller vibrational frequencies.

***Exercise 19.15**

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 required information is found in Table A.22 of Appendix A.

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 occupied by the same molecule is

$$p_{\mathrm{vib,rot}}(v, J) = p_{\mathrm{vib}}(v) p_{\mathrm{rot}}(J) \qquad (19.4\text{-}6)$$

The same result can be obtained by combining the two contributions to the energy.

EXAMPLE 19.9

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,

$$(\text{Probability}) = (4.728)(2.84 \times 10^{-5}) = 1.34 \times 10^{-4}$$

Exercise 19.16

Use the energy of the level with $v = 1, J = 2$ directly in the Boltzmann formula of Eq. (19.4-1b) to obtain the result of Example 19.9 by a different calculation.

The probabilities of electronic energy levels are also governed by the Boltzmann probability distribution. Since most electronic states are even more widely spaced than vibrational states, excited electronic states of most molecules are almost unpopulated at room temperature.

*Exercise 19.17

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.

Summary of the Chapter

The motion of the nuclei of molecules consists of translational, rotational, and vibrational motions. To a good approximation, these three types of motion make separate contributions to the molecular energy of a diatomic molecules. The translational energy for 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 is taken to be that of normal modes, each one of which oscillates like a harmonic oscillator.

The populations of rotational, vibrational, and electronic states of molecules are described by the Boltzmann probability distribution.

$$(\text{Population of vibrational level}) \propto e^{-E_v/k_B T}$$

PROBLEMS

Problems for Section 19.1

19.18. Repeat the calculation of Example 19.1 for a box 1.00 m on a side. Compare your answer with that of Example 19.1 and comment on any qualitative difference.

***19.19.** Find the values of the three translational quantum numbers (assume 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.

19.20. Find the values of the three translational quantum numbers (assume 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.

Problems for Section 19.2

***19.21.** **a.** Calculate the reciprocal wavelength of the light absorbed by H_2 in making the transition from $J = 1$ to $J = 2$.

b. Using information on the normal H_2 molecule, predict the reciprocal wavelength of the light absorbed by HD in making the transition from $J = 1$ to $J = 2$. The isotope D is deuterium, ^2H.

19.22. 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 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.

***19.23.** Using information on the normal H_2 molecule, find the frequencies of vibration of the HD and D_2 molecules, where D is deuterium, ^2H. Compare these with the vibrational frequency of normal H_2.

19.24. 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,

c. ^{35}Cl is replaced by ^{37}Cl and ^{1}H is replaced by ^{2}H.

***19.25.** 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.

19.26. 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.

***19.27.** We will find in Chapter 20 that when electromagnetic radiation is emitted or absorbed by 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.

19.28. We will find in Chapter 20 that when electromagnetic radiation is emitted or absorbed by 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.

19.29. Show that the formula for the moment of inertia in Eq. (19.3-2) gives the same result as the formula in Eq. (19.2-30) for a diatomic molecule.

Problems for Section 19.3

19.30. Classify each of the following molecules as linear, spherical top, prolate symmetric top, oblate symmetric top, or asymmetric top:

a. H_2O **b.** CO_2 **c.** CH_3Cl
d. $CHCl_3$ **e.** CH_2Cl_2 **f.** CCl_4

***19.31.** Classify each of the following molecules as linear, spherical top, prolate symmetric top, oblate symmetric top, or asymmetric top:

a. C_6C_6 **b.** C_2H_6 **c.** C_2H_5Cl
d. C_2H_4 **e.** C_2H_2 **f.** *trans*-$C_2H_2F_2$

19.32. Determine the number of vibrational normal modes for each of the molecules in Problem 19.30.

***19.33.** Determine the number of vibrational normal modes for each of the molecules in Problem 19.31.

19.34. Without doing any calculations, assign principal axes for the molecules in Problem 19.30.

19.35. Without doing any calculations, assign principal axes for the molecules in parts (a), (b), (d), and (e) of Problem 19.31.

19.36. 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 the isotopes ^{16}O and ^{1}H. Pick a product of inertia and show that it vanishes.

***19.37. 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 a oblate symmetric top.

b. Find the rotational energy of the $J = 1$, $K = 1$ level of chloroform. The energy of a oblate symmetric top is given by the formula[8]

$$E = J(J+1)\frac{\hbar^2}{2I_B} + K^2\left(\frac{1}{I_C} - \frac{1}{I_B}\right)\frac{\hbar^2}{2}$$

c. Find the ratio of the population of the $J = 1$, $K = 1$ level of chloroform to the population of the rotational ground state at 298.15 K.

19.38. 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]

$$E = J(J+1)\frac{\hbar^2}{2I_B} + K^2\left(\frac{1}{I_A} - \frac{1}{I_B}\right)\frac{\hbar^2}{2}$$

c. Find the ratio of the population of the $J = 1$, $K = 1$

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[8] Jeff C. Davis, Jr., *op. cit.*, p. 316 (Note 1).

[9] Jeff C. Davis, Jr., *op. cit.*, p. 315 (Note 1).

level of chloromethane to the population of the rotational ground state at 298.15 K.

***19.39.** 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?

19.40. 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

***19.41.** 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

Problems for Section 19.4

19.42. 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. Normal H_2
b. HD,
c. D_2, where D is deuterium, ^2H

***19.43.** 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.

19.44. **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.

***19.45.** Find the rotational level of maximum population for H_2 at 298 K. Do it separately for ortho and para hydrogen.

19.46. Find the rotational level of maximum population for I_2 at 298 K.

General Problems

19.47. 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.

c. Find the ratio of the populations of the first two energy levels.

19.48. **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 LCAO-MO treatment in Chapter 17, 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.

c. 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.

d. 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.

***19.49.** 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 further 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.

20

Spectroscopy and Photochemistry

OBJECTIVES

After studying this chapter, a student should:

1. understand the Bohr frequency rule and be able to solve problems related to it;
2. understand the origin of selection rules and be able to use them in interpretation of spectra;
3. be able to solve problems using the Beer–Lambert law;
4. understand the principles of photochemistry;
5. understand the principles of Raman spectroscopy and be able to predict which normal modes of a polyatomic molecule will be Raman active;
6. be able to deduce molecular structural information from infrared, microwave, and Raman spectral features;
7. understand the principles of electron spin resonance and nuclear magnetic resonance spectroscopy;
8. be able to deduce molecular structural information from electron spin resonance and nuclear magnetic resonance spectra;
9. understand the principles used in Fourier transform infrared and NMR spectroscopy.

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 interaction.
2. Emission/absorption spectroscopy is based on 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. Measurement of the wavelengths of emitted or absorbed light allows the determination of energy level differences.
4. Selection rules predict which transitions between pairs of levels will occur with absorption or emission of radiation.
5. Concentrations can be determined spectroscopically using the Beer–Lambert law.
6. The spectroscopy of atoms involves electronic energy levels.
7. Transitions between rotational states of molecules produce spectra in the microwave region.
8. Transitions between vibrational states of molecules produce spectra in the infrared region.
9. Transitions between electronic states of molecules produce spectra in the visible and ultraviolet regions.
10. Photochemistry is closely related to spectroscopy and involves chemical reactions that are initiated by absorption of radiation.
11. Other types of optical spectroscopy such as Raman spectroscopy, can supplement emission/absorption spectroscopy.
12. Magnetic resonance spectroscopy involves transitions between states that have different energies in a magnetic field.
13. Some modern spectrometers use Fourier transform techniques.

20.1 Emission/Absorption Spectroscopy and Energy Levels

In Chapters 14 through 19, we studied the energies and wave functions of atoms and molecules theoretically. These energy levels can be studied experimentally by measuring the wavelengths of the light that is emitted, absorbed, or scattered in processes that involve transitions between energy levels. We begin with a discussion of optical spectroscopy, involving the emission and absorption of photons by atoms or molecules.

The Bohr Frequency Rule

According to the Planck–Einstein relation of Eq. (14.3-8), the energy of a photon is

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda} \tag{20.1-1}$$

where h is Planck's constant, ν is the frequency of the radiation, c is the speed of propagation of electromagnetic radiation and λ is the wavelength. Since wavelengths of radiation can be measured very accurately, photon energies can be determined with great accuracy. The fundamental 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 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**,

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda} = E_{\text{upper}} - E_{\text{lower}} \tag{20.1-2}$$

where E_{upper} and E_{lower} are the energy values for the upper and lower levels of the atom or molecule. If a photon is absorbed, the upper level is the final level and the lower level is the initial level. If a photon is emitted, the lower level is the final level and the upper level is the initial level. In either event, Eq. (20.1-2) applies as written. The Bohr frequency rule is based on the assumption that only one photon is absorbed or emitted at a time. Multiphoton transitions can be studied, but we do not discuss them.[1]

The spectrum of electromagnetic radiation is arbitrarily divided into several regions, as shown in Table 20.1. Typical spacings between electronic energy levels are roughly 2 eV to 10 eV, corresponding to photon energies in the visible and ultraviolet region. Spacings between vibrational energy 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 of molecules are too small to observe spectroscopically. The absorption of photons can also break chemical bonds or cause transitions to reactive excited states, which is the basis of photochemistry. Bond energies are usually expressed in kilojoules per mole,

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[1] See for example C. K. Rhodes, *Science*, **229**, 1345 (1985).

Table 20.1 Regions of the Electromagnetic Spectrum

Name of Region	Wavelength	Photon Energy/eV
Gamma radiation	<10 pm	>124,000
X-radiation	10 pm–10 nm	124,000–124
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	0.00124–0.0000124
Radiofrequency radiation (including AM, FM, TV)	10 cm–10 km	<0.0000124

and typical chemical bond energies are near 400 to 500 kJ mol^{-1}. Photons with energies large enough to break chemical bonds lie in the ultraviolet region.

EXAMPLE 20.1

Find the frequency and wavelength of a photon with enough energy to break a chemical bond whose bond energy is 4.31 eV (corresponding to 416 kJ mol^{-1}, the average bond energy of a C–H bond).

Solution

$$\nu = \frac{E}{h} = \frac{(4.31\ \text{eV})(1.602\times 10^{-19}\ \text{J eV}^{-1})}{6.6261\times 10^{-34}\ \text{J s}} = 1.04\times 10^{15}\ \text{s}^{-1}$$

$$\lambda = \frac{2.9979\times 10^{8}\ \text{m s}^{-1}}{1.04\times 10^{15}\ \text{s}^{-1}} = 2.88\times 10^{-7}\ \text{m} = 288\ \text{nm}$$

*Exercise 20.1

An einstein is a mole of photons.

Find the energy per photon and per einstein for

a. Microwave radiation with $\lambda = 1.0$ cm

b. X-radiation with $\lambda = 1.0\times 10^{-10}$ m

The Quantum Mechanics of Spectroscopic Transitions. Selection Rules

Our discussion of quantum mechanics 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 an atom or a molecule plus radiation. The standard approximate treatment uses a time-dependent version of perturbation theory that treats the atom or molecule quantum mechanically but treats the radiation as a classical wave consisting of an oscillating electric field and an oscillating magnetic field (see Section 14.2).[2] If the radiation is plane polarized, the electric field oscillates in a plane containing the

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[2] Jeff C. Davis, *Advanced Physical Chemistry*, The Ronald Press, New York, 1965, pp. 243ff.

direction of propagation, and the magnetic field oscillates in the plane perpendicular to this plane and also containing the direction of propagation, as in Figure 14.9.

Since an electric field exerts a force on any charged particle and a magnetic field exerts a force on any 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 field is many times more effective in causing atomic and molecular transitions than the magnetic field, and is more important in optical spectroscopy. However, the transitions between nuclear spin states in NMR spectroscopy are magnetic dipole transitions.

In the time-dependent perturbation treatment of electric dipole transitions, the Hamiltonian operator of the molecule in the presence of radiation is written in a way somewhat similar to Eq. (17.2-1):

$$\hat{H} = \hat{H}^{(0)} + \hat{H}' \tag{20.1-3}$$

This differs from Eq. (17.2-1) in that $\hat{H}^{(0)}$ is the complete time-independent Hamiltonian operator of the molecule in the absence of radiation. The time-dependent perturbation term $\hat{H}'$ describes the interaction between the molecule and the electric field of the radiation. We now assume that the zero-order time-independent Schrödinger equation has been solved to a usable approximation:

$$\hat{H}^{(0)}\psi_j^{(0)} = E_j^{(0)}\psi_j^{(0)} \tag{20.1-4}$$

The wave function $\psi_j^{(0)}$ is the coordinate wave function (energy eigenfunction) of the molecule in the absence of radiation. We would usually approximate it as a product of a translational factor, a rotational factor, a vibrational factor, and an electronic factor.

Inclusion of the perturbation produces a time-dependent wave function, which is written as a linear combination of the zero-order functions as in Eq. (15.2-14):

$$\Psi(q,t) = \sum_j a_j(t)\psi_j^{(0)}(q) \tag{20.1-5}$$

where q stands for all of the coordinates of the particles in the molecule and where a scheme must be found to determine the coefficients $a_1, a_2, \ldots$. Since the zero-order wave functions are time-independent, these coefficients contain all of the time dependence of the wave function, and we obtain approximate expressions for them using perturbation theory.

In order to observe transitions we specify that at time $t = 0$ the wave function is equal to one of the zero-order functions, $\psi_n^{(0)}$,

$$\Psi(q,0) = \psi_n^{(0)}(q) \tag{20.1-6}$$

so that at $t = 0$,

$$a_j(0) = \delta_{jn} = \begin{cases} 1 & \text{if } j = n \\ 0 & \text{if } j \neq n \end{cases} \tag{20.1-7}$$

where δ_{jn} is the **Kronecker delta**, introduced in Eq. (15.4-29). Its definition is exhibited in the second equality of Eq. (20.1-7). 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 $\psi_j^{(0)}$. More than one coefficient can become nonzero. For a new student of quantum mechanics, it is sometimes difficult to accept the fact that a single wave function can describe different possible outcomes. We already found this kind of behavior in Chapter 14 in the discussion of a free particle. In that chapter, we had a single wave function that corresponded to a certain probability that a traveling wave was moving from left to right and another probability that it was moving from right to left. In this case we have a single wave function corresponding to a certain probability that the molecule makes a transition from state n to state j and at the same time corresponding to another probability that it makes a transition to another state or remains in state n. It is possible to think of a wave function as representing a large number of identical systems (an ensemble of systems) instead of one system. All of the systems in the ensemble are in the same zero-order state at time zero, but at a later time the systems can occupy different zero-order states.

Time-dependent perturbation theory allows a formula to be derived that gives the coefficients as functions of time. The probability that the system is in the state corresponding to $\psi_j^{(0)}$ is proportional to $|a_j|^2$. If the radiation is polarized 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 integral[3]

$$(\mu_z)_{jn} = \int \psi_j^{(0)*} \hat{\mu}_z \psi_n^{(0)} \, dq \tag{20.1-8}$$

where $\hat{\mu}_z$ is the z component of the operator for the electric dipole of the atom or molecule, as in Eq. (18.4-9). The integration is over all values of all of the coordinates of the system, abbreviated by the symbol q. The integral in Eq. (20.1-8) is the z component of a vector quantity, $(\mu)_{jn}$, called the **transition dipole moment** for the transition from state n to state j.

For two states that have a nonzero transition dipole moment, a transition between them can 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. Only the electric dipole transitions are considered, and the perturbation theory is an approximate theory. Most of the selection rules are therefore not exactly obeyed. Forbidden transitions occur, but with lower probabilities than allowed transitions, so that spectral features corresponding to them have low intensities.

Inspection of Eq. (20.1-8) shows that the value of the transition dipole moment is unchanged if the initial and final states' wave functions are switched. This means that incident radiation will induce transitions from a lower-energy state to a higher-energy state with the same probability as it will induce transitions in the other direction. A transition that raises the energy of the atom or molecule corresponds to absorption, while one that lowers the energy corresponds to emission of a photon. This emission is called **stimulated emission**, since it is stimulated (caused to occur) by the radiation field. Radiation emitted in stimulated emission has the same wavelength as the incident photons, 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, a strong beam of undirectional radiation can result, with all of its waves in phase. Such radiation is said to be **coherent**, and this kind of radiation is emitted by lasers, which amplify electromagnetic radiation by adding radiation to an incident beam by stimulated

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[3] Davis, *loc. cit.* (Note 2).

emission. ("Laser" is an acronym for "light amplification by stimulated emission of radiation.") Transitions resulting in emission of photons can also occur in the absence of stimulating radiation. Such emission 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. Since there is no inducing radiation to specify a direction and phase, spontaneously emitted radiation emitted by a collection of many molecules is emitted in all directions and is not coherent.

Optical spectroscopy is of two principal types. In **absorption spectroscopy** the attenuation of an incident beam due to absorption is observed. In **emission spectroscopy** spontaneously emitted radiation from excited atoms or molecules is observed. The intensity of absorption of radiation due to a given transition depends on three factors: the intensity of the radiation, the inherent probability that the transition will take place, and the numbers of molecules in the upper and lower states (the "population" of the state). If the lower-energy state has a greater population absorption will be observed, but if the two states are equally populated the absorption and the stimulated emission will cancel and nothing will be observed. The intensity of spontaneous emission depends only the inherent probability of the transition and on the number of molecules in the upper state.

In a system of many atoms or molecules at thermal equilibrium, the number of atoms or molecules occupying a given state of energy E is proportional to the Boltzmann factor of Eq. (1.5-17) or Eq. (10.2-35):

$$(\text{Number of molecules with energy } E) \propto e^{-E/k_{\mathrm{B}}T} \qquad (20.1\text{-}9)$$

where k_{B} is Boltzmann's constant ($1.3807 \times 10^{-23}\ \mathrm{J\,K^{-1}}$) and T is the absolute temperature. The number of atoms or molecules occupying excited states drops rapidly with increasing energy so that states of energy values much higher than $k_{\mathrm{B}}T$ will at equilibrium be occupied by very few atoms or molecules. Absorptive or emissive transitions from such states cannot be observed unless these states are significantly populated by an input of energy that raises the effect temperature. For emission spectroscopy, these states can be populated with an electric arc, a spark, or a flame.

*Exercise 20.2

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 $E_2 = 10.2\ \mathrm{eV}$.

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 since light is transmitted in a medium at a speed that depends on wavelength and on the material of the medium. Light that strikes a boundary between two materials is refracted (has its path 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.

Diffraction gratings are also used to disperse the radiation. Figure 20.1a shows schematically how radiation is dispersed by a prism and Figure 20.1b shows how it is dispersed by a transmission grating, which passes radiation through a set of equally spaced parallel slits at which the radiation is diffracted. Figure 20.1b is very similar to Figure 14.6b. In the radiation that passes through the grating, crests that are in

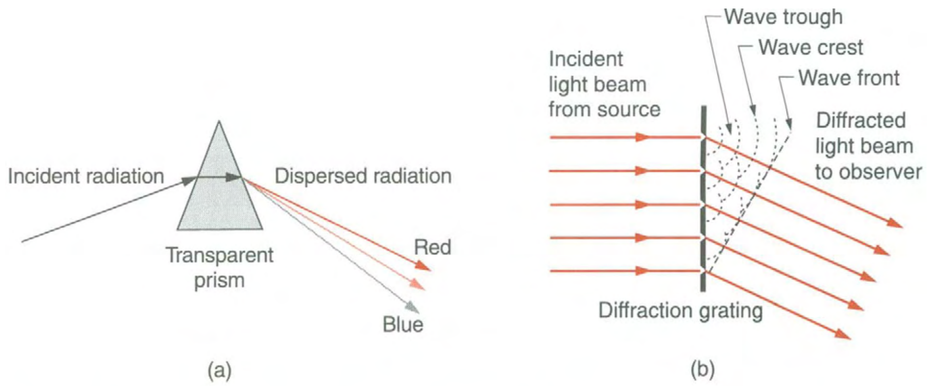

Figure 20.1. The Dispersion of Electromagnetic Radiation. **(a) Prism.** Since the refractive index depends on wavelength, different wavelengths are refracted through different angles. **(b) Transmission grating.** Since constructive interference is necessary to give the diffracted beam, different wavelengths are diffracted through different angles. The diagram shows first order, in which there is a difference of one wavelength in the paths from adjacent scattering centers. Second order corresponds to two wavelengths difference, and so on.

constructive interference produce a beam in a direction determined by the wavelength of the radiation and the slit spacing, so that different wavelengths produce beams at different angles. A reflection grating functions in a similar way.

In a simple spectroscope, the wavelengths of emitted light are observed by viewing the locations of bright images of the slit. If only narrow bands of wavelengths are emitted, the slit images look like line segments and these features are called **spectral lines**. In a spectrograph the dispersed light falls on a photographic film or plate and a permanent record of the spectrum is obtained, which allows accurate measurement of the line positions. Figure 20.2 shows a simulation of the visible portion of the emission spectrum of atomic hydrogen at low pressure.

Absorption Specroscopy. The Beer–Lambert Law

Absorption spectroscopy has been carried out in a **spectrophotometer** such as the one shown schematically in Figure 20.3. The light is dispersed by a prism or grating, collimated into a beam of nearly parallel rays, and passed through a cell containing the

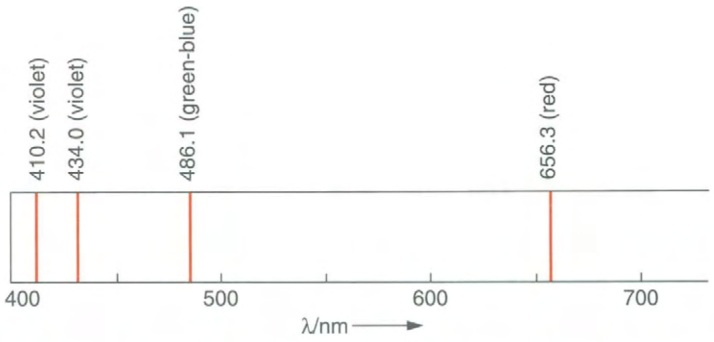

Figure 20.2. The Visible Portion of the Hydrogen Atom Emission Spectrum (Simulated). Each wavelength represented produces an image of the slit of the spectrograph. If only discrete wavelengths are present, as in this case, the spectrum is called a line spectrum.

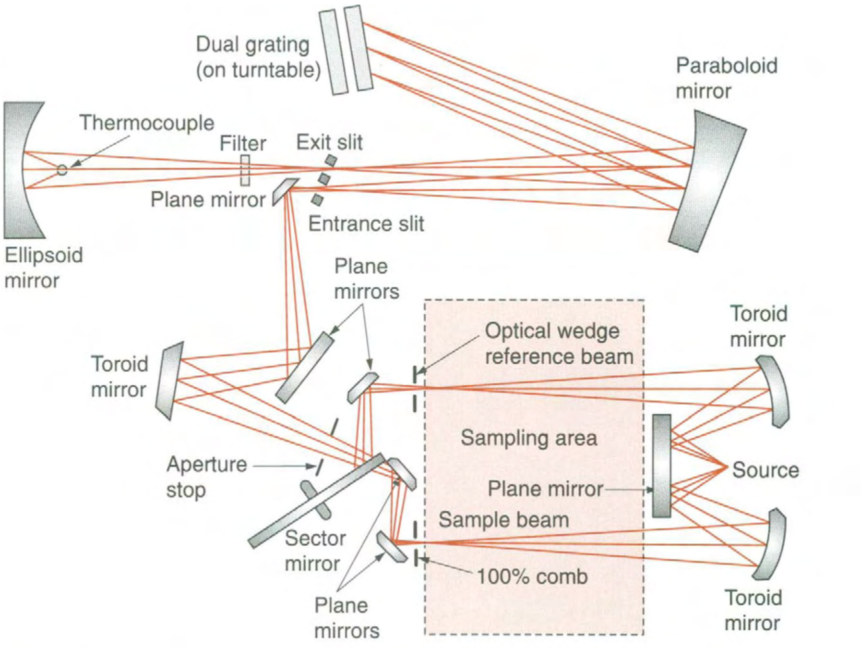

Figure 20.3. Schematic Diagram of a Filter-Grating, Double-Beam Infrared Spectrophotometer. This diagram shows a scanning instrument. The wavelength passed is determined by the angular position of the grating, which is mounted on a turntable, and generally rotated automatically by a motor. (Courtesy of Perkin-Elmer Corporation.)

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. More modern instruments use a Fourier transform technique, which we will discuss later in the chapter.

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, $I(\lambda)$, such that the energy carried by radiation with wavelengths in the infinitesimal wavelength range between λ and $\lambda + d\lambda$ is

$$\text{(Energy in range } d\lambda \text{ per unit time per unit area)} = I(\lambda)\, d\lambda \qquad (20.1\text{-}10)$$

A variable that is commonly plotted to represent an absorption spectrum is the transmittance, T, usually expressed in percent:

$$T(\lambda) = \left(\frac{I(\lambda)_{\text{out}}}{I(\lambda)_{\text{in}}}\right) \times 100\% \quad \text{(definition)} \qquad (20.1\text{-}11)$$

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.

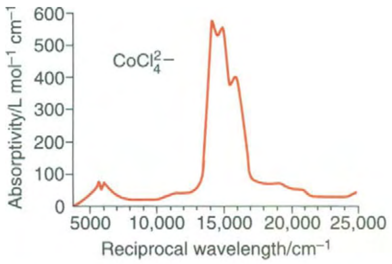

Figure 20.4. The Absorption Spectrum of 0.001 mol L^{-1} CoCl$_4^{2-}$ in 10 mol L^{-1} HCl Solution. This continuous spectrum arises because of the broadening of the spectral lines due to solvent interaction. From Russell S. Drago, *Physical Methods in Chemistry*, W.B. Saunders, Philadelphia, 1977, p. 392.

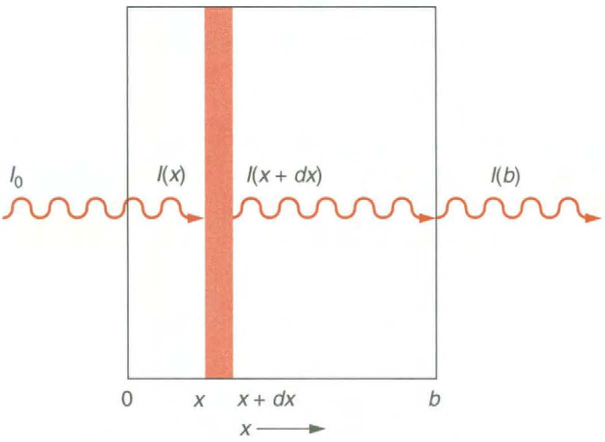

Figure 20.5. Absorption of Light in a Thin Slab. The attenuation of the light due to the absorbing substance in the thin slab is assumed proportional to the concentration of the substance and to the thickness of the slab.

Figure 20.4 shows an absorption spectrum for a sample in liquid solution, plotted as a function $1/\lambda$, measured in cm^{-1}. This spectrum shows absorption over broad ranges of wavelength, and not just at a few wavelengths. This is common for absorbing substances dissolved in liquid solvents. The interactions with solvent molecules broaden the spectral lines due to 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 lifetime of the states, introduced in Eq. (15.4-25).[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. A spectral line with a very narrow inherent width appears to have a larger line width due to the limitations of the instrument. The difference in wavelength of the most closely spaced narrow spectral lines that an instrument can resolve is called the **resolution** of the instrument.

Absorption spectroscopy can be used to measure the concentration of a substance. Figure 20.5 shows a cell containing an absorbing substance with concentration c and with 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 $c\,dx$ 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 the farther it travels into the cell, because of absorption. The amount of light absorbed in the slab per unit time is proportional to the intensity of light and to the amount of absorbing substance, so the change in I from one side of the thin slab to the other is

$$-dI = k(\lambda)Ic\,dx \tag{20.1-12}$$

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[4] V. B. E. Thomas, *J. Chem. Educ.*, **72**, 616 (1995).

The proportionality factor k is a function of wavelength but not of concentration. It will be different from zero only for wavelengths such that the photon energy equals the energy difference between a significantly occupied molecular energy level and a higher level.

Equation (20.1-12) is a differential equation that can be solved for the intensity of light as a function of position. Division by I separates the variables, giving

$$-\frac{dI}{I} = k(\lambda)c\,dx \tag{20.1-13}$$

This differential equation is solved by 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,

$$-\ln\left(\frac{I(\lambda, b)}{I(\lambda, 0)}\right) = \ln\left(\frac{I(\lambda, 0)}{I(\lambda, b)}\right) = k(\lambda)cb \tag{20.1-14}$$

The **absorbance** A (formerly called the **optical density**) is defined as the common logarithm of the same ratio as in the second natural logarithm in Eq. (20.1-14). Equation (20.1-14) can be transformed into the **Beer–Lambert law**:

$$A(\lambda) = \log_{10}\left(\frac{I(\lambda, 0)}{I(\lambda, b)}\right) = a(\lambda)bc \tag{20.1-15}$$

where $a(\lambda)$ is the **absorptivity** (formerly called the **extinction coefficient**):

$$a(\lambda) = \frac{k(\lambda)}{\ln(10)} = \frac{k(\lambda)}{2.302585} \tag{20.1-16}$$

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 any). If the concentration is measured in $\mathrm{mol\,L^{-1}}$, the absorptivity is called the **molar absorptivity**. The Beer–Lambert law is well obeyed by many substances at low 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, which provides one way to study molecular association.

EXAMPLE 20.2

A solution of a certain dye has a molar absorptivity of $1.8 \times 10^5\ \mathrm{L\,mol^{-1}\,cm^{-1}}$ 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

$$c = \frac{A}{ab} = \frac{1.65}{(1.8 \times 10^5\ \mathrm{L\,mol^{-1}\,cm^{-1}})(1.000\ \mathrm{cm})} = 9.2 \times 10^{-6}\ \mathrm{mol\,L^{-1}}$$

*Exercise 20.3

A solution of a certain dye has a concentration of $0.000100\ \mathrm{mol\,L^{-1}}$ and gives an absorbance of 1.234 at a wavelength of 587 nm in a cell of length 1.000 cm. Find the molar absorptivity at this wavelength.

20.2 The Spectra of Atoms

The only energy levels of atoms that can ordinarily be studied experimentally are electronic levels. For a hydrogen atom, when the orbitals are substituted in the integral of Eq. (20.1-8) the following selection rules are found:[5]

Hydrogen Atom Selection Rules

$$\Delta m = m_{\text{final}} - m_{\text{initial}} = 0, \pm 1 \tag{20.2-1a}$$

$$\Delta l = l_{\text{final}} - l_{\text{initial}} = \pm 1 \tag{20.2-1b}$$

$$\Delta n \text{ — no restrictions} \tag{20.2-1c}$$

These selection rules correspond to conservation of angular momentum in the atom–radiation system, since the angular momentum of a photon is $\pm\hbar$. Since $\Delta l = \pm 1$, a hydrogen atom in an s subshell can make a transition only to a p subshell, while 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 20.1. Figure 20.6 shows schematically some of the transitions that take place, with line segments connecting each pair of states between which transitions can occur.

*Exercise 20.4

From the expression for the energy of a hydrogen atom in Eq. (16.2-19), find the wavelength and frequency of the photons emitted by a hydrogen atom undergoing the $n = 2 \rightarrow n = 1$ transition, the $n = 3 \rightarrow n = 2$ transition, and the $n = 4 \rightarrow n = 3$ transition. In what spectral range (visible, ultraviolet, or infrared) does each lie?

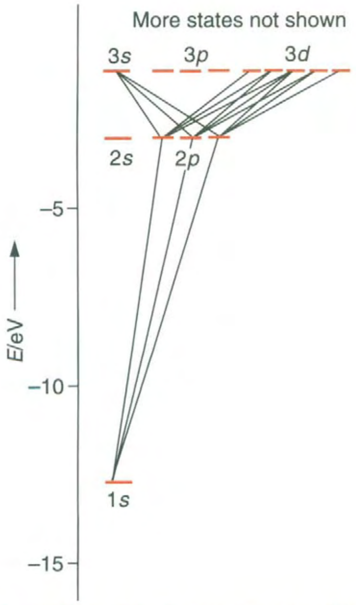

Figure 20.6. The Energy Levels of the Hydrogen Atom and the Allowed Transitions between Them. This type of diagram is known as a Grotrian diagram. It is constructed by interpreting the spectrum of the substance.

For multielectron atoms, most spectra can be understood in terms of orbital wave functions made up of hydrogenlike orbitals. If such wave functions are used to calculate transition dipole moments, the following selection rules result:[6]

Selection Rules for Multielectron Atoms

$$\Delta L = \pm 1 \tag{20.2-2a}$$

$$\Delta S = 0 \tag{20.2-2b}$$

$$\Delta J = 0, \pm 1 \qquad (0 \rightarrow 0 \text{ not allowed}) \tag{20.2-2c}$$

$$\Delta M_J = 0, \pm 1 \qquad (0 \rightarrow 0 \text{ not allowed for } \Delta J = 0) \tag{20.2-2d}$$

where J is the quantum number for the total electronic angular momentum and M_J is the quantum number for its z component. The most important of these selection rules is that of Eq. (20.2-2b), that $\Delta S = 0$. Transitions between singlet and triplet states, etc., are forbidden. Forbidden transitions do occur (with low probabilities) and we will later discuss the forbidden transitions from triplet excited states to singlet ground states that account for phosphorescence.

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[5] Davis, *op. cit.*, pp. 256–257 (Note 2).

[6] Davis, *op. cit.*, pp. 256–257 (Note 2).

20.3 Rotational and Vibrational Spectra of Diatomic Molecules

Transitions between rotational, vibrational, and electronic states of diatomic molecules can be observed. All three kinds of transition can occur simultaneously, but the selection rules also allow transitions to occur in which only the rotational and vibrational states change, as well as transitions in which only the rotational states change. Transitions in which only the vibrational states change are forbidden.

Rotational Spectra of Diatomic Molecules

If a diatomic molecule can be represented as a rigid rotor, the transition dipole moment integral for a rotational transition is

$$(\mu)_{J''M'',J'M'} = \int Y^*_{J''M''}\mu Y_{J'M'}\sin(\theta)\,d\theta\,d\phi \tag{20.3-1}$$

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[7]

$$\Delta J = \pm 1 \text{ for nonzero permanent dipole moment} \tag{20.3-2a}$$

$$\text{All } \Delta J \text{ values forbidden for zero permanent dipole moment} \tag{20.3-2b}$$

where J is the quantum number for the magnitude of the rotational angular momentum and M is the quantum number for its z component. The rotational selection rules are well obeyed by diatomic molecules with $^1\Sigma$ electronic states. The selection rule of Eq. (20.3-2b) can be understood qualitatively by considering what would happen if the molecules obeyed classical mechanics. In order for an interaction to occur between the molecule and the radiation, the molecule must exhibit a periodically varying electric dipole moment as it undergoes the classically pictured motion. If a diatomic molecule has a permanent dipole moment, rotation does present a periodically varying dipole to the radiation, since the dipole's direction is changing, even though its magnitude is not. A homonuclear diatomic molecule has no permanent dipole moment so it has no rotational spectrum.

Rotational transitions give photon wavelengths in the microwave region. The radiation sources in microwave spectrometers are klystron tubes, which were originally designed 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 is usually employed by specialists rather than as a routine laboratory technique.

From the selection rule, the photon energy for an allowed transition is

$$E_{\text{photon}} = h\nu = \frac{hc}{\lambda} = E_{v,J+1} - E_{vJ} \tag{20.3-3}$$

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[7] Ira N. Levine, *Molecular Spectroscopy*, Wiley, New York, 1975, pp. 162ff.

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. The reciprocal of the wavelength is

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{1}{hc}(E_{v,J+1} - E_{vJ}) \tag{20.3-4}$$

where we introduce the symbol $\tilde{\nu}$ for the reciprocal wavelength. The reciprocal wavelength is usually expressed in cm^{-1}, and is sometimes called a "frequency," since it is proportional to the frequency of the light through the relation $c/\lambda = \nu$.

Equation (19.2-44) gives the required energy levels. For a first approximation, we neglect the terms in $\tilde{\alpha}$ and $\tilde{\mathfrak{D}}$, obtaining the result corresponding to a rigid rotor:

$$\begin{aligned}\tilde{\nu} = \frac{1}{\lambda} &= \tilde{B}_e[(J+1)(J+2) - J(J+1)] \\ &= \tilde{B}_e[J^2 + 3J + 2 - J^2 - J] = 2\tilde{B}_e(J+1)\end{aligned} \tag{20.3-5}$$

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 $2\tilde{B}_e$, $4\tilde{B}_e$, etc. Figure 20.7a shows the

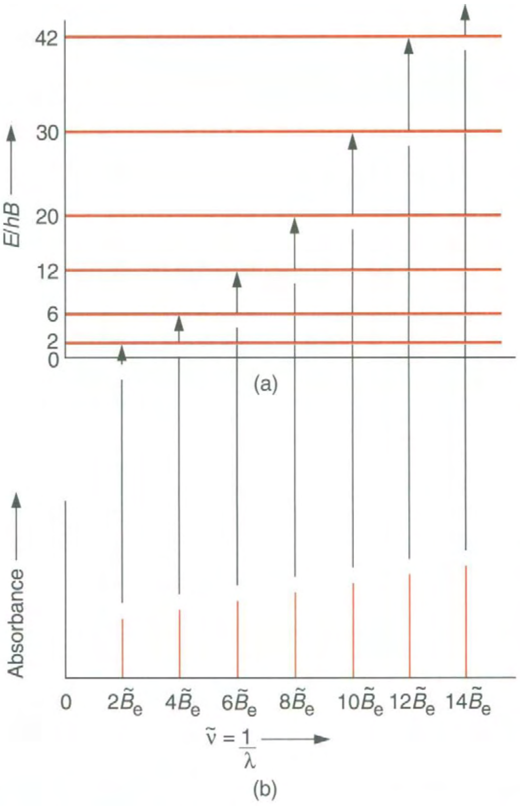

Figure 20.7. A Microwave Spectrum. (a) **The allowed transitions.** (b) **The simulated spectrum.** The positions of the spectral lines are correlated with the transitions that produce the lines. The intensities are related to the populations of the rotational levels.

energy levels with the allowed transitions and Figure 20.7b shows a simulated spectrum for carbon monoxide.

EXAMPLE 20.3

The splitting between the spectral lines in the CO spectrum is 3.8626 cm^{-1}. Find the value of r_e, the equilibrium internuclear distance.

Solution

The splitting is equal to $2\tilde{B}_e$, so the value of $\tilde{B}_e$ is 1.9313 cm^{-1}. We assume that the molecule contains the principal isotopes, ^{12}C and ^{16}O, with masses 12.0000 amu and 15.994915 amu.

$$\mu = \left(\frac{(12.0000\ \text{amu})(15.994915\ \text{amu})}{12.0000\ \text{amu} + 15.994915\ \text{amu}}\right)\left(\frac{0.001\ \text{kg}}{6.02214\times 10^{23}\ \text{amu}}\right)$$

$$= 1.1385\times 10^{-26}\ \text{kg}$$

$$r_e^2 = \frac{h}{8\pi^2\mu\tilde{B}_e c}$$

$$= \frac{6.6261\times 10^{-34}\ \text{J s}}{8\pi^2(1.1385\times 10^{-26}\ \text{kg})(1.9313\ \text{cm}^{-1})(2.9979\times 10^{10}\ \text{cm s}^{-1})}$$

$$= 1.2731\times 10^{-20}\ \text{m}^2$$

$$r_e = 1.1283\times 10^{-10}\ \text{m} = 112.83\ \text{pm} = 1.1283\ \text{Å}$$

The expression in Eq. (20.3-5) can be improved on by including the correction terms in the energy level expression of Eq. (19.2-47).

Exercise 20.5

a. Find an expression for the reciprocal wavelengths of the microwave spectrum of a diatomic molecule including all of the terms in Eq. (19.2-47). 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. (20.3-5).

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*Exercise 20.6

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 or transitions producing the line and by the number of molecules occupying the initial state or states for the spectral line. The rotational levels have a degeneracy of $2J + 1$. At equilibrium the rotational states have population proportional to the Boltzmann factor of Eq. (1.5-17). Therefore,

$$(\text{Population of energy level } J) \propto (2J + 1)e^{-E_J/k_B T} \qquad (20.3\text{-}6)$$

The degeneracy increases and the Boltzmann factor decreases as J increases, so the population rises to a maximum and then decreases as J increases. In Example 19.7 of the previous chapter, we found that the most populated rotational level for the CO molecule at room temperature is the $J = 7$ level. 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 20.7**

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 levels, the emitted or absorbed radiation is in the infrared region of the spectrum. Vibrational transitions do not occur without rotational transitions since $\Delta J = 0$ is forbidden for diatomic molecules. The infrared spectrum is a vibration–rotation spectrum and information about rotational levels as well as vibrational levels can be obtained. The vibrational selection rules are derived in the Born–Oppenheimer approximation by evaluating the transition dipole moment integral

$$(\mu_x)_{v'v''} = \int \psi_{v'}^* \hat{\mu}(x) \psi_{v''}\, dx \tag{20.3-7}$$

where $\psi_{v'}$ and $\psi_{v''}$ are two vibrational wave functions, expressed in terms of $x = r - r_e$, and where $\hat{\mu}(x)$ 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 products no significant numerical error, but does contribute to the fact that vibrational selection rules are only approximately correct.

The expression for the dipole moment would be determined by solution of the electronic Schrödinger equation in the Born–Oppenheimer approximation. We represent the expression for the dipole moment by the truncated Taylor series:

$$\mu(x) = \mu(0) + \left(\frac{d\mu}{dx}\right)_0 x + \cdots \tag{20.3-8}$$

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. (20.3-8), the selection rule is

$$\Delta v = 0, \pm 1 \text{ for nonzero dipole moment} \tag{20.3-9a}$$

$$\text{All } \Delta v \text{ values forbidden for zero dipole moment} \tag{20.3-9b}$$

Transitions for which $\Delta v = 0$ give the pure rotational spectrum in the microwave region. Transitions for which $\Delta v = \pm 1$ give the vibration–rotation spectrum in the infrared region. The transition dipole moment vanishes for homonuclear diatomics because the dipole moment $\mu(x)$ vanishes for all values of x.

Exercise 20.8

Using the $v = 0$ harmonic oscillator function of Eq. (14.6-8), show that a nonzero value of the $\mu(0)$ term on the right-hand side of Eq. (20.3-8) leads to a nonzero value of the transition dipole moment for the $v = 0$ to $v = 0$ transition. Use the $v = 0$ function and the $v = 1$ function from Eq. (14.6-9) 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.

It is possible to understand qualitatively the selection rule of Eq. (20.3-9b) by assuming a diatomic molecule described by classical mechanics. In order for such a vibrating molecule to interact with electromagnetic radiation, the molecule must present a fluctuating dipole to the radiation as the molecule vibrates, and the molecule must be differently charged at its two ends in order to do this.

Figure 20.8 shows the allowed transitions that occur between the ground vibrational state ($v = 0$) and the first excited vibrational state ($v = 1$). The resulting set of spectral lines is called a **band**, and the band corresponding to the allowed transitions shown 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

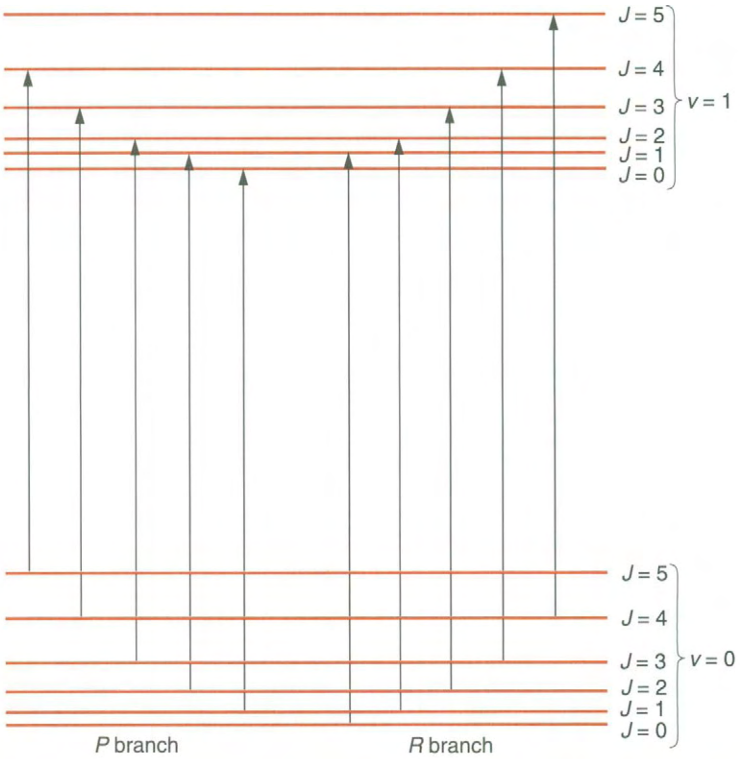

Figure 20.8. Allowed Transitions Leading to a Vibration–Rotation Spectral Band of a Diatomic Substance. In the R branch, the value of J in the upper level is greater than that in the lower level, and in the P branch, the opposite is the case. There is no Q branch, which would correspond to the same value of J in the upper and lower energy levels.

J in both states were the same, they would constitute the ***Q* branch**. The rotational selection rules forbid this branch for diatomic molecules, but the location that the Q branch would have if it were present is the **band center**. Vibrational selection rules are less well obeyed than rotational selection rules, and forbidden vibrational transitions are frequently observed, although with lower intensities than the allowed transitions. A forbidden spectral band with $\Delta v = \pm 2$ is called a **first overtone**, one with $\Delta v = \pm 3$ is called a **second overtone**, and so on.

If we neglect the x_e, α, and $\mathfrak{D}$ terms in the energy level expression of Eq. (19.2-47), the reciprocal wavelength of a line of the R branch of the fundamental band is given by

$$\tilde{\nu}_R = \frac{1}{\lambda_R} = (E_{1,J+1} - E_{0,J})/hc = \tilde{\nu}_e + 2\tilde{B}_e(J+1) \qquad (J = 0, 1, 2, \ldots) \qquad (20.3\text{-}10)$$

where J is the value of the rotational quantum number in the lower ($v = 0$) state. The R branch consists of a set of equally spaced lines with spacing $2\tilde{B}_e$. It looks like the rotational spectrum except that these lines start from the band center instead of from zero reciprocal wavelength.

The reciprocal wavelengths of lines of the P branch are given by

$$\tilde{\nu}_P = \frac{1}{\lambda_P} = (E_{1,J-1} - E_{0,J})/hc = \tilde{\nu}_e - 2\tilde{B}_e J \qquad (J = 1, 2, 3, \ldots) \qquad (20.3\text{-}11)$$

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 a lower value of J. The P branch consists of a set of equally spaced lines with spacing $2\tilde{B}_e$ 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 $4\tilde{B}_e$.

Exercise 20.9

Show that Eqs. (20.3-10) and (20.3-11) are correct.

EXAMPLE 20.4

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, neglecting the correction terms.

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.

$$\tilde{\nu}_{BC} = \frac{1}{\lambda_{BC}} = \tilde{\nu}_e = 2169.81\ \mathrm{cm}^{-1}$$

$$\Delta\tilde{\nu} = \Delta(1/\lambda) = 2\tilde{B}_e = 2(1.93127\ \mathrm{cm}^{-1}) = 3.86254\ \mathrm{cm}^{-1}$$

b. From Eq. (19.2-29), and using the value of μ from Example 14.6,

$$\nu = \tilde{\nu}_e c = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \quad \text{or} \quad k = 4\pi^2 \mu \tilde{\nu}_e^2 c^2$$

$$k = 4\pi^2 (1.1385 \times 10^{-26}\ \text{kg})(2169.81\ \text{cm}^{-1})^2 (2.9979 \times 10^{10}\ \text{cm s}^{-1})^2$$
$$= 1901.8\ \text{kg s}^{-2} = 1901.8\ \text{N m}^{-1} = 1901.8\ \text{J m}^{-2}$$

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 19.7, 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 20.9 shows the fundamental band of the HCl molecule. The double lines are due to the two isotopes of chlorine that are present. The lines are not equally spaced, mostly due to the effect of the α term in the energy level expression of Eq. (19.2-47). In HCl, as in most molecules, the $\mathfrak{D}$ 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 $v = 1$. Transitions from the $v = 1$ and higher levels are generally not seen in absorption spectra near room temperature due to the small population of excited vibrational states (see Example 19.8).

Using the energy level expression of Eq. (19.2-47), the reciprocal wavelength of the band center of the fundamental band is

$$\tilde{\nu}_{BC} = \frac{1}{\lambda_{BC}} = \tilde{\nu}_e - \tilde{\nu}_e x_e[(3/2)^2 - (1/2)^2]$$
$$= \tilde{\nu}_e - 2\tilde{\nu}_e x_e \quad \text{(center of the fundamental band)} \qquad (20.3\text{-}12)$$

and the reciprocal wavelength of the band center of the first overtone is

$$\tilde{\nu}_{BC} = \frac{1}{\lambda_{BC}} = 2\tilde{\nu}_e - 6\tilde{\nu}_e x_e \quad \text{(center of the first overtone band)} \qquad (20.3\text{-}13)$$

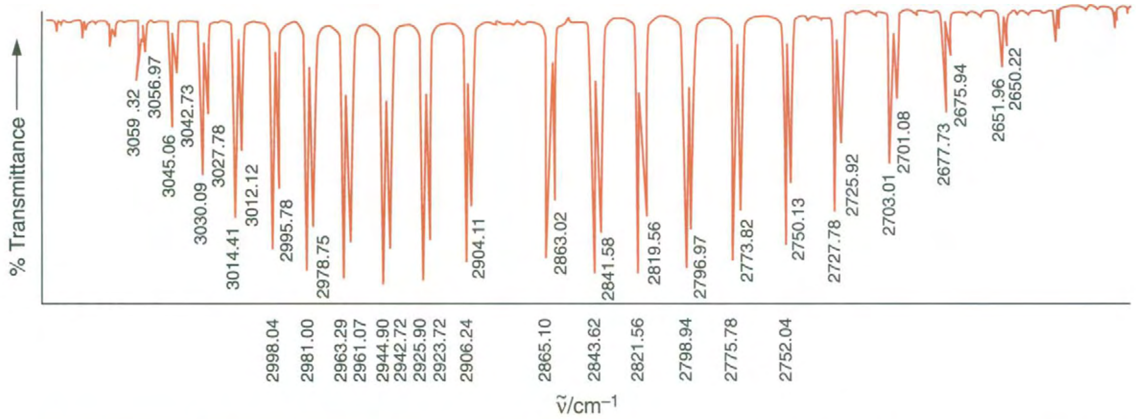

Figure 20.9. The Fundamental Band of the Vibration–Rotation Spectrum of HCl. In this figure, we see the *R* and *P* branches. The resolution of the spectrum is sufficient to show the lines for $H^{35}Cl$ and $H^{37}Cl$. The ^{35}Cl is the more abundant isotope of chlorine, and produces the more intense lines. From N. L. Alpert, W. E. Keiser and H. A. Szymanski, *IR Theory and Practice of Infrared Spectrscopy*, 2d ed., Plenum Press, New York, 1970.

If the overtone band can be observed, it is possible to evaluate the anharmonicity parameter $\tilde{\nu}_e x_e$ from it.

EXAMPLE 20.5

Find the reciprocal wavelengths for the band centers of the fundamental and the first overtone of the CO molecule, including correction terms.

Solution

For the fundamental, the reciprocal wavelength of the band center is

$$\tilde{\nu}_{BC} = \frac{1}{\lambda_{BC}} = 2169.81\ \mathrm{cm}^{-1} - 2(13.294\ \mathrm{cm}^{-1}) = 2167.22\ \mathrm{cm}^{-1}$$

For the first overtone.

$$\tilde{\nu}_{BC} = \frac{1}{\lambda_{BC}} = 2(2169.81\ \mathrm{cm}^{-1}) - 6(13.294\ \mathrm{cm}^{-1}) = 4259.86\ \mathrm{cm}^{-1}$$

Exercise 20.10

a. Using the expression for the energy levels in Eq. (19.2-49) 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.

Exercise 20.11

If the energy level expression of Eq. (19.2-49) is used, the reciprocal wavelength of a line in the *R* branch of the first overtone band is

$$\tilde{\nu}_R = \frac{1}{\lambda_R} = 2\tilde{\nu}_e - 6\tilde{\nu}_e x_e + 2\tilde{B}_e(J + 1) - 4\tilde{\mathfrak{D}}(J + 1)^3 - \tilde{\alpha}(2J^2 + 7J + 4) \qquad (20.3\text{-}14)$$

a. Verify Eq. (20.3-14).

b. Obtain the analogue of Eq. (20.3-14) 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.

20.4 Electronic Spectra of Diatomic Molecules

The electronic energy levels of typical molecules are even more widely spaced than the vibrational energy levels, so that the electronic spectra for most diatomic molecules are found in the ultraviolet or visible region. Transitions of a diatomic molecule from one electronic state to another are complicated by the fact that rotational and vibrational transitions take place simultaneously with the electronic transitions. The selection rules for these transitions are derived much as in the other cases we have considered, by determining which transitions correspond to nonzero transition dipole moments. The following selection rules are obtained:[8]

$$\Delta\Lambda = 0, \pm 1 \tag{20.4-1a}$$

$$\Delta S = 0 \tag{20.4-1b}$$

$$\text{Parity of electronic state changes: } (u \rightarrow g \text{ or } g \rightarrow u) \tag{20.4-1c}$$

$$\Delta J = \pm 1 \tag{20.4-1d}$$

$$\Delta v\text{—not restricted} \tag{20.4-1e}$$

where Λ is the quantum number for the magnitude of the projection of the total electronic orbital angular momentum on the internuclear axis, S is the total electron spin quantum number, J is the rotational quantum number (not the quantum number for the total electronic angular momentum), and v is the vibrational quantum number.

*Exercise 20.12

The lowest-lying excited singlet state of the CO molecule lies 8.0278 eV above the ground state. Find the wavelength of the light absorbed in the transition to this state from the ground state, neglecting changes in rotational and vibrational energy.

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. It is possible to use electronic spectra to determine rotational and vibrational properties of homonuclear diatomic molecules, which have no infrared or microwave spectrum. Figure 20.10 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.

In order to understand electronic spectra 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 20.10 a line segment is drawn to represent a typical electronic transition. The line is vertical, corresponding to the Franck–Condon principle. The probability of a transition is proportional to the square of the transition dipole moment. One factor in the transition dipole moment is the overlap integral of the vibrational wave functions in the initial and final states. The square of this overlap integral is called the **Franck–Condon factor**. The value of this overlap integral 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 must be drawn from one of the regions of relatively large value of a vibrational wave function to another region of relatively large value. Since the equilibrium internuclear distance of the upper electronic state in Figure 20.10 is somewhat larger than that of the lower state, the most probable transitions will take place to excited vibrational states of the upper electronic state. Figure 20.11 shows the electronic band spectrum of nitrogen.

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[8] Levine, *op. cit.*, pp. 298ff (Note 7).

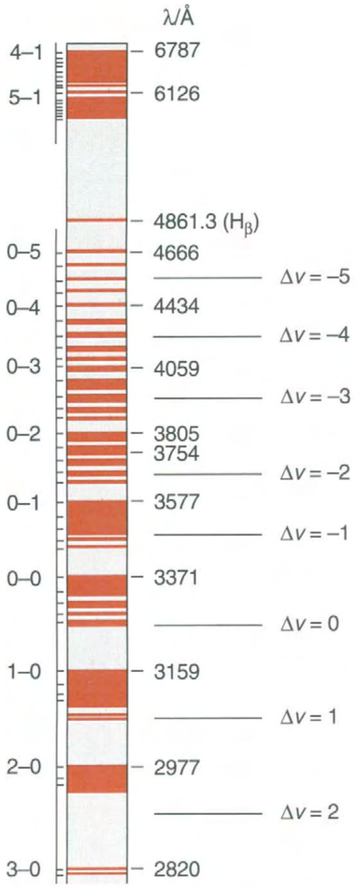

Figure 20.11. The Electronic Spectrum of Diatomic Nitrogen. This spectrum shows a number of bands corresponding to different final vibrational states, and sets of lines within each band corresponding to different initial and final rotational states.

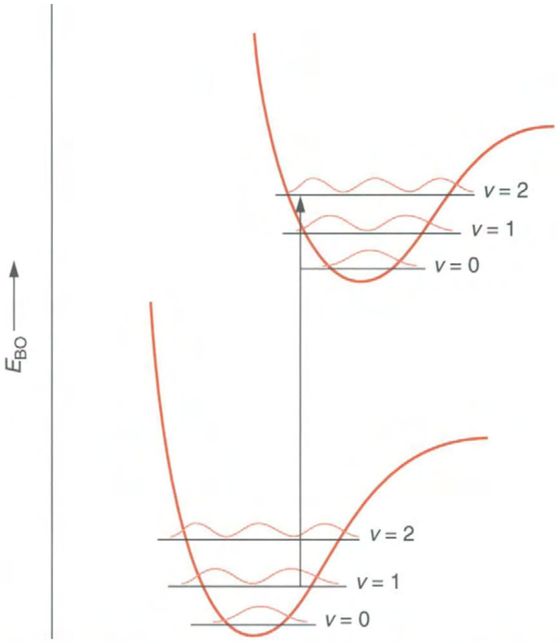

Figure 20.10. An Electronic Transition According to the Franck–Condon Principle. The vertical lines in this figure illustrate the Franck–Condon principle. The Franck–Condon factor giving the strength of the transition is proportional to the overlap integral for the initial and final vibrational states. 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.

As with atoms, there is a selection rule forbidding transitions that change the value of S. Since our selection rules are approximate, forbidden transitions between triplet ($S = 1$) states and singlet ($S = 0$) states do occur, but with low probabilities and corresponding low intensities compared with singlet–singlet transitions. 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 the electron makes a transition from a π bonding orbital to a π antibonding orbital, the transition is called a $\pi \to \pi^*$ ("pi to pi-star") transition. If the electron goes from a nonbonding orbital to a π antibonding orbital, the transition is said to be an $n \to \pi^*$ ("n to pi-star") transition.

20.5 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

The rotational transitions of polyatomic molecules produce a microwave spectrum as described for diatomic molecules. As in that case, we assume that a rotating molecule is rigid and cannot vibrate. We have already divided polyatomic molecules into four classes: linear molecules, spherical top molecules, symmetric top molecules, and asymmetric top molecules. As is the case with diatomic molecules, 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. Analysis of a spectrum yields the value of the two equal moments of inertia, but not necessarily the values of individual bond lengths. Spherical top molecules are so symmetrical that they cannot have a nonzero dipole moment, which forbids all rotational transitions and no spectrum is observed. A rotational spectrum is always observed for an asymmetric top molecule, because it has so little symmetry that it must have a dipole moment. We will not discuss the microwave spectra of symmetric top molecules and asymmetric top molecules.[9]

Vibrational Spectra of Polyatomic Molecules

As with diatomic molecules, vibrational transitions are accompanied by rotational transitions, giving bands of lines. The vibration of polyatomic molecules is that of normal modes, each acting approximately like an independent harmonic oscillator. We number the normal modes with an index i, ranging from 1 to $3n - 5$ (linear molecules) or $3n - 6$ (nonlinear molecules). The selection rules for vibrational transitions are:

$$\Delta v_i = 0, \pm 1 \text{ for some one value of } i, \;\; \Delta v = 0 \text{ for all other values} \tag{20.5-1a}$$

The motion of the normal mode i must modulate the molecule's dipole moment (20.5-1b)

The rule of Eq. (20.5-1a) means that only one normal mode changes its quantum number at a time. The case in which all Δv's vanish corresponds to a rotational spectrum. The statement that the motion must modulate the dipole moment of the molecule means that the classically pictured motion must cause the dipole moment to oscillate in value. These selection rules lead to a fundamental band in the infrared region for each normal mode that modulates the molecule's dipole moment. If a polyatomic molecule possesses a permanent dipole moment, all of its normal modes can modulate the dipole and give rise to vibrational bands. For example, in a nonlinear triatomic molecules such as H_2O or SO_2, all three of the normal modes shown in Figure 19.5 will give fundamental bands in the infrared spectrum. Transitions that violate the selection rules do occur, but with small probabilities. There are overtones like those of diatomic molecules, and also **combination bands**, in which two (or more) normal modes change their quantum numbers at once. These forbidden bands are generally less intense than the fundamental bands.

EXAMPLE 20.6

The infrared spectrum of hydrogen sulfide, H_2S, shows three strong bands at $1290\,\text{cm}^{-1}$, $2610.8\,\text{cm}^{-1}$, and $2684\,\text{cm}^{-1}$. There are weaker bands at $2422\,\text{cm}^{-1}$, $3789\,\text{cm}^{-1}$, and $5154\,\text{cm}^{-1}$. Interpret the spectrum.

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[9] Davis, *op. cit.*, pp. 322ff (Note 2).

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 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_2, and also roughly equal to $\nu_2 + \nu_3$. It has been assigned both ways but is more likely to be the combination band, by analogy with the water spectrum.[10]

In Example 20.6 we see a general pattern for triatomic molecules stated in Section 19.3: The bend has the lowest frequency, the symmetric stretch has an intermediate frequency, and the asymmetric stretch has the highest frequency. The weak bands are identified by trial and error, seeing whether their frequencies approximate a multiples of a fundamental frequency or a sum of two fundamental frequencies.

Even in molecules without a permanent dipole, some of the normal modes can produce a fluctuating dipole that oscillates about zero magnitude, and thus produce spectral lines. For example, the CO_2 molecule is linear and therefore has no permanent dipole moment, although each C=O bond is polar. The normal modes of CO_2 were shown in Figure 19.5. 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 correspond to a single vibrational band that is called a **perpendicular band**. The asymmetric stretch produces an oscillating dipole parallel to the molecule axis since 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 changing 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 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 $\Delta J = \pm 1$.[11] Figure 20.12 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. The situation with nonlinear molecules is similar. If there is a single symmetry axis, vibrational motions in which the dipole oscillates perpendicular to the axis correspond to a band with a Q branch as well as P and R branches.

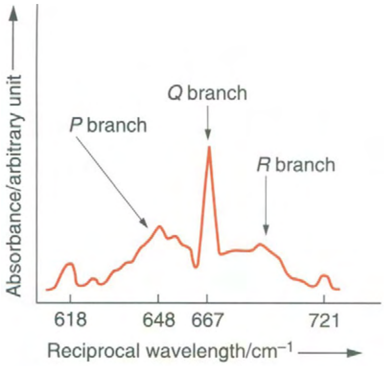

Figure 20.12. The Perpendicular Band of Carbon Dioxide. This spectrum shows the occurrence of a Q branch, which occurs when the normal mode produces a modulation of the dipole moment of the molecule perpendicular to the principal symmetry axis of the molecule. From G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. II, Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand Reinhold, New York, 1945, p. 273.

With larger polyatomic molecules the determination of which normal modes will be infrared active is harder than with triatomic molecules. There are more normal modes and each normal mode involves a more complicated motion. 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

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[10] G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. II, Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand Reinhold, New York, 1945, p. 283.

[11] Levine, *op. cit.*, pp. 255ff (Note 7).

normal modes needs to be nonzero. This integral is somewhat similar to an overlap integral, except for the occurrence of the dipole moment operator, and the transition dipole moment integrals can be studied by group theory in a way similar to overlap integrals.[12] However, it is often possible by inspection of the normal modes to identify those that modulate the dipole moment of the molecule.

EXAMPLE 20.7

The normal modes of cyanogen, C_2N_2, are shown in Figure 20.13. (The last two diagrams represent two modes each, of equal frequency.) Say which are infrared active.

Solution

The molecule is symmetrical, and has a zero dipole moment in the 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.

***Exercise 20.13**

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?

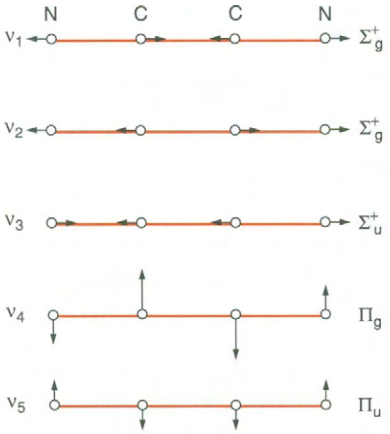

Figure 20.13. The Vibrational Normal Modes of Cyanogen, C_2N_2. The arrows show the directions of motion of the nuclei during half of the period of vibration, and the lengths are proportional to the amplitudes of the nuclear oscillations. From G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. II, Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand Reinhold, New York, 1945, p. 181.

Electronic Spectra of Polyatomic Molecules

Electronic transitions in polyatomic molecules are similar to those in diatomic molecules. Vibrational and rotational transitions take place along with electronic transitions. The Franck–Condon principle applies as in diatomic molecules 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 selection rules for electronic transitions in polyatomic molecules are also more complicated than in diatomic molecules, and we will not discuss them. However, one 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:

$$\Delta S = 0 \quad \text{(rule for all molecules and atoms)} \tag{20.5-2}$$

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, much as it is used to determine which overlap integrals vanish.[13] We state only the general rule: The symmetry of the electronic wave function in the final state must be different from the

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[12] P. W. Atkins, *Molecular Quantum Mechanics*, 2d ed., Oxford University Press, Oxford, 1983, pp. 303ff.

[13] B. S. Tsukerblat, *Group Theory in Chemistry and Spectroscopy*, Academic Press, San Diego, 1994, pp. 223ff.

symmetry of the initial state. For example, a transition from a u state to a g state is ordinarily allowed (and vice versa), while a transition from a g state to another g state or from a u state to another u state is not allowed.

The molecular electronic selection rules are not exact since they are derived with approximate wave functions. "Forbidden" transitions are often observed, but they 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. A transition from an excited triplet state to a singlet ground state 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).

If orbital wave functions are used for a polyatomic molecule, the electronic transitions can be classified by specifying the initial and final orbitals. As with diatomic molecules, if an absorption corresponds to a transition from a nonbonding to an antibonding π orbital, we call it an "n to pi-star" ($n \to \pi^*$) transition, and similarly for a "pi to pi-star" ($\pi \to \pi^*$) 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 $\pi \to \pi^*$ transition and another absorption near 300 nm corresponding to an $n \to \pi^*$ transition.

20.6 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. We use the benzophenone molecule as a typical example, and include photochemical processes, which are chemical reactions that occur only after the absorption of a photon.

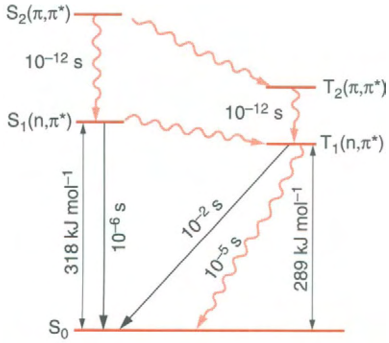


Figure 20.14. Some Energy Levels of the Benzophenone Molecule. The wavy arrows represent radiationless transitions, and the straight arrows represent emissions of photons. The times shown are relaxation times for the transitions. Data from D. L. Pavia, G. M. Lampman, and G. S. Kriz, Jr., *Introduction to Organic Laboratory Techniques*, 2d ed., Saunders College Publishing, Philadelphia, 1982, p. 364.

Fluorescence and Phosphorescence

Benzophenone ($Ph_2C{=}O$, where Ph stands for the phenyl group, C_6H_5) is a substance that exhibits fluorescence and phosphorescence as well as undergoing a photochemical reaction. Figure 20.14 shows schematically some low-lying electronic energy levels of benzophenone. The excited levels correspond to excitation of electrons in the carbonyl group. An excited level that is reached from the ground level by an $n \to \pi^*$ transition is labeled (n, π^*) and an excited level that is reached by a $\pi \to \pi^*$ transition is labeled (π, π^*).

There are two levels labeled (n, π^*) and two levels labeled (π, π^*). These differ in the value of the total spin quantum number S, with singlet levels corresponding to $S = 0$ and with triplet levels corresponding to $S = 1$. The ground level is a singlet level, and the selection rules allow transitions only to excited singlet levels. Transitions to the two excited singlet levels give rise to two absorptions, one near 330 nm ($n \to \pi^*$) and one near 260 nm ($\pi \to \pi^*$). Transitions to the triplet levels from the ground level are forbidden and we can ignore them. Polyatomic molecules do not have the same kind of term symbols as do diatomic molecules, so we follow a common notation and label the singlet levels as S_0, S_1, S_2, etc., in order of increasing energy, and the triplet levels T_1, T_2, etc. in order of increasing energy. We reserve the subscript 0 for the ground level (the S_0 level) so that there is no T_0 level.

If a molecule absorbs a photon to make a transition to an excited singlet level, there is some probability that the molecule will make the reverse transition and emit a photon of the same wavelength as the photon originally absorbed, but this is not the only thing that can happen. The molecule will probably be in an excited vibrational state after the upward transition (see the discussion of the Franck–Condon principle in Section 20.4), so that the molecule can make a transition to a lower-energy vibrational level within the excited electronic level, thus losing some vibrational energy. This energy can be emitted as a photon, which would be in the infrared region. A **radiationless transition** can also occur. The vibrational energy lost by the molecule can be 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 electronic 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 photon will be less energetic than the photon originally absorbed and the emitted light will have a longer wavelength than the absorbed light. Many common objects, including human teeth, certain minerals and "black-light" posters can fluoresce, emitting visible light when irradiated with 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. A radiationless transition in which the value of S changes is called an **intersystem crossing**. To each of the excited singlet levels in Figure 20.14 there corresponds a triplet level with the same electron configuration and a lower energy that can be reached with an intersystem crossing. If a molecule is in an excited state with a value of S different from that of the ground state, it might make a forbidden radiative transition to the ground state. This process is called **phosphorescence**. A typical mean time for phosphorescence is longer than for fluorescence (typically 1 ms to 10 s). In Figure 20.14, the approximate values of mean transition times are indicated near each arrow.

Photochemistry

A molecule in an excited state can often undergo chemical reactions that are inaccessible to a molecule in the ground level. If the excited state was reached directly or indirectly by absorption of radiation, the reaction is a **photochemical reaction**. We have already discussed the rate of a photochemically initiated reaction in Section 13.5. 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. This is similar to the statement of the Bohr frequency rule of spectroscopy, that the absorption or emission of a single photon accompanies a transition between atomic or molecular energy levels.

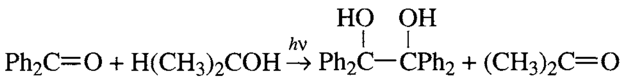
The Stark–Einstein law does not imply that every photon necessarily leads to the reaction of one molecule, since some of the excited molecules might undergo internal conversion, intersystem crossing, fluorescence, or phosphorescence processes leading to unreactive states. A **chain reaction** might occur in which the reaction of one molecule can lead to the reaction of other molecules without absorption of further radiation, as in the reaction of H_2 and Br_2 discussed in Section 13.5. The **quantum yield** of a photochemical reaction, Φ, is defined by

$$\Phi = \frac{\text{total number of molecules reacted}}{\text{number of photons absorbed}} \tag{20.6-1}$$

In a chain reaction, Φ can exceed unity, but in a non-chain reaction unity is its maximum value. Equation (20.6-1) can be restated in terms of moles of reactant and moles of photons. One mole of photons is called an **einstein**, so that

$$\Phi = \frac{\text{amount reacted in moles}}{\text{amount of photons absorbed in einsteins}} \tag{20.6-2}$$

An example of a photochemical reaction involves benzophenone.[14] Its energy level diagram has already been presented in Figure 20.14. Upon irradiation with ultraviolet light of 300 nm to 350 nm wavelength, benzophenone undergoes reaction with 2-propanol to form benzpinacol and acetone:



$$\mathrm{Ph_2C{=}O + H(CH_3)_2COH} \xrightarrow{h\nu} \mathrm{Ph_2\overset{\overset{HO}{|}}{C}{-}\overset{\overset{OH}{|}}{C}Ph_2 + (CH_3)_2C{=}O} \tag{20.6-3}$$

Since radiation of 300 nm wavelength has photons of insufficient energy to reach the singlet (π, π^*) level, and since 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 singlet (n, π^*) level:

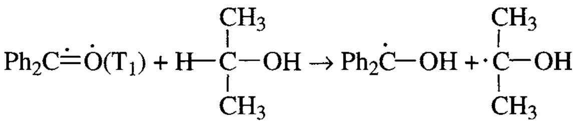
$$\mathrm{Ph_2C{=}O} + h\nu \rightarrow \mathrm{Ph_2C\overset{\cdot}{=}\dot{O}}\ (\mathrm{S_1}) \tag{20.6-4}$$

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:

$$\mathrm{Ph_2C\overset{\cdot}{=}\dot{O}(S_1)} \rightarrow \mathrm{Ph_2C\overset{\cdot}{=}\dot{O}(T_1)} \tag{20.6-5}$$

This step is followed by the abstraction of a hydrogen atom (complete with one electron) from a 2-propanol molecule:



$$\mathrm{Ph_2C\overset{\cdot}{=}\dot{O}(T_1) + H{-}\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}OH \rightarrow Ph_2\dot{C}{-}OH + \cdot\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}{-}OH} \tag{20.6-6}$$

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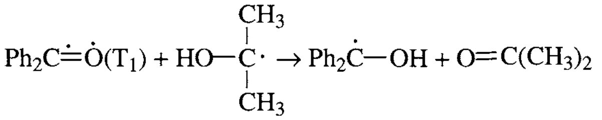
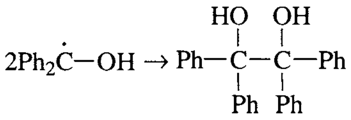
[14] D. L. Pavia, G. M. Lampman, and G. S. Kriz, Jr., *Introduction to Organic Laboratory Techniques*, 2d ed., Saunders College Publishing, Philadelphia, 1982, pp. 362ff.

The next step is the abstraction of a second hydrogen atom from the 2-propanol molecule by another excited benzophenone molecular, forming another molecule of the radical and an acetone molecule:



$$\mathrm{Ph_2C\dot{=}\dot{O}(T_1) + HO{-}\overset{CH_3}{\underset{CH_3}{\dot{C}}}\cdot \rightarrow Ph_2\dot{C}{-}OH + O{=}C(CH_3)_2} \qquad (20.6\text{-}7)$$

The final step is combination of two radicals:



$$\mathrm{2Ph_2\dot{C}{-}OH \rightarrow Ph{-}\overset{HO}{\underset{Ph}{C}}{-}\overset{OH}{\underset{Ph}{C}}{-}Ph} \qquad (20.6\text{-}8)$$

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.

Exercise 20.14

Borosilicate glass blocks almost all radiation of wavelength less than 300 nm. 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 (the reaction is **quenched**). The explanation is that 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 ground level and a triplet (π, π^*) level 2.7 eV above the ground level. There is a well-obeyed selection rule that 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, and that 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 the 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 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.

Photosynthesis

The process of photosynthesis is an important set of photochemical reactions occurring in plants, “fixing” carbon dioxide and producing carbohydrates and O_2. In the cells of photosynthetic plants are found organelles called **chloroplasts**, in which are found several chromophores called **chlorophylls**. Chlorophyll molecules absorb blue and red light, giving the chloroplasts their characteristic green color. Chlorophyll molecules have four pyrrole rings, quite similar to the heme groups in hemoglobin, myoglobin, and the cytochromes. However, the chlorophylls contain a magnesium atom instead of the iron atom found in the heme group. It is important to the functioning of the cytochromes that the iron can be oxidized to iron(III) and reduced to iron(II). It is important to the functioning of the chlorophyll that the magnesium occurs in only one oxidation state.

The accepted mechanism of the initial photochemical reaction is as follows:[15] First, the chlorophyll molecule absorbs a photon of red light, making a transition to an excited singlet state from its singlet ground state. Second, the excited chlorophyll molecule loses an electron to some other substance involved in the chain of reactions that eventially produces carbohydrates and oxygen. Since the magnesium atom possesses only a single oxidation state, this electron comes from a delocalized orbital in the ring system, producing a radical cation. Third, some electron donor gives an electron to the chlorophyll. This electron goes into the orbital from which the first electron made its original transition, so that the chlorophyll is restored to its ground state.

The whole process depends on the fact that the excited singlet chlorophyll is a much stronger reducing agent than the ground-state chlorophyll, which has a half-cell reduction potential under biological conditions of about 0.5 V. Since the excitation energy is about 1.5 eV, the effective half-cell potential of the excited chlorophyll is about -1.0 V. However, the chlorophyll radical cation is easy to reduce, since it is reduced to form the ground state of the chlorophyll molecule, not the excited state.

The chlorophyll does not react directly with carbon dioxide, and in fact at least eight photons are required for each oxygen molecule evolved in the photosynthetic process, so that the chlorophyll cycles repeatedly from its ground state to its excited state to its oxidized state and back to its ground state in order to produce one oxygen molecule. The later steps in the process occur in the liquid outside of the membrane in which the chlorophyll is bound.

Linear polyenes called carotenoids occur in the chloroplasts. In addition to other functions, they prevent the formation of singlet O_2, which is extremely toxic to the plant cells. The ground level of O_2 is a ${}^3\Sigma_g^-$ level, and 0.98 eV is required to excite oxygen molecules to a ${}^1\Delta_g$ excited level. The excited chlorophyll molecule has absorbed 1.5 eV from a photon of red light, and can undergo intersystem crossing to a triplet state of slightly lower energy. Because of the selection rule requiring constancy of the sum of the spin quantum numbers, the excited singlet state of the chlorophyll cannot excite the oxygen to its singlet state, but the triplet state can do so. The carotenoid molecules have an excited triplet state that is lower in energy than the excited triplet state of chlorophyll, and accept the energy from any chlorophyll molecules that have undergone intersystem crossing before significant numbers of singlet oxygen molecules can be produced. The excited triplet states of the carotenoids do not have enough energy to excite the oxygen, thus preventing formation of singlet oxygen.

Vision

Another interesting set of photochemical reactions is involved in vision in vertebrates.[16] There are two kinds of light-sensitive cells in the retina of the vertebrate eye, called

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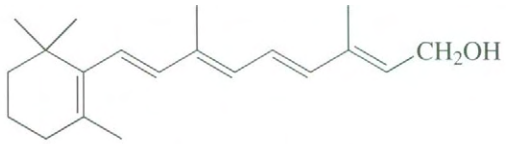
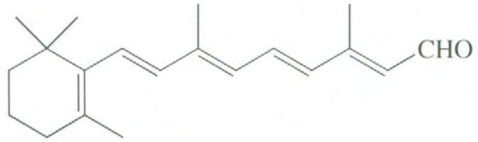
[15] G. Zubay, *Biochemistry*, Addison-Wesley, Reading, MA, 1983, pp. 409ff.

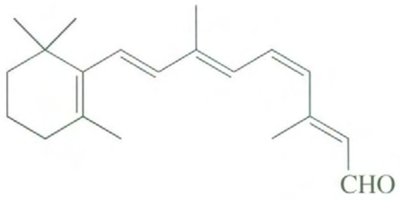
[16] Zubay, *op. cit.*, pp. 169ff (Note 15).



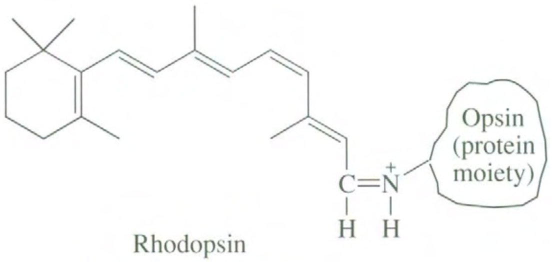
all-*trans*-Retinol (vitamin A_1)
(a)



all-*trans*-Retinal
(b)



11-*cis*-Retinal
(c)



Rhodopsin
(d)

Figure 20.15. The Structures of Retinal and Rhodopsin. (a) **All-*trans* retinol (vitamin A).** (b) **All-*trans* retinal.** (c) **11-*cis* retinal.** (d) **Rhodopsin.** The absorption of a photon by the 11-*cis* retinal that is bound to the protein opsin begins the vision process.

rods and **cones**. The rods provide for vision in dim light but do not give 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 moiety called **opsin** and a polyene called **retinal**. Retinal is related to retinol, which is known as vitamin A, and which is depicted in Figure 20.15a. 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 20.15b and 20.15c. The 11-*cis* form attaches to the free $-NH_2$ group of a lysine residue, forming a Schiff base, as shown in Figure 20.15d. The all-*trans* isomer does not bond to the opsin. Each variety of cone cell has one of three proteins that are similar to rhodopsin, but absorbs light only in either the red, green, or blue wavelength region. 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, so that the unbound retinal cannot be responsible for vision in the visible region.

Exercise 20.15

a. Using the structural formulas in Figure 20.15 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 π 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-degree 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 sequence of identifiable proteins called lumirhodopsin, metarhodopsin I, and metarhodopsin II. Over a period of several minutes, the metarhodopsin II dissociates into a 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 eye to become dark-adapted but is much too slow to be involved in the actual process of vision. The process by which a signal is sent into a fiber of the optic nerve is somehow associated with the conformational changes in the protein that result from the isomerization of the retinal, and apparently occurs with metarhodopsin II.

20.7 Other Types of Spectroscopy

The spectroscopy that we have discussed involves the emission or absorption of ultraviolet, visible, or infrared radiation. There are a number of types of spectroscopy that utilize different processes, and we discuss a few of them in this section.

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 up or accepting energy from the sample in the scattering process. Radiation of one wavelength is incident on the sample and radiation of a different wavelength comes out from the sample. You can also think of the process as consisting of absorption of photons of one frequency accompanied by immediate emission of

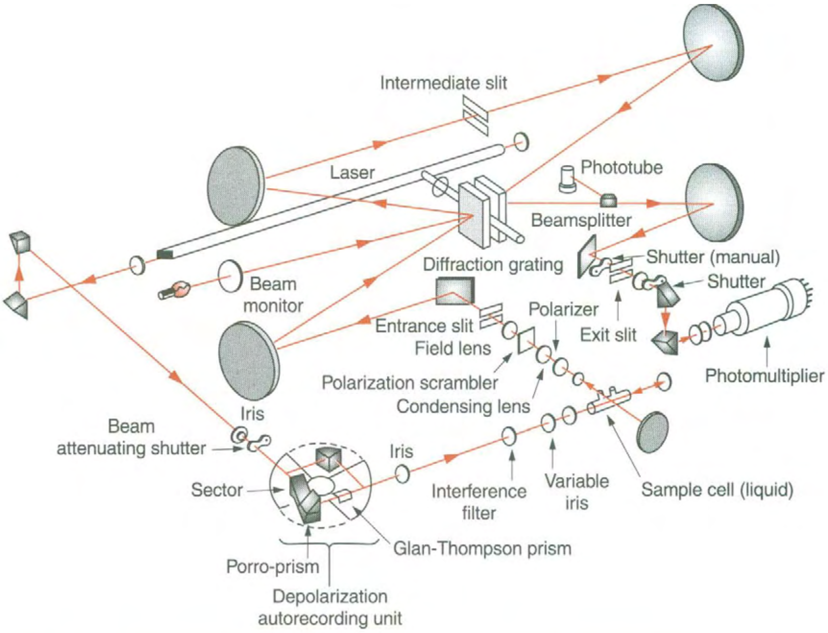


Figure 20.16. Schematic Diagram of a Laser Raman Spectrophotometer. In the diagram, there are two distinct beams: the incident beam, and the scattered beam at right angles to the incident beam. (Courtesy of Jeol, Ltd.)

photons of a different frequency, with the difference in photon energy being absorbed or given off by the sample. The scattered radiation is ordinarily observed in a direction at right angles to the incident beam's direction. Figure 20.16 schematically shows a Raman spectrometer. The scattered beam is generally much weaker than the incident beam, and the use of lasers to provide an intense incident beam has greatly improved the performance of Raman spectrometers.

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. Let the frequency of the incident radiation denoted by ν and the frequencvy of the scattered radiation be denoted by ν'. If the radiation loses energy to the molecules,

$$h\nu - h\nu' = E_{\text{upper}} - E_{\text{lower}} \tag{20.7-1}$$

and if the molecules lose energy to the radiation,

$$h\nu' - h\nu = E_{\text{upper}} - E_{\text{lower}} \tag{20.7-2}$$

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. (20.7-1) are called **Stokes lines** and those corresponding to Eq. (20.7-2) are called **anti-Stokes lines**. Incident light of a fixed frequency is used, and the scattered light can be dispersed to determine the wavelengths at which inelastic scattering occurs.

Since Raman spectroscopy uses a different physical process from that of ordinary optical spectroscopy, the selection rules are different, and this can make it possible to observe transitions that are forbidden in emission or absorption spectroscopy. The Raman selection rules for rotational and vibrational transitions are:

Raman Selection Rules

$\Delta J = 0, \pm 2$ (±1 also allowed for nonlinear molecules) (20.7-3a)

$\Delta v = 0, \pm 1$ (20.7-3b)

The nuclear motion must modulate the polarizability of the molecule (20.7-3c)

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 17.37). For a molecule with the same properties in all directions (an isotropic molecule) the induced moment μ_{ind} is proportional to the electric field $\boldsymbol{\mathscr{E}}$ and in the same direction as the electric field:

$$\boldsymbol{\mu}_{\text{ind}} = \alpha \boldsymbol{\mathscr{E}} \tag{20.7-4}$$

where α is the polarizability, and where $\boldsymbol{\mathscr{E}}$ is the electric field (a vector quantity). A symmetric top molecule such as methane or sulfur hexafluoride obeys Eq. (20.7-4). For an anisotropic molecule (with different properties in different directions) the x component of the induced moment is given by

$$\mu_{x,\text{ind}} = \alpha_{xx}\mathscr{E}_x + \alpha_{xy}\mathscr{E}_y + \alpha_{xz}\mathscr{E}_z \tag{20.7-5}$$

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 (20.7-5) and its analogues become the same as Eq. (20.7-4) if

$$\alpha_{xx} = \alpha_{yy} = \alpha_{zz} \tag{20.7-6}$$

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 two different indexes vanish. The components of the induced dipole are then given by

$$\mu_{x',\text{ind}} = \alpha_{x'x'}\mathscr{E}_{x'} \tag{20.7-7a}$$

$$\mu_{y',\text{ind}} = \alpha_{y'y'}\mathscr{E}_{y'} \tag{20.7-7b}$$

$$\mu_{z',\text{ind}} = \alpha_{z'z'}\mathscr{E}_{z'} \tag{20.7-7c}$$

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."[17] 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 due to the motion.

There are two contributions to the polarizability of a molecule: the distortion of the electronic wave function and the distortion of the nuclear framework. In most molecules the major contribution is from the electrons. The electronic polarizability parallel to a bond is different from the polarizability perpendicular to the bond. As a diatomic molecule or linear polyatomic molecule rotates, all of the bonds rotate in the same way

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[17] N. B. Colthup, L. H. Daly, and S. E. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, 3d ed., Academic Press, San Diego, 1990, pp. 65ff.

and the components of the polarizability fluctuate periodically. The rotation will be Raman active (produce a Raman spectrum). For a nonlinear polyatomic molecule, the polarizabilities of the individual bonds add vectorially to make a total polarizability. If the molecule is sufficiently symmetrical, the total polarizability is the same in all directions and the ellipsoid of polarizability is a sphere. This is the case with a spherical top molecule, which has no rotational Raman spectrum. Symmetric tops and asymmetric tops have anisotropic polarizabilities and have rotational Raman spectra.

The stretching or compression of a bond changes the electronic wave function, so that the vibration of a diatomic molecule will be Raman active. A vibrational normal mode in a polyatomic molecule will be Raman active if it produces a periodic change in the shape of the ellipsoid of polarizability or in the case of a nonspherical ellipsoid if it changes the orientation of the ellipsoid of polarizability. The normal modes of carbon dioxide are shown in Figure 19.5. 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. One end of the molecule moves inward while the other end moves outward, and the ellipsoid of polarizability does not change. In the symmetric stretch, the whole molecule stretches and compresses. The ellipsoid of polarizability also stretches and compresses, and is thus modulated by the motion. The bending modes, which are seen in the infrared, are not seen in the Raman spectrum, since the bonds do not stretch appreciably as the bond angle bends. The ends of the molecule remain at the same distance from each other and move up and down together, as do the ends of the ellipsoid of polarizability. 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 will not be seen in the Raman, and vice versa.*[18] The normal modes of carbon dioxide illustrate this rule. In molecules with more than three atoms, the analysis can be more complicated, and group theory is often used to simplify the analysis.

EXAMPLE 20.8

Identify the normal modes of cyanogen shown in Figure 20.13 that will give rise to Raman lines.

Solution

In modes 1 and 2, 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 in that the bonds do not change their lengths appreciably, and this mode will not be seen in the Raman spectrum. Mode 4 is a little more complicated, although we can conclude immediately from the rule of mutual exclusion that it must be Raman active, since the molecule has a center of symmetry and this mode is not infrared active. Although the ends of the molecule do not appreciably change their distance from each other, there is a rocking motion of the molecule. The ellipsoid of polarizability follows this, changing its orientation, so that the motion does modulate the polarizability.

*Exercise 20.16

Figure 20.17 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

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[18] Levine, *op. cit.*, p. 268 (Note 7).

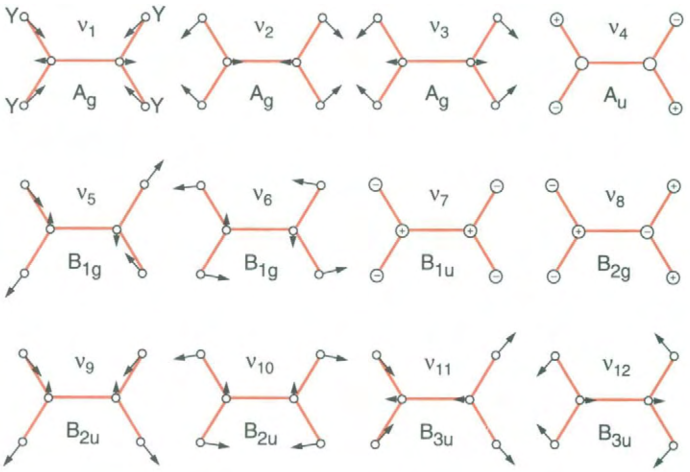

Figure 20.17. The Vibrational Normal Modes of Ethylene, C_2H_4. The arrows show the direction of motion of each nuclei in one half of the period. The length of each arrow is proportional to the amplitude of motion of the nucleus. From G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. II, Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand Reinhold, New York, 1945, p. 107.

the plane, a positive sign (+) indicates upward motion and a negative sign (−) indicates downward motion. Say which modes are infrared active and which are Raman active. There is a center of symmetry, so the rule of mutual exclusion can be used.

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. (20.7-3a), the Raman shift of the Stokes rotational lines of a diatomic molecule is given by

$$\tilde{\nu} - \tilde{\nu}' = (E_{J+2} - E_J)/hc = \tilde{B}_e(4J + 6) \tag{20.7-8}$$

where terms in α and $\mathfrak{D}$ have been neglected.

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. (19.3-7):

$$E_J = \frac{\hbar^2}{2I_B} J(J+1)$$

Equation (20.7-8) can be used for a linear polyatomic molecule if $\tilde{B}_e$ is replaced by

$$\tilde{B} = \frac{h}{8\pi^2 I_B c} \tag{20.7-9}$$

EXAMPLE 20.9

Carbon dioxide has no microwave spectrum, so its rotational Raman spectrum can be used to determine the bond lengths. Figure 20.18 shows this spectrum. From the splitting between the lines, 3.09 cm^{-1}, calculate the equilibrium bond lengths.

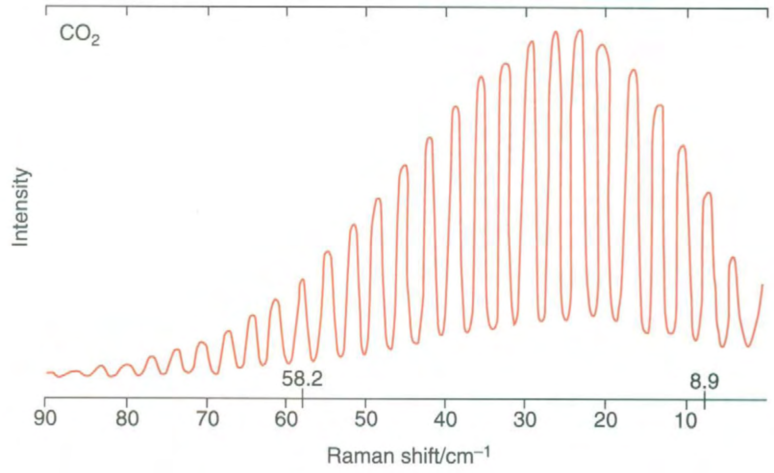

Figure 20.18. Rotational Raman Spectrum of Carbon Dioxide. The axis is the difference between the reciprocal wavelength of the incident and that of the scattered radiation. The peak at zero Raman shift is the scattered radiation with no change in energy of the molecules. From L. Claron Hoskins, *J. Chem. Educ.*, **54**, 642 (1977).

Solution

Since the carbon nucleus is at the center of mass it makes no contribution to the moments of inertia and 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 $\tilde{B}$ is given by

$$\tilde{B} = \frac{h}{8\pi^2 I_B c} = \frac{h}{8\pi^2 2m_O r_e^2 c}$$

The CO_2 molecule has a symmetry number equal to 2. Since the ^{16}O nuclei have zero spin (they are bosons), and since the electronic ground state is a sigma state, only even values of J can occur, just as with a homonuclear diatomic molecule with nuclei of zero spin. The first spectral line should occur at $6\tilde{B}$, and the splitting between lines should equal $8\tilde{B}$. The first full line shown in the figure is the second line, corresponding to the transition from $J = 2$ to $J = 4$.

Using the symbol $\Delta\tilde{\nu}$ for the splitting, we obtain

$$\begin{aligned} r_e^2 &= \frac{h}{2\pi^2 m_O c\,\Delta\tilde{\nu}} \\ &= \frac{6.6261 \times 10^{-34}\ \text{J s}}{2\pi^2(2.656 \times 10^{-26}\ \text{kg})(3.09\ \text{cm}^{-1})(2.9979 \times 10^{10}\ \text{cm s}^{-1})} \\ &= 1.364 \times 10^{-20}\ \text{m}^2 \end{aligned}$$

$$r_e = 1.17 \times 10^{-10}\ \text{m} = 117\ \text{pm} = 1.17\ \text{Å}$$

This result agrees fairly well with the accepted value, 116.15 pm. This bond length is quite short, since a typical carbonyl C=O bond length is 122 pm. It has roughly the same length as the carbon–oxygen triple bond in carbon monoxide.

From the vibrational selection rule, $\Delta v = \pm 1$, the Raman shift of the band center in a vibrational spectrum of a heteronuclear diatomic molecule will be the same as the frequency of the band center in an infrared spectrum. A homonuclear diatomic molecule has no infrared or microwave spectrum, so the Raman spectrum can be used to determine the intermolecular distance and the vibrational frequency. A band in the vibrational Raman spectrum of a diatomic molecule has three branches. For the Stokes band, there is the Q branch corresponding to $\Delta J = 0$, the O branch corresponding to $\Delta J = -2$, and the S branch corresponding to $\Delta J = +2$. These branches consist of sets of lines with the same spacings as the lines in the rotational Raman spectrum.

Exercise 20.17

***a.** From data in Table A.22 of Appendix A find the Raman shift in reciprocal wavelength 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?

Photoelectron Spectroscopy

In photoelectron spectroscopy, high-energy ultraviolet radiation is absorbed by the sample substance, causing ejection of an electron:

$$M + \text{photon} \rightarrow M^{+} + e^{-} \tag{20.7-10}$$

where M represents a molecule (or atom) 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 particular electron ejected.

Several different energies are observed. If the electronic wave function is approximated as an orbital wave function, we can identify the orbitals from which electrons are ejected. The wave function of the ion will be like that of the molecule except that one spin orbital will be vacant that is occupied in the molecule. If the other orbital energies do not change appreciably, the ionization energy will be equal to the magnitude of the orbital energy of this spin orbital, so that photoelectron spectroscopy affords a direct means for measuring the orbital energies. This is the content of **Koopman's theorem.**[19]

Figure 20.19 shows the photoelectron spectrum of N_2, using 58.4 nm ultraviolet radiation from a helium arc. 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. Since the sample is at room temperature, only the ground vibrational state of the molecule is significantly occupied in the initial state, so the separate lines within each set correspond to different vibrational states of the ion produced by the ionization. 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

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[19] T. C. Koopman, *Physica*, **1**, 104 (1933).

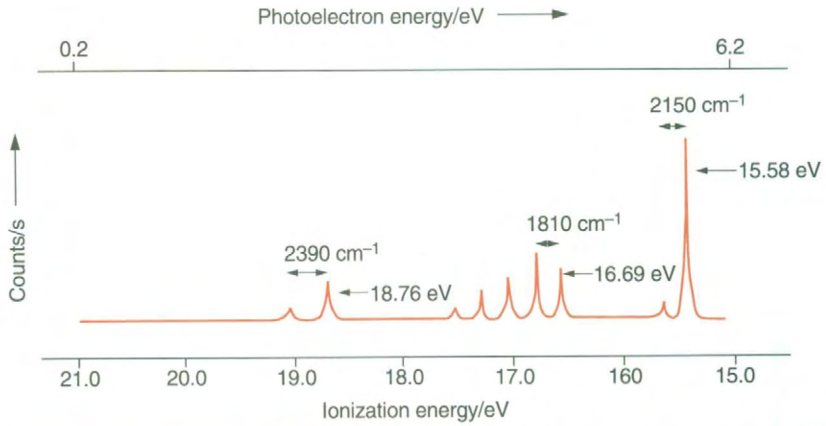

Figure 20.19. Photoelectron Spectrum of Nitrogen. Electrons ejected from three different orbitals are shown. The splittings are for different vibrational states in the product ions. From Ira N. Levine, *Molecular Spectroscopy*, Wiley, New York, 1975, p. 316.

orbital, and the leftmost set of lines arises from removal of an electron from the σ_u^*2s antibonding orbital.

The absorption of a photon with removal of an electron is quite similar to absorption of a photon to make a transition to an excited electronic state, and the Franck–Condon principle applies. The ionization potential that is determined through photoelectron spectroscopy is referred to as the "vertical" ionization energy, since the ionization is represented by a vertical line in a diagram such as that of Figure 20.10. 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.

EXAMPLE 20.10

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

$$\begin{aligned}\Delta E_{\text{zero-point}} &= \frac{h\nu_{\text{molecule}}}{2} - \frac{h\nu_{\text{ion}}}{2} = \frac{hc}{2}(\tilde{\nu}_{\text{molecule}} - \tilde{\nu}_{\text{ion}}) \\ &= \frac{(6.6261 \times 10^{-34}\ \text{J s})(2.9979 \times 10^{10}\ \text{cm s}^{-1})}{2}(209\ \text{cm}^{-1}) \\ &= 2.08 \times 10^{-21}\ \text{J} = 0.0130\ \text{eV}\end{aligned}$$

$$\Delta E_{\text{e-e}} = \Delta E_{0\text{-}0} + 0.013\ \text{eV} = 15.58\ \text{eV} + 0.013\ \text{eV} = 15.59\ \text{eV}$$

Exercise 20.18

Explain why the spacing between the lines in the leftmost set in Figure 20.19 is greater than 2359 cm^{-1}, the vibrational spacing of the ground level, while 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. The method has not been extensively exploited until fairly recently.

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 through 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 intensity of the sound wave can be measured electronically as the wavelength of the light is varied, giving an absorption spectrum. 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 principal advantage of the method is that an opaque sample can be used, such as a strongly colored liquid or solid.

Circular Dichroism and Optical Rotatory Dispersion

These two types of spectroscopy involve study of optically active substances. An optically active substance is one that rotates the plane of plane-polarized light, and is generally one that has molecules without a plane of symmetry and without an improper rotation axis. Plane-polarized light was described in Figure 14.4 as an oscillating electric field remaining in one plane containing the direction of propagation and an oscillating magnetic field in a plane perpendicular to the first plane. To understand optical activity one must consider **circularly polarized light**, which is equivalent to 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 as depicted in Figure 20.20, which shows the electric field. The sum of the two electric fields follows a helix, and the light is said to be circularly polarized. If the wave shown in the figure propagates to the right of the figure, a stationary observer facing the source of radiation observes an electric field that rotates clockwise. Such radiation is called **right-polarized** radiation, while 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.

Although we depicted a ray of circularly polarized light as being the sum of two plane-polarized rays, it is also possible to depict plane-polarized light as being the sum of two circularly polarized rays. Figure 20.21a 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 have the same frequency and the same amplitude. Plane-polarized light should be visualized as being made up of equal numbers of left circularly polarized photons and right circularly polarized photons.

As light passes through a transparent or translucent medium, its speed is less than the speed of light in vacuum. This can be thought of as absorption of the light by the

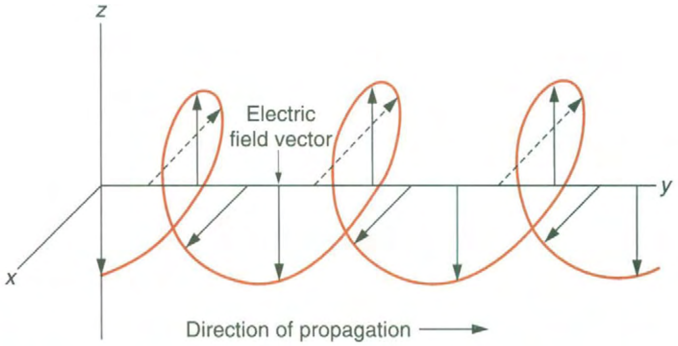

Figure 20.20. Circularly Polarized Light from Plane-Polarized Light. The circularly polarized light corresponds to the electric field vector moving in a helical pattern. Plane-polarized light in the *y*–*z* and *x*–*z* planes can interfere to form circularly polarized light.

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:

$$n = \frac{c(\text{vacuum})}{c(\text{medium})} \quad \text{(definition of refractive index)} \tag{20.7-11}$$

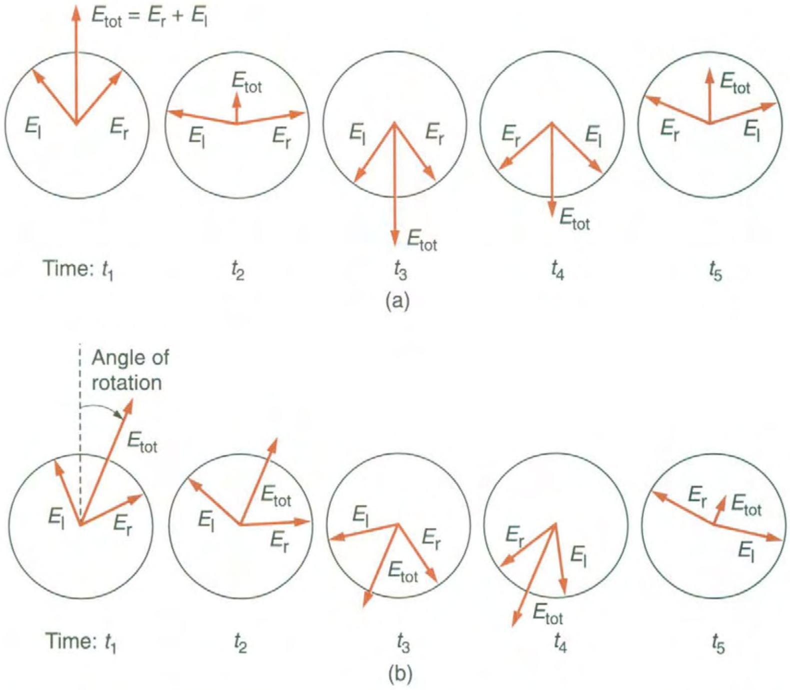

Figure 20.21. Plane-Polarized Light (E_{tot}) from Right-Polarized Light (E_r) and Left-Polarized Light (E_l). (a) **Plane-polarized light in a vertical plane.** This diagram shows how the two vectors from the right- and left-polarized light add to produce a sum vector that oscillates in one plane. (b) **Plane-polarized light (E_{tot}) from right-polarized light (E_r) and left-polarized light (E_l) which is delayed relative to (a).** 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).

The refractive index depends on the wavelength of light as well as on the identify of the medium.

Molecules that have a plane of symmetry are identical to their enantiomorphs. They 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 20.21b. 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

$$\alpha = \frac{\pi(n_R - n_L)L}{\lambda} \qquad (20.7\text{-}12)$$

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

$$[\alpha] = \frac{\alpha}{\rho L} \quad \text{(definition)} \qquad (20.7\text{-}13)$$

where α is the angle of rotation, ρ is the density of the substance, and L is the length of the sample. If, instead of a pure substance, 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 identity 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, however, 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.[20]

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.

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[20] S. C. Stinson, *Chem. Eng. News*, **63**(45), 21 (Nov. 11, 1985).

20.8 Magnetic Resonance Spectroscopy

When an atom or molecule is in a magnetic field, different spin states of electrons or nuclei have different energies. Transitions between the spin states give rise to absorption of radiation at characteristic frequencies depending on the magnetic field and on the properties of the molecule, allowing information about the molecular structure to be deduced. The spectroscopy that exploits transitions between different electronic spin states is called **electron spin resonance** (ESR) spectroscopy or **electron paramagnetic resonance** (EPR) spectroscopy, and the spectroscopy that exploits transitions between different nuclear spin states is called **nuclear magnetic resonance** (NMR) spectroscopy. Nuclear magnetic resonance is also used in medicine to obtain images of internal organs of patients (or at least their densities of hydrogen atoms) by focusing on the NMR absorption of hydrogen nuclei and creating images of the density of hydrogen atoms. This is generally called magnetic resonance imaging (MRI).

Magnetic Fields

The strength of a magnetic field is commonly specified by the **magnetic induction B** or the **magnetic field strength H**. These two quantities are proportional to each other. We 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:

$$B = |\mathbf{B}| = \frac{\mu_0 I}{2\pi r} \tag{20.8-1}$$

where μ_0 is the permeability of a vacuum, introduced in Section 14.2:

$$\mu_0 = 4\pi \times 10^{-7}\ \mathrm{T\ m\ A^{-1}} \quad \text{(exactly, by definition)} \tag{20.8-2}$$

The current is measured in amperes (A, equal to coulombs per second), the distance is measured in meters and the magnetic field is measured in teslas (T). There is another unit of magnetic field, called the **gauss**, defined by

$$1 \times 10^4\ \text{gauss} = 1\ \mathrm{T} \quad \text{(exactly)} \tag{20.8-3}$$

The earth's magnetic field is roughly equal to 1 gauss at most locations on the earth's surface. The direction of the magnetic induction can be obtained from a right-hand rule: If the right thumb points in the direction of the current, then **B** points in the direction of the curled fingers, tangent to a circle perpendicular to the wire and centered on it. 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 a particle of charge Q is moving with velocity **v** through a magnetic field **B** there is a force on the particle given by

$$\mathbf{F} = Q\mathbf{v} \times \mathbf{B} \tag{20.8-4}$$

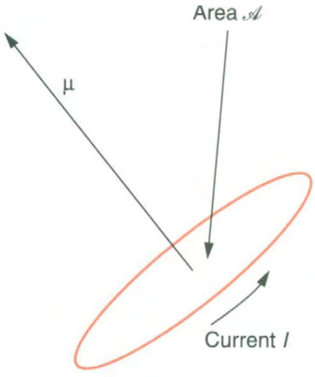
where × stands for the vector product (cross product) of the two vectors, defined and discussed in Appendix B. The direction of the force is given as in Appendix B and corresponds to another right-hand rule: If the thumb points in the direction of **v** and the index finger points in the direction of **B**, the middle finger points in the direction of **F** when perpendicular to the other two digits.

Magnetic Dipoles

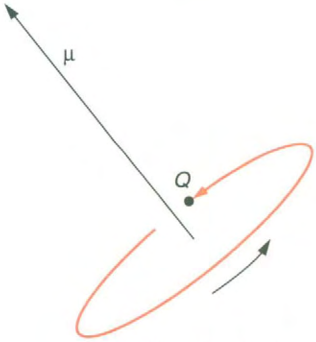
Magnetic dipoles are like bar magnets, with a "north-seeking" pole at one end and a "south-seeking" pole at the other. Just as an electric field applies a torque to an electric dipole, a magnetic field applies a torque to a magnetic dipole. An electric dipole can be made up of a positive and a negative charge (two electric monopoles) separated from each other in space. It is not yet certain whether magnetic monopoles can exist separately.[21] If they do exist, they are not commonly observed.

According to classical electromagnetic theory, a magnetic dipole can be produced by an electric current flowing in a closed loop of a conducting material, as shown in Figure 20.22a. The magnetic dipole $\boldsymbol{\mu}$ is a vector whose magnitude is given by the product of the current, I, and the area of the loop, $\mathscr{A}$:

$$|\boldsymbol{\mu}| = \mu = I\mathscr{A} \tag{20.8-5}$$



A current in a ring
(a)



An orbiting charge, Q
(b)

Figure 20.22. 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.

Do not confuse the symbol μ for the magnitude of a magnetic dipole with the same letter used for the permeability. The direction of the magnetic dipole vector is as shown in the figure, perpendicular to the plane of the loop. If the fingers of the right hand point in the direction of the current the thumb points in the direction of the magnetic dipole.

The potential energy of a magnetic dipole in a magnetic field is given by

$$E_{\mathrm{mag}} = \boldsymbol{\mu} \cdot \mathbf{B} = -|\boldsymbol{\mu}||\mathbf{B}| \cos(\alpha) \tag{20.8-6}$$

where the dot (·) stands for the scalar product (dot product) of the two vectors, defined in Appendix B, and where α is the angle between the dipole and the field. 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. A compass needle approximates a magnetic dipole and tends to orient itself in the direction of minimum potential energy.

If a particle of charge Q is moving in a circular orbit as in Figure 20.22b, its motion is equivalent to an average electric current with magnitude equal to the particle's charge divided by t_{orbit}, the time required to make one circuit of the orbit:

$$I = \frac{Q}{t_{\mathrm{orbit}}} = \frac{Qv}{2\pi r} \tag{20.8-7}$$

where r is the radius of the particle's orbit and v is its speed. Combining Eqs. (20.8-5) and (20.8-7) gives

$$\mu = |\boldsymbol{\mu}| = \frac{\pi r^2 Qv}{2\pi r} = \frac{Qvr}{2} \tag{20.8-8}$$

This can be restated in terms of the angular momentum, which for a circular orbit is given by Eq. (D-18) of Appendix D as

$$L = |\mathbf{L}| = mvr \quad \text{(circular orbit)} \tag{20.8-9}$$

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[21] J. E. Dodd, *The Ideas of Particle Physics*, Cambridge University Press, New York, 1984, pp. 169ff.

so that

$$\mu = |\boldsymbol{\mu}| = \frac{Q}{2m}|\mathbf{L}| \quad \text{(circular orbit)} \tag{20.8-10}$$

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):

$$\boldsymbol{\mu} = \frac{Q}{2m}\mathbf{L} \quad \text{(general relation)} \tag{20.8-11}$$

Electronic and Nuclear Magnetic Dipoles

Equation (20.8-11) is a convenient form to use in discussing quantum-mechanical magnetic moments. The operators and eigenvalues for the angular momentum of an orbiting particle are known from Chapters 15 and 16 and allow the operators for the magnetic dipole to be constructed. For an orbiting electron, the charge Q is equal to $-e$, and the operator for the magnetic dipole is

$$\hat{\boldsymbol{\mu}} = -\frac{e}{2m_e}\hat{\mathbf{L}} \tag{20.8-12}$$

where m_e is the mass of the electron, 9.10939×10^{-31} kg.

Equation (20.8-12) must be modified to hold for spin and angular momenta. The operator of the magnetic dipole due to the spin angular momentum of an electron is

$$\hat{\boldsymbol{\mu}} = -g\frac{e}{2m_e}\hat{\mathbf{S}} \tag{20.8-13}$$

where $\hat{\mathbf{S}}$ is the spin angular momentum operator. The quantity g is a correction factor that accounts for the failure of the electron to obey nonrelativistic mechanics, and is known as the **anomalous *g* factor of the electron**. Its value is 2.0023 .... The only eigenvalue that the operator $\hat{\mathbf{S}}^2$ possesses is $\hbar^2(1/2)(3/2)$, so that the magnitude of the magnetic dipole due to the spin of an electron is

$$|\boldsymbol{\mu}| = g\frac{e}{2m_e}\hbar[(1/2)(3/2)]^{1/2} = g\beta_e[(1/2)(3/2)]^{1/2} \tag{20.8-14}$$

The constant β_e is called the **Bohr magneton**:

$$\beta_e = \frac{e\hbar}{2m_e} = 9.2740 \times 10^{-24}\ \mathrm{J\,T^{-1}} \tag{20.8-15}$$

If a magnetic dipole is placed in a magnetic field, its energy is given by Eq. (20.8-6). For a magnetic field in the direction of the z axis,

$$E_{\text{mag}} = -\mu_z B_z \tag{20.8-16}$$

For an electron, $\hat{S}_z$ has two eigenvalues, $\pm\hbar/2$, so that

$$E_{\text{mag}} = \pm g\frac{e}{2m_e}\frac{\hbar}{2}B_z = \pm\frac{g\beta_e B_z}{2} \quad \text{(electron)} \tag{20.8-17}$$

The difference between the two energies is exploited in ESR spectroscopy.

EXAMPLE 20.11

For a magnetic field of 0.500 T, find the difference in the energies of the two electron spin states.

Solution

$$\Delta E_{\text{mag}} = g\beta_e B_z = (2.0023)(9.2740 \times 10^{-24}\ \text{J T}^{-1})(0.500\ \text{T}) = 9.28 \times 10^{-24}\ \text{J}$$

Exercise 20.19

***a.** Find the frequency and wavelength of photons with energy equal to the energy difference in Example 20.11.

b. Find the ratio of the populations of the two energy levels in Example 20.11 at 298.15 K.

Many nuclei have nonzero spin angular momenta and possess magnetic moments. For a proton the magnetic dipole operator is analogous to that of the electron,

$$\hat{\boldsymbol{\mu}} = g_p \frac{e}{2m_p} \hat{\mathbf{I}} \tag{20.8-18}$$

where $\hat{\mathbf{I}}$ is the spin angular momentum operator of the proton. The proton has the same spin angular momentum properties as the electron. The only magnitude that $\boldsymbol{\mu}$ can have is

$$|\boldsymbol{\mu}| = \mu = g_p \frac{e}{2m_p} \hbar[(1/2)(3/2)]^{1/2} = g_p \beta_N [(1/2)(3/2)]^{1/2}$$
$$= \sqrt{3/4} g_p \beta_N \tag{20.8-19}$$

The factor g_p is analogous to the g factor of the electron, and is called the **nuclear *g* factor** of the proton. Its value is 5.58569. The constant β_N is analogous to the Bohr magneton, and is called the **nuclear magneton**:

$$\beta_N = \frac{e\hbar}{2m_p} = 5.050787 \times 10^{-27}\ \text{J T}^{-1} \tag{20.8-20}$$

The magnitude of $\boldsymbol{\mu}$ for the proton is equal to 2.44×10^{-26} J T^{-1}. 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 $g_p \beta_N (1/2) = 1.41 \times 10^{-26}$ J T^{-1}.

Exercise 20.20

a. Verify the value of the magnitude of the magnetic moment of the proton.

***b.** 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 20.11 for the electron.

c. Find the ratio of the populations of the two energy levels in part (a).

There are other nuclei besides the proton that have nonzero spin angular momentum. Chemists ordinarily encounter nuclei only in their ground states, so a given nucleus (a given **nuclide**) can be taken to have a fixed magnitude of its spin angular momentum:

$$|\mathbf{I}| = \hbar\sqrt{I(I+1)} \tag{20.8-21}$$

where I is a fixed quantum number for a given nucleus. For example, $I = 1$ for ^{2}H, $I = 1/2$ for ^{13}C, and $I = 0$ for ^{12}C and ^{16}O. Each nucleus has a characteristic magnetic dipole moment:

$$|\boldsymbol{\mu}| = |g_{\mathrm{N}}|\beta_{\mathrm{N}}\sqrt{I(I+1)} \tag{20.8-22}$$

where g_{N} is a characteristic factor for the given nucleus, called the **nuclear *g* factor**.

The nuclear magneton β_{N} of Eq. (20.8-20) 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.23 of Appendix A lists the nuclear g factors and spin quantum numbers of some common nuclides. It is remarkable that some nuclides have negative values of the nuclear g factor. In these cases the magnetic dipole of the nucleus has the direction that would be expected for a negative particle.

The values that I_z can take on are

$$I_z = \hbar M_I = \hbar I, \hbar(I-1), \hbar(I-2), \ldots, -\hbar I \tag{20.8-23}$$

where M_I is a quantum number that ranges in integral steps from I to $-I$. For a proton, M_I can equal $1/2$ or $-1/2$. For a ^{2}H nucleus M_I can equal 1, 0, or -1, and other nuclei follow the standard pattern determined by their values of I. The number of values of M_I is $2I + 1$. The z component of the magnetic dipole can take on values

$$\mu_z = g_{\mathrm{N}}\beta_{\mathrm{N}}M_I \tag{20.8-24}$$

If a nucleus is placed in a magnetic field B_z, the magnetic energy is proportional to B_z:

$$E_{\mathrm{mag}} = -g_{\mathrm{N}}\beta_{\mathrm{N}}B_z M_I \tag{20.8-25}$$

A proton could be in either of two energy states, as could a ^{13}C nucleus. A deuterium nucleus could be in any of three energy states, and so on. Transitions between such states are observed in NMR spectroscopy.

Electron Spin Resonance Spectroscopy

In ESR spectroscopy, electrons are placed in a magnetic field and transitions are observed between the two possible spin states. These are magnetic dipole transitions and the selection rule is

$$\Delta m_s = \pm 1 \tag{20.8-26}$$

Transitions between the two possible states, $m_s = 1/2$ and $m_s = -1/2$, are allowed. The frequency of radiation absorbed or emitted is

$$\nu = \frac{E_{\mathrm{mag}}}{h} = \frac{g\beta_e B_z}{h} \tag{20.8-27}$$

Radiation that can be absorbed or emitted is said to be in "resonance" with the electrons. The "resonance" terminology will seem reasonable if we compare the radiation frequency and the frequency of precession of the angular momentum about its cone of possible directions (see Problem 20.65).

EXAMPLE 20.12

Find the magnetic field necessary to cause ESR absorption or emission of radiation with wavelength 1.000 cm.

Solution

$$B_z = \frac{hc}{g\beta_e\lambda} = \frac{(6.6261\times 10^{-34}\text{ J s})(2.9979\times 10^{10}\text{ cm s}^{-1})}{(2.0023)(9.2740\times 10^{-24}\text{ J T}^{-1})(1.000\text{ cm})} = 1.070\text{ T}$$

It might seem that every substance would absorb radiation at the same frequency if placed in the same magnetic field since all substances contain electrons. However, most substances do not absorb at all because all of their electrons occupy space orbitals in pairs with opposite spins. Such electrons cannot change their spins unless both members of a pair change simultaneously because of the Pauli exclusion principle. One electron gains the same amount of energy that the other electron loses and no absorption takes place. Only a substance containing unpaired electrons will exhibit an electron spin resonance spectrum. It would still seem that no useful information about the substance would be obtained except to find out whether it contains unpaired electrons. 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, the z component of the field is

$$B_z = B_0 + B_{\text{internal},z} = B_0 + \sum_{j=1}^{n} a_j M_{Ij} \tag{20.8-28}$$

where a_j is called a **coupling constant** for the jth nucleus and where M_{Ij} is the quantum number for the z component of the nuclear spin angular moment of nucleus number j. The coupling constants for nuclei in many molecules have values near 1 gauss (1×10^{-4} T), but they depend on the orbital in which the electron is found as well as on the identity of the nucleus.

It is found that B_{internal} is a short-range interaction and is known as the **Fermi contact interaction**. It has an effect only if the electron approaches very closely to the nucleus. If an unpaired electron occupies an orbital with a nodal surface at a particular nucleus, its probability of being found at that nucleus is very small and the coupling constant for that nucleus and that orbital will be negligibly small. Since atomic orbitals with $l = 0$ (s orbitals) are the only atomic orbitals without nodal surfaces passing through the nucleus, the coupling constant at a specific nucleus is sometimes said to be a measure of the "s character" of the orbital at that nucleus.

An ESR spectrometer uses microwave radiation with wavelengths around 1 cm. 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 actually "felt" by an unpaired electron reaches the value B_{res}, the value such that Eq. (20.8-27) is satisfied for the frequency being used:

$$B_0 + B_{\mathrm{internal}} = B_0 + \sum_{j=1}^{n} a_j M_{Ij} = B_{\mathrm{res}} = \frac{h\nu}{g\beta_e} \tag{20.8-29}$$

A sample of a substance with several nuclear dipoles in its molecules can have several spectral lines, or values of B_0 at which resonance occurs, since a variety of nuclear spin states will be found in different molecules in the sample. In a symmetrical molecule, an unpaired electron will often occupy an orbital that has equal magnitudes at two or more nuclei of the same element. In this case the coupling constants are equal. For example, consider a hydrogen molecule ion, H_2^+, with an unpaired electron that couples equally with two protons. The molecule could be in a state with both proton spins up ($M_I = 1$), in either of two states with one proton spin up and one down ($M_I = 0$), or in a state with both proton spins down ($M_I = -1$). Since the sum of the M_I values has three different values, we obtain a spectrum with three lines. Each molecule produces only one line in the spectrum, and the three lines are produced by three sets of molecules. The differences between the energies of the different nuclear spin states are so small that the populations of the different nuclear spin states are very nearly equal. The middle line will be twice as intense as the other two, since there are two states with one spin up and one spin down.

EXAMPLE 20.13

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

Since all of the coupling constants are equal, there will be just 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 coefficient. The intensities of the spectral lines will be proportional to the number of molecules in each level. 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 differing by unity is given by Eq. (20.8-5):

$$\Delta E_{\mathrm{mag}} = g_N \beta_N B_z = (5.5857)(5.0508 \times 10^{-27}\ \mathrm{J\,T^{-1}})(0.500\ \mathrm{T})$$
$$= 1.411 \times 10^{-26}\ \mathrm{J}$$

At 300 K the ratio of the populations of two such states is

$$e^{-\Delta E_{\mathrm{mag}}/k_B T} = \exp\left(-\frac{1.411 \times 10^{-26}\ \mathrm{J}}{(1.3807 \times 10^{-23}\ \mathrm{J\,K^{-1}})(300\ \mathrm{K})}\right)$$
$$= 0.9999966$$

Since the states are almost equally populated, the population of a level will be approximately 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 and a subset of $n - m$ is

$$\mathrm{Number} = \frac{n!}{m!(n-m)!} \tag{20.8-30}$$

which is the formula for binomial coefficients. The intensities of the lines are in the ratios 1 : 6 : 15 : 20 : 15 : 6 : 1.

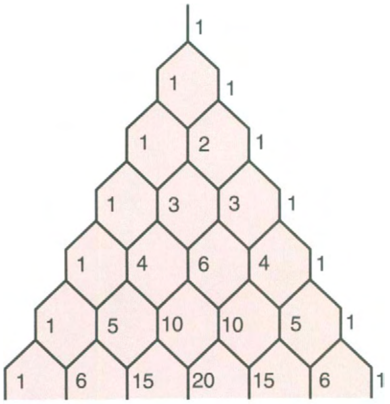

Figure 20.23. Diagram to Find the Splittings in the ESR Spectrum of the Benzene Negative Ion, $C_6H_6^-$. The use of this diagram requires that all of the splitting constants are equal. Otherwise the lines will not coincide, and there will be more than seven lines.

Figure 20.23 shows another way of arriving at the spectrum of Example 20.13. Starting with the spectral line that would occur without any splitting by proton spins, 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 this gives 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 20.21

Predict the ESR spectrum of the hydrogen atom.

If an unpaired electron is affected by a nucleus with a spin quantum number other than $1/2$, a single 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 equal intensity, since there is only one state with each value of M_I. A nucleus with $I = 3$ would produce seven lines of equal intensity.

Nuclear Magnetic Resonance Spectroscopy

In NMR spectroscopy, transitions of nuclei from one spin state to another are observed in a magnetic field. Earlier NMR instruments were "continuous-wave" NMR instruments (or "scanning" instruments), similar to the ESR instruments previously described. A fixed-frequency source of radiation is used and the magnetic field is varied (scanned). The frequency is smaller than in ESR spectroscopy, and the radiofrequency energy is conducted by coaxial cable to the probe in which a liquid or solid sample is placed in the magnetic field. Every type of nucleus that has a nonzero spin has its characteristic g factor. Since presently available magnets cannot scan over a very large range of magnetic fields without losing the necessary field homogeneity, a single scanning instrument is usually built to take the spectrum of only one type of nucleus. The most common scanning instruments obtain NMR spectra only of protons.

Modern NMR instruments are **Fourier-transform NMR spectrometers**, which use pulses of radiofrequency energy that cover a band of frequencies. 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 simple spectra that we now discuss are the same whether they are generated by a continuous-wave or a Fourier-transform instrument.

The selection rule for transitions of nuclear spins with absorption or emission of radiation is

$$\Delta M_I = \pm 1 \tag{20.8-31}$$

so that from Eq. (20.8-25),

$$E_{\text{photon}} = h\nu = |g_N|\beta_N B_z \tag{20.8-32a}$$

If absorption is to occur the magnetic field at the nucleus must equal the value required for the radiation being used:

$$B_z = B_{\text{res}} = \frac{h\nu}{g_N \beta_N} \tag{20.8-32b}$$

where g_N is the nuclear g factor for the particular type of nucleus.

EXAMPLE 20.14

Find the value of the magnetic field necessary for protons to absorb at a frequency of 200.00 MHz.

Solution

$$B_z = \frac{h\nu}{g_N\beta_N} = \frac{(6.6261 \times 10^{-34}\ \text{J s})(200.00 \times 10^6\ \text{s}^{-1})}{(5.5857)(5.050787 \times 10^{-27}\ \text{J T}^{-1})} = 4.6973\ \text{T}$$

*Exercise 20.22

Find the magnetic field necessary for ^{13}C nuclei to absorb at 200.00 MHz.

If the externally applied field were the only contribution to the magnetic field at the nucleus, every proton would absorb at a fixed value of the field, every ^{13}C nucleus would absorb at another fixed value of the field, and so on. No information could be obtained except to identify which nuclei with nonzero spins were present. However, there are two additional contributions to the magnetic field at a nucleus. The first molecular contribution to the magnetic field at a nucleus comes from the electrons around the nucleus. The externally applied magnetic field, B_0, induces a net current in the electrons of the molecule, which produces a contribution to the magnetic field that is in the opposite direction to the externally applied field. This phenomenon is called **diamagnetism**. 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 the jth nucleus,

$$B_{j\text{diamagnetic}} = -\sigma_j B_0 \tag{20.8-33}$$

where σ_j is called the **shielding constant** of the jth nucleus. It has a larger value when the probability of finding electrons around the nucleus is larger. Typical values for σ range from 15×10^{-6} to 35×10^{-6} (15 to 35 parts per million).

We will later discuss the second contribution to the field at a given nucleus, known as spin–spin coupling and due to the other nuclei in the molecule. A spectrum with sufficient resolution to give information about the shielding constants but not the spin–spin coupling is called a low-resolution NMR spectrum. If we ignore the spin–spin coupling, the magnetic field at the jth nucleus is

$$B_j = (1 - \sigma_j)B_0 \tag{20.8-34}$$

and the applied magnetic field at which absorption by the jth nucleus occurs is

$$B_{0j} = \frac{h\nu}{g_N\beta_N} + \sigma_j B_{0j} \tag{20.8-35}$$

An NMR spectrum is observed with a continuous-wave instrument by scanning B_0 over a range of 10 or 20 parts per million and observing the values of B_0 at which absorption occurs.

It is not possible to use a system of bare nuclei as a reference, so it is customary to choose a reference substance to serve as a zero point for our NMR spectra. For proton NMR, the standard reference substance is tetramethylsilane, $Si(CH_3)_4$, abbreviated TMS, which has a single sharp spectral line and a rather large shielding constant, 31 ppm. In a later discussion of spin–spin splitting, we will be able to see why TMS has a single spectral line, making it a good choice for a reference compound.

The difference between the applied field necessary for the reference substance to absorb and that necessary for a given nucleus to absorb is called the **chemical shift** of that nucleus. One variable used to specify the chemical shifts is δ, which is usually expressed in parts per million (ppm). For nucleus number j,

$$\delta_j = \frac{B_{0\text{ref}} - B_{0j}}{B_{0\text{ref}}} \times 10^6 \text{ ppm} \tag{20.8-36}$$

Since the first term on the right-hand side of Eq. (20.8-35) is the same for both $B_{0\text{ref}}$ and B_{0j},

$$\delta_j = \frac{\sigma_{\text{ref}} B_{0\text{ref}} - \sigma_j B_{0j}}{B_{0\text{ref}}} \times 10^6 \text{ ppm} \approx (\sigma_{\text{ref}} - \sigma_j) \times 10^6 \text{ ppm} \tag{20.8-37}$$

The variable δ ordinarily lies between 0 and 15 ppm for proton NMR, but there are some substances containing protons with negative values of δ (larger shielding constants than TMS). The approximate equality in Eq. (20.8-37) holds to four significant digits because the different values of the applied field will differ only by 10 or 20 parts per million. A second variable used to specify the chemical shift is τ:

$$\tau = 10 \text{ ppm} - \delta \tag{20.8-38}$$

Larger values of τ correspond to larger values of the shielding constant and therefore to larger values of the magnetic field.

The values of the shielding constants and of the chemical shifts are related to the structure of the molecule since a higher electron density around a given nucleus generally corresponds to a larger shielding constant. If a nucleus 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 different chemical environments for protons. The values will be slightly different in different substances with similar functional groups, but the values in the table are useful as a general guide.

An NMR spectrum is ordinarily a graph in which a spectral line corresponding to absorption is represented by a peak and in which the intensity of the line is proportional to the area under the peak. The area under the peak is proportional to the number of nuclei producing the spectral line.

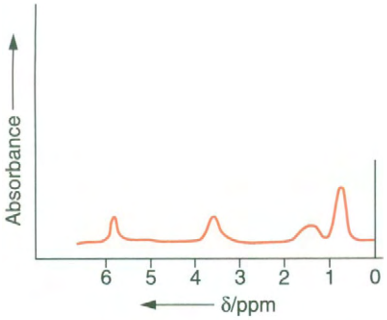

Figure 20.24. The Low-Resolution Proton NMR Spectrum of 1-Propanol (Simulated). The line near 6 ppm is from the hydroxyl proton, the line near 3.5 ppm is from the methylene closest to the hydroxyl group, the line near 1.5 ppm is from the other methylene, and the line near 0.8 ppm is from the methyl group.

EXAMPLE 20.15

Figure 20.24 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 $\delta = 1.5$. 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 20.23

Sketch the low-resolution proton NMR spectrum you would expect from propanal (propionaldehyde).

The second molecular contribution to the magnetic field at a given nucleus is due to the presence in the molecule of other nuclei with magnetic dipoles. The direct interaction between one nuclear dipole and another is unimportant. The important interaction occurs because a magnetic dipole in one nucleus induces a current in the electrons of the molecule that move close to both this nucleus and a second nucleus, and this produces a contribution to the magnetic field at the second nucleus. The effect is called **spin–spin coupling**. The field at the jth nucleus due to this effect is given by

$$B_{\text{spin-spin},j} = \sum_{i=1}^{n} J_{ji} M_{Ii} \tag{20.8-39}$$

where the sum includes a term for each other nucleus with nonzero spin. M_{Ii} is the quantum number for the z projection of the spin angular momentum of nucleus number i, and the coefficient J_{ij} is called the **spin–spin coupling constant** for nuclei numbers i and j. The spin–spin coupling constant depends on the electronic environments of both nuclei. It is found that nucleus j affects nucleus i in the same way that nucleus i affects nucleus j, so that

$$J_{ij} = J_{ji} \tag{20.8-40}$$

The spin–spin coupling constants are sometimes expressed in terms of frequency. The ratio of J_{ij} expressed in hertz to the instrument's frequency is the same as the ratio of J_{ij} expressed in tesla to the field used in the instrument.

In the case of proton NMR in organic molecules, almost all of the carbon atoms are carbon-12 atoms, which have no magnetic dipole. Almost all of the oxygen atoms are oxygen-16 atoms, which also have no magnetic dipole. If no other atoms with spin are present, only the other protons provide a spin–spin coupling for a given proton.

The spin–spin coupling leads to a splitting of spectral lines into multiple lines that can be seen in a high-resolution spectrum. For example, in a molecule that contains no magnetic nuclei except for two protons, the field at the first proton is

$$B_1 = B_0(1 - \sigma_1) + J_{12} M_{I2} \tag{20.8-41}$$

There will be one value of B_0 at which the molecules with $M_{I2} = 1/2$ will resonate and another value at which the molecules with $M_{I2} = -1/2$ will resonate. Since the energy difference between these states is small compared with k_BT, the numbers of molecules in the two sets will be nearly equal to each other. If the chemical shifts of the two protons differ by an amount that is somewhat larger than J_{12}, both transitions will be observed and two spectral lines will be observed, with a difference in B_0 at resonance equal to J_{12}. This is the **spin–spin splitting** that arises from the spin–spin coupling. The spin–spin splitting is a reciprocal effect, as indicated in Eq. (20.8-40). The proton that produces the splitting in the first proton's line will exhibit two lines with the same splitting as the first proton.

If the difference in chemical shift between protons on two different atoms is not large compared with the splitting constant, one does not get a splitting exactly equal to J_{12}, and the two lines are not of equal intensity. In the limit that the two protons have exactly the same chemical shift, although spin–spin coupling occurs, the transitions are governed by a selection rule that forbids transitions in such a way that spin–spin splitting is not observed.[22] Some nuclei exhibit spin–spin coupling but do not produce spin–spin splitting in the spectrum. For example ^{35}Cl nuclei and protons couple, but do not produce spin–spin splitting.

The spin–spin coupling is a short-range phenomenon, and two nuclei must be fairly close to each other to have an appreciable coupling constant. Two protons that are bonded to a pair of atoms that are bonded directly together will ordinarily exhibit spin–spin splittings, and protons that are more distant from each other than this will not usually exhibit significant spin–spin splitting if the substance is an aliphatic compound. In aromatic compounds, spin–spin splitting from *meta* or *para* protons is observed, due to the delocalized bonding. Another way of stating the rule for aliphatic compounds is that two protons will have appreciable spin–spin splitting if the number of bonds from one to the other is no greater than three.

If there are n protons on the second carbon atom, there are $n + 1$ possible values for the sum in Eq. (20.8-39). There can be n protons with spin up, there can be $n - 1$ with spin up, and so on down to no protons with spin 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 out of a set of n members:

$$\text{Degeneracy} = \frac{n!}{m!(n-m)!} \tag{20.8-42}$$

which is the formula for the binomial coefficients. Two protons on the first atom will thus cause the line of a proton on an adjacent atom to be split into three lines with intensities in the ratios $1:2:1$, three protons will produce four lines with intensities in the ratios $1:3:3:1$, and so on.

If a proton is bonded to an atom that is bonded to two or three adjacent atoms to which protons are bonded, more than one value of the splitting constant can be involved, since the splitting constants depend on the electronic environment of both protons and on the distance between the protons. One way to predict the effect of the

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[22] John D. Roberts, *Nuclear Magnetic Resonance*, McGraw-Hill, New York, 1959, pp. 55ff.

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, and so on.

EXAMPLE 20.16

Predict the high-resolution NMR spectrum of pure 2-propanol.

Solution

The spectral line of the –OH proton will be split into two lines by the proton on the –CH– carbon. The spectral line of the proton on the –CH– carbon will be split into seven lines by the six protons on the $-CH_3$ carbons, with relative intensities 1 : 6 : 15 : 20 : 15 : 6 : 1, and each of these lines will be split into two lines by the single –OH proton. Figure 20.25 shows the high-resolution spectrum.

The shielding term in Eq. (20.8-41), which gives rise to the chemical shift, is proportional to the applied field, while 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. In terms of parts per million of the magnetic field, the chemical shift will be the same and the spin–spin splittings will be smaller in the higher-frequency instrument. Comparison of the spectra of the same substance from

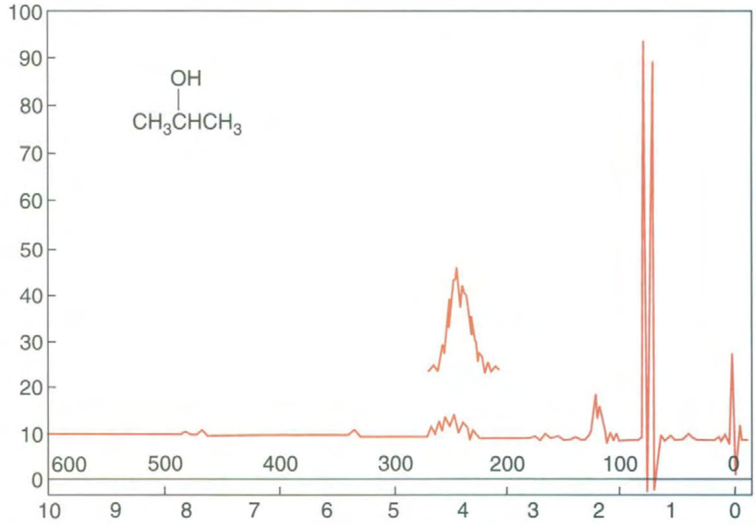

Figure 20.25. The High-Resolution Proton NMR Spectrum of 2-Propanol. This spectrum is from a sample dissolved in deuterated chloroform. Because of solvent interaction, the line from the hydroxyl proton occurs near 2 ppm instead of further downfield. The peak near 4 ppm is from the proton on the carbon attached to the hydroxyl group. It is split into seven lines by the six methyl protons, and each of these lines is split into two lines by the hydroxyl proton. These 14 lines overlap and are not completely resolved. From Charles J. Pouchert and John R. Campbell, *The Aldrich Library of NMR Spectra*, The Aldrich Chemical Co., 1974, Vol. I, p. 85.

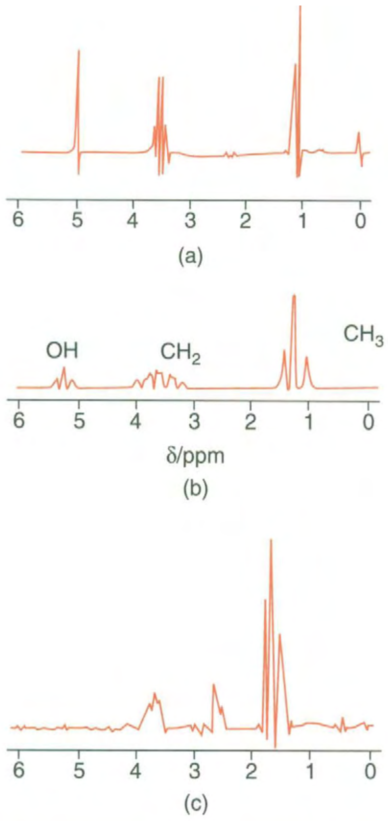

Figure 20.26. The Proton NMR Spectrum of Ethanol. (a) **With a trace of water present.** Because of exchange of the hydroxyl proton with water protons, the hydroxyl proton shows no spin–spin splitting. From Gilbert W. Castellan, *Physical Chemistry*, 3d ed., Addison-Wesley, Reading, MA, 1983, p. 606. (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 Ira N. Levine, *Molecular Spectroscopy*, Wiley, New York, 1975, p. 353. (c) **In deuterated chloroform.** In this spectrum, the dilution with chloroform moves the hydroxyl line to near 2.6 ppm. The splitting into three lines is not quite resolved. From Charles J. Pouchert and John R. Campbell, *The Aldrich Library of NMR Spectra*, The Aldrich Chemical Co., 1974, Vol. I, p. 79.

two such instruments can aid in interpretation of a spectrum with a number of overlapping sets of lines.

If a substance is mixed with other substances, they can modify its chemical shifts. Figure 20.26 shows three different high-resolution proton NMR spectra of ethanol. Figure 20.26a shows the spectrum of ethanol with a trace of water present. Figure 20.26b shows the spectrum of carefully purified ethanol, and Figure 20.26c shows the spectrum of a dilute solution of ethanol in deuterated chloroform. In the first spectrum, the spectral line of the $-$OH proton is at $\delta = 5$ ppm. In the carefully purified ethanol, this peak is in approximately the same place, at $\delta = 5.3$ ppm. In the solution this spectral line is at $\delta = 2.6$ ppm. Ethanol molecules strongly hydrogen-bond to other ethanol molecules. 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 hydroxyl proton, although adjacent to the electronegative oxygen atom, has a larger shielding constant than the protons on the carbinol carbon. The O–H bond distance, approximately 96 ppm, is so small that the proton is "buried" in the electron density close to the oxygen. When a hydrogen bond forms, the proton is "deshielded" moving to a greater distance from the oxygen nucleus and to a region of lower electron density.

There is another difference between the two spectra. In the spectrum of the carefully purified ethanol the line of the $-$OH proton exhibits spin–spin splitting, being split into three lines and also splitting the $-$CH$_2$ protons' lines. In the solution spectrum this splitting is also present although poorly resolved. In the first spectrum the absence of the spin–spin splitting in the $-$OH proton line is due to exchange of the proton with a small amount of water present in the ethanol. The alcohol molecules, which are slightly acidic, can exchange their $-$OH protons 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. Since these protons will be a random mixture of spin-up and spin-down protons, an average line with no spin–spin splitting is observed.

The difference in energy between the two states of protons in a typical magnetic field is much smaller than $k_{\mathrm{B}}T$, so that the populations of the two states are nearly equal. If the populations were 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 20.17

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

$$\text{(Population ratio)} = e^{-\Delta E/k_{\mathrm{B}}T} = e^{-g_{\mathrm{P}}\beta_{\mathrm{N}}B/k_{\mathrm{B}}T}$$

$$= \exp\left(\frac{-(5.5857)(5.05079\times10^{-27}\ \mathrm{J\,T^{-1}})(4.6973\ \mathrm{T})}{(1.3807\times10^{-23}\ \mathrm{J\,K^{-1}})(298\ \mathrm{K})}\right)$$

$$= e^{-3.2205\times10^{-5}} = 0.9999678$$

20.9 Fourier Transform Spectroscopy

Fourier transform spectroscopy is a technique that is used in both infrared and NMR spectroscopy. A spectrum is obtained without having to disperse radiation or to scan over different frequencies or magnetic fields. There are several advantages over the use of continuous-wave instruments. Since it is not necessary to spend time scanning, an instrument can take a spectrum repeatedly in a short period of time and average the separate spectra, allowing weak spectral lines to be seen and allowing random "noise" to be reduced by the averaging procedure. In ^{13}C NMR, ^{13}C atoms constitute only 1% of the carbon atoms in ordinary carbon and therefore give only a weak spectrum in scanning techniques, but averaging several repeated spectra allows a good spectrum to be obtained with Fourier transform instruments. Furthermore, advanced techniques involving two-dimensional spectra, etc. are essentially impossible with continuous-wave techniques but can be carried out routinely with high-field Fourier transform NMR instruments. Magnetic resonance imaging for medical diagnosis would be impossible with continuous-wave techniques. In this technique, the patient is placed in a large superconducting magnet, and the density of protons is determined as a function of position from the NMR signal and processed into an image.

In a Fourier transform infrared spectrometer a pulse of infrared radiation containing many frequencies is passed through an **interferometer**, as depicted in Figure 20.27.[23] The beamsplitter 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, and an interferogram corresponding to a number of frequencies encodes the intensities of the various frequencies.

An interferogram is taken without a sample in position and another is taken with a sample in position, and the difference between the two interferograms contains the information corresponding to the absorption spectrum. 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. The intensity of radiation as a function of time can be written as a Fourier transform:

$$I(t) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} c(\omega) e^{i\omega t}\, d\omega \tag{20.9-1}$$

Equation (20.9-1) is a kind of linear combination of basis functions, $e^{i\omega t}$, but with an integration instead of a sum. The basis functions are oscillatory functions with frequencies given by

$$\nu = \frac{\omega}{2\pi} \tag{20.9-2}$$

The variable ω is sometimes called the "circular frequency." The function $c(\omega)$ plays the same role as the expansion coefficients in a linear combination and is called the Fourier transform of $I(t)$.[24] It contains the same information as $I(t)$, but encoded as a

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[23] W. D. Perkins, *J. Chem. Educ.*, **63**, A5 (1986), **64**, A269 (1987), and **64**, A296 (1987).

[24] See L. Glasser, *J. Chem. Educ.*, **64**, A261 (1987) and *J. Chem. Educ.*, **64**, A306 (1987) for an introduction to Fourier series and transforms.

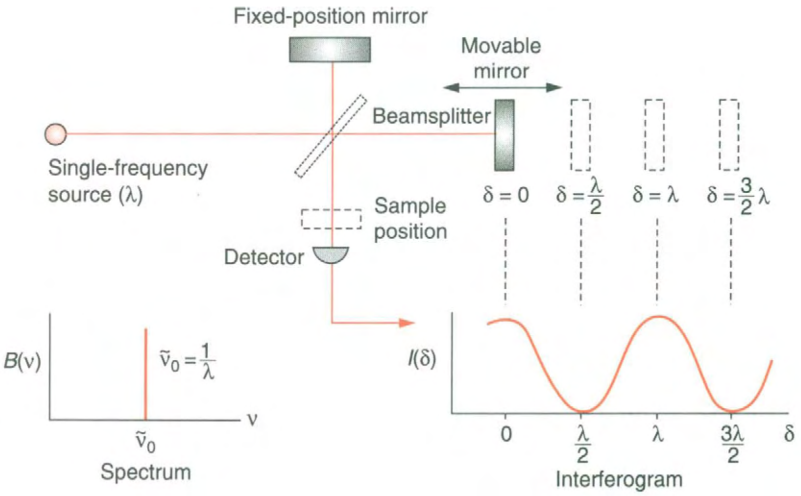

Figure 20.27. The Radiation Path in a Fourier Transform Infrared Spectrophotometer (Schematic). If only one wavelength is present, the sinusoidal interferogram at the lower right is observed as the movable mirror in the Michelson–Morley interferometer changes its position. The Fourier transform of this signal is a single sharp line, as shown at the lower left. If many frequencies are present, the Fourier transform will show all frequencies present in the proper intensities. From W. D. Perkins, *J. Chem. Educ.*, **63**, A5 (1986).

function of frequency instead of time and is therefore the infrared spectrum of the sample. Appendix B contains a brief introduction to Fourier series and transforms and more information is contained in reference 24.

To find the spectrum $c(\omega)$, one must invert the Fourier transform, which is done by calculating the integral

$$c(\omega) = \frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} I(t)e^{-i\omega t}\,dt \tag{20.9-3}$$

Since Eq. (20.9-1) and Eq. (20.9-3) differ only in the sign of the exponent, $I(t)$ is also called the Fourier transform of $c(\omega)$.

EXAMPLE 20.18

Find the Fourier transform of the function $f(\omega) = \dfrac{1}{a^2+\omega^2}$, 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 ∞:

$$I(t) = \frac{2}{\sqrt{2\pi}}\int_{0}^{\infty}\frac{\cos\omega t}{a^2+\omega^2}\,d\omega = \frac{2}{\sqrt{2\pi}}\frac{\pi}{2a}e^{-a|t|} = \sqrt{\frac{\pi}{2}}\,\frac{1}{a}\,e^{-a|t|}$$

Where we have looked the integral up in a table.[25]

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[25] H. B. Dwight, *Tables of Integrals and Other Mathematical Data*, 4th ed., Macmillan, New York, 1961.

Exercise 20.24

***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 $t_0 = 0$.

Fourier transform NMR spectroscopy can be described qualitatively in terms of the semiclassical picture of **Larmor precession**.[26] In a magnetic field, each nuclear spin precesses like the motion of the gyroscope depicted in Figure D.3 of Appendix D. The possible directions of the nuclear spin of a proton are like those of an electron, depicted in Figure 16.11, so a proton spin precesses about one of two possible cones. A calculation of this precession frequency is assigned in Problem 20.65. In the presence of the external magnetic field, more of the protons' magnetic dipoles will be in one cone than the other, according to the Boltzmann distribution, but will be randomly distributed about the cone. The vector sum of the magnetic dipoles is a macroscopic magnetization vector pointing parallel to the external field. A strong pulse of radiofrequency radiation is delivered to the sample, much like the pulse of infrared radiation used in Fourier transform infrared spectroscopy. The direction of the radiation and the length of the pulse are carefully controlled so that the magnetization vector rotates to become perpendicular to the z axis (the direction of the external magnetic field) at the end of the pulse.

After the end of the pulse, the magnetization vector precesses in a plane perpendicular to the external magnetic field, with equal numbers of spins up and spins down. This vector decays as the individual spins return to their original Boltzmann distribution and the magnetization vector again becomes parallel to the external magnetic field. There are two mechanisms of decay, each of which leads to 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 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. These relaxation times are related to line widths and can be used to gain information about the systems being studied.

The precessing magnetization vector induces an alternating voltage in a coil around the sample. The detected signal is called the **free induction decay spectrum** (abbreviated FIDS). Since the different nuclei experience different total fields due to different chemical shifts and different spin–spin couplings, they precess at slightly different frequencies. The free induction decay spectrum is like an infrared interferogram, encoding the NMR spectrum as a function of time. The Fourier transform of the free induction decay spectrum provides the spectrum.

Various special techniques have been devised that are carried out with carefully controlled pulses of radiation, including various pulse sequences that result in spectra that are plotted in two dimensions instead of one dimension. The interested reader can

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[26] R. S. Macomber, *J. Chem. Educ.*, **62**, 212 (1985).

read more about Fourier transform infrared and NMR spectroscopy in some of the works listed at the end of the book, as well as in the references listed in the article of footnote 23.

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

$$\Delta J = \pm 1$$

which leads to a spectrum of equally spaced lines with a spacing in terms of reciprocal wavelength equal to $2\tilde{B}_e$. 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 $\tilde{\nu}_e$. 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 are equally spaced with a spacing of $4\tilde{B}_e$.

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 the 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.

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 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 must be such that the magnetic field at a given nucleus is

$$B_{\text{res}} = \frac{h\nu}{g_{\text{N}}\beta_{\text{N}}}$$

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.

PROBLEMS

Problems for Section 20.1

***20.25.** A solution of phenylalanine in neutral water with concentration equal to 0.110×10^{-3} mol L^{-1} has an absorbance at 206.0 nm of 1.027 in a 1.000-cm cell. Find the molar absorptivity.

20.26. 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.

20.27. 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.

20.28. The absorptivity of hemoglobin at 430 nm is found to be 532 L mol^{-1} cm^{-1}. The molar mass of hemoglobin is 68,000 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.

Problems for Section 20.2

***20.29.** A positronium atom 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.

20.30. 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:

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.

***20.31.** Crudely approximate the electronic motion in a hydrogen atom by assuming that the electron moves in a cubical three-dimensional 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 box be to make the transition have the same wavelength as the correct $n = 2$ to $n = 1$ transition?

20.32. 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 16 and 17. Draw a Grotrian diagram for these states and the ground state of the He atom.

b. Using energies from Figure 17.3, estimate the wavelengths at which spectral lines would be found from the transitions of part (a).

Problems for Section 20.3

20.33. Using an identity from Appendix F, derive the selection rule for a harmonic oscillator, $\Delta v = 0, \pm 1$.

20.34. 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.

***20.35.** 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, ^2H. Assuming equal oscillator strengths, find the line of maximum intensity at 298 K.

20.36. 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

Explain your answers.

***20.37.** 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

Explain your answers.

20.38. Using the $\tilde{\nu}_e$ and $\tilde{\nu}_e x_e$ 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 $v = 2$.

20.39. Using the $\tilde{\nu}_e$ and $\tilde{\nu}_e x_e$ 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 (high-temperature) band corresponding to the transition from $v = 1$ to $v = 2$.

20.40. 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?

Problems for Section 20.5

***20.41.** The infrared spectrum of HCN shows strong bands at $712.1\ \text{cm}^{-1}$ and at $3312.0\ \text{cm}^{-1}$. There is a strong Raman band at $2089.0\ \text{cm}^{-1}$. There are weaker infrared bands at $1412.0\ \text{cm}^{-1}$, at $2116.7\ \text{cm}^{-1}$, at $2800.3\ \text{cm}^{-1}$, at $4004.5\ \text{cm}^{-1}$, at $5394\ \text{cm}^{-1}$, and at $6521.7\ \text{cm}^{-1}$. Identify these bands as fundamental, overtone, or combination bands and give the shape of the molecule.

20.42. The N_2O molecule has three strong bands in its IR spectrum, at $588.8\ \text{cm}^{-1}$, at $1285.0\ \text{cm}^{-1}$, and at $2223.5\ \text{cm}^{-1}$. All have been shown to be fundamentals, and the molecule has been shown to be linear. Explain why CO_2, which is also linear, has only two fundamental IR bands while N_2O has three.

***20.43.** Using the frequencies in Problem 20.42, indicate where to look for overtone and combination bands in the spectrum of N_2O.

20.44. The H_2S molecule has strong infrared bands at $1290\ \text{cm}^{-1}$, $2610.8\ \text{cm}^{-1}$, and $2684\ \text{cm}^{-1}$. There are weaker bands at $2422\ \text{cm}^{-1}$, $3789\ \text{cm}^{-1}$, and $5154\ \text{cm}^{-1}$. Assign these bands as fundamentals, overtones, or combination bands, and specify which normal mode corresponds to each fundamental.

20.45. The NO_2 molecule has strong infrared bands at $648\ \text{cm}^{-1}$, $1320\ \text{cm}^{-1}$, and $1621\ \text{cm}^{-1}$. There are weaker bands at $1373\ \text{cm}^{-1}$, $2220\ \text{cm}^{-1}$, and $2910\ \text{cm}^{-1}$. Assign these bands as fundamentals, overtones, or combination bands, and specify which normal mode corresponds to each fundamental.

Problems for Section 20.6

20.46. In a photochemical reaction, 0.00100 W of radiant energy of wavelength 254 nm is incident on the reaction vessel, and 61.2% of this energy is absorbed. If 2.45 mol of the absorbing reactant reacts to form products in 30.0 s, find the quantum yield.

***20.47.** Find the frequency and wavelength of light given off by the benzophenone molecule (a) in fluorescence from the S_1 state, and (b) in phosphorescence from the T_1 state.

20.48. Which one of the following substances could quench the photochemical reaction of benzophenone discussed in Section 20.6?

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

Problems for Section 20.7

***20.49.** The rotational Raman spectrum of H_2 has lines at Raman shifts of $354\ \text{cm}^{-1}$, $586\ \text{cm}^{-1}$, $814\ \text{cm}^{-1}$, and $1034\ \text{cm}^{-1}$. At room temperature, the line of greatest intensity is at $586\ \text{cm}^{-1}$. Explain the relative intensities and calculate the internuclear distance for H_2.

20.50. From the frequency in Figure 19.6, 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.

***20.51.** Which of the following substances will have a rotational Raman spectrum?

a. CCl_4
b. BF_3
c. CO_2

20.52. Which of the following substances will have a rotational Raman spectrum?

a. SF_6
b. PCl_5
c. NH_3

***20.53.** Which of the substances in Problem 20.36 will have a rotational Raman spectrum?

20.54. Which of the normal modes of cyanogen will produce Raman bands? See Example 20.7.

20.55. Use computer software such as CAChe or Spartan to find the normal modes of vibration of the following molecules. Compare the calculated frequencies with the experimental frequencies.[27] 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

Problems for Section 20.8

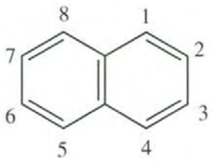
20.56. The manganese nucleus has a spin quantum number $I = 5/2$. Describe the ESR spectrum of manganese atoms.

***20.57.** Describe the ESR spectrum of a deuterium atom.

20.58. The Hückel molecular orbital method gives the following LCAO-MO 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 nonhybridized 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.

***20.59.** For electrons in a magnetic field such that ESR absorption occurs at a frequency of $9.159 \times 10^9\ \mathrm{s}^{-1}$, calculate the ratio of the populations of the two spin states at 298 K.

20.60. For electrons in a magnetic field of 1.44 T, calculate the ratio of the populations of the two spin states at 298 K.

20.61. 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.

20.62. 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.

20.63. 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.

20.64. 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.

***20.65.** According to classical mechanics, a magnetic dipole

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[27] G. Herzberg, *Molecular Spectra and Molecular Structure, Vol. II, Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand Reinhold, New York, 1945.

$\boldsymbol{\mu}$ in a magnetic field **B** precesses about the field direction. That is, the direction of the dipole vector traces out a cone with the axis of the cone in the direction of the field. This precession is called the Larmor precession. 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) is given by

$$\nu_{\text{Larmor}} = \frac{1}{2\pi}\frac{Q}{2m}B$$

The Larmor precession frequency of the magnetic moment of a proton is given by

$$\nu_{\text{Larmor}} = \frac{1}{2\pi}g_{\text{p}}\frac{e}{2m_{\text{p}}}B$$

Find the Larmor precession frequency of a proton in a magnetic field of 1.4092 T. Compare this frequency with the frequency of the radiation absorbed by protons in an NMR apparatus at this field. (See Example 20.14 for the radiation frequency.) Comment on why the term "magnetic resonance" is an appropriate name for the interaction of the radiation and the precessing spins.

20.66. Nuclear magnetic moments are sometimes expressed in terms of the **magnetogyric ratio** γ, defined by

$$|\mu| = \gamma\hbar[I(I+1)]^{1/2}$$

This quantity has a different value for each nuclide.

a. Find the value of the magnetogyric ratio for protons.
b. Find the value of the magnetogyric ratio for ^{13}C nuclei.

Problems for Section 20.9

***20.67.** Find the Fourier transform $I(t)$ of the function $e^{-a|\omega|}$.

20.68. Find the inverse Fourier transform $c(\omega)$ of the function $I(t) = e^{-at^2}\sin(bt)$.

20.69. Find the inverse Fourier transform $c(\omega)$ of the function $I(t) = e^{-at}\sin(bt)$.

20.70. 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 $g(x)$.[28] 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 20.69.

General Problems

20.71. 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. (19.2-44) 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.

20.72. 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. (19.2-44). 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.

20.73. a. 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

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[28] Philip M. Morse and Herman Feshbach, *Methods of Theoretical Physics*, Part I, McGraw-Hill, New York, 1953, pp. 464ff.

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.

20.74. 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 20.72 and 20.73, use your computer program 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.

20.75. Say how you would distinguish between each pair of substances, using spectroscopic techniques. If possible specify two different techniques.

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.)

d. Methyl acetate and propanoic acid

e. Acetone (propanone) and propionaldehyde (propanal)

f. $^1H^{35}Cl$ and $^2H^{35}Cl$.

g. $HC{\equiv}CH$ and $HC{\equiv}CCl$

20.76. 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. Every molecule exhibits an electron spin resonance spectrum.

j. Every molecule exhibits a nuclear magnetic resonance spectrum.

k. A nonpolar molecule cannot exhibit an infrared spectrum.

l. A molecule that is a spherical top exhibits $3n-6$ vibrations that lead to infrared spectral lines.

m. A molecule that is a spherical top exhibits the same kind of infrared spectrum as a heteronuclear diatomic molecule.

n. Most organic substances are colorless in the visible region and also do not absorb in the ultraviolet region.

o. A linear polyatomic molecule exhibits the same type of infrared spectrum as a diatomic molecule.

p. A linear polyatomic molecule exhibits the same kind of microwave spectrum as a diatomic molecule.

22

The Structure of Solids and Liquids

OBJECTIVES

After studying this chapter, a student should:

1. understand the crystal systems and lattices, and be able to solve problems related to them;
2. understand the Einstein and Debye theories of crystal vibrations, and be able to solve problems related to them;
3. understand the simple band theory of electronic structure in solids;
4. know the principal facts about the structure of simple liquids and understand the basic approach of cell model theories and distribution function theories of liquids;
5. know the principal facts about polymer structure and formation, including molecular mass distributions and polymer conformation;
6. understand the simple theories of polymer conformations and rubber elasticity.

PRINCIPAL FACTS AND IDEAS

1. The properties of liquids and solids are primarily determined by intermolecular forces.
2. The study of crystalline solids is based on the regular lattice structure.
3. The Einstein and Debye theories describe vibrations in crystals.
4. The band theory explains the electronic structure of solids.
5. Liquids can be modeled as though they were very dense gases or as though they were disordered solids.
6. Polymers are made up of long chainlike molecules.

22.1 General Features of Solids

Section 22.1 is a brief review of material included in general chemistry courses, and can be skipped without loss of continuity.

In both liquid and solid phases, the molecules or other formula units (such as atoms or ions) are close together. Because of this proximity, the intermolecular forces are strong, with a balance between attractive and repulsive forces holding the substance at an almost constant volume. Several forces are known: gravity, the strong and weak forces in nuclei, and electromagnetic forces. The most important electromagnetic force for chemistry is the Coulomb force (electrostatic force) that corresponds to repulsions between like charges and attraction unlike charges. It is common practice in chemistry to subdivide the effects of electrostatic forces into several classes: ionic chemical bonds, covalent chemical bonds, ion–dipole forces, dipole–dipole forces, hydrogen bonds, ion-induced dipole forces, London dispersion forces, interatomic repulsions, etc. We group solids ito four classes according to the principal cohesive (attractive) force that holds the solid together. The first class is **molecular solids**, which consist of atoms or molecules that are attracted to each other by forces other than chemical bonds. Examples of molecular solids are solid water (ice), solid carbon dioxide (dry ice), and solid argon. The usual attractive intermolecular force in molecular solids is the London dispersion force, but in solid water the principal intermolecular attraction is hydrogen bonding. The melting temperature of a solid is a rough measure of the strength of its cohesive forces. The stronger the attractions, the higher the melting temperature. Because of the relative weakness of their intermolecular attractions, molecular solids generally melt at low temperatures.

The second class is **ionic solids**, which contain positive and negative ions. The ions are always arranged so that a given ion is closer to ions of the opposite charge than to ions of the same charge. The attractive electrostatic forces thus exceed the repulsive electrostatic forces in magnitude, and provide the cohesive force that holds the solid together. The net cohesive force is a sum of attractive and repulsive electrostatic forces, and there is considerable variation in melting temperatures among ionic solids, although melting temperatures are generally higher than those of molecular solids. Sodium chloride melts at 801°C, and ammonium nitrate melts at 170°C.

The third class is **network covalent solids**, in which the principal cohesive forces are provided by covalent bonds. A sample of a covalent solid can be considered to be one giant molecule. Solid carbon in either of its naturally occurring allotropic forms, diamond and graphite, is a network of atoms bonded together by covalent bonds. In diamond, each carbon atom is bonded to four other carbon atoms in a tetrahedral geometry. In graphite, the atoms are arranged in sheets, in which each carbon is bonded to three other carbons at bond angles of 120°, forming a sheet of hexagons. There are weaker London forces between the sheets, which can fairly easily be cleaved from each other. Quartz (one of the forms of silica, or silicon dioxide) is a network of silicon atoms each of which is covalently bonded to four oxygen atoms in a tetrahedral conformation. Each oxygen atom is bonded to two silicon atoms, and holds the crystal in a rigid lattice. Due to the strength of the covalent bonds, network covalent solids generally melt at very high temperatures. Graphite sublimes at 1 atm at 3367°C (its triple point is at a higher pressure than 1 atm, like that of carbon dioxide). One of the forms of quartz melts at 1610°C.

The fourth class of solids consists of **metallic solids**. The bonding in metallic solids is primarily delocalized covalent bonding. This bonding can be represented by molecular orbitals that are linear combinations of atomic orbitals from many atoms. The electrons occupying these orbitals move over large regions of the solid, and can easily conduct electrical currents. There are large variations in the melting temperatures of metals. Mercury melts at −38°C, but most metals melt at temperature considerably above room temperature, although generally not at temperatures as high as covalent solids.

A **crystalline** solid consists of a regular geometric array of repeating identical molecular units. Most common samples of crystalline substances are **polycrystalline** and are made up of many pieces of crystal lattice struck together in various orientations. If you look at a broken piece of cast iron you can usually see grains that might be single crystals. If a single crystal can be grown, it usually has a greater mechanical strength than a polycrystalline sample of the same material.

Solids that are not crystalline are **amorphous**. They do not have a regular array of many repeating identical units, but have a more disordered structure. **Glasses** are amorphous materials that soften gradually as they are heated, becoming liquid without a definite melting temperature. They are often considered to be supercooled liquids, although they can be very rigid. Silica readily forms a glass called "fused silica" or "fused quartz." Fused silica is an amorphous solid, in which the silicon tetrahedra are disordered instead of being in a repeating lattice as in quartz. Some of the silicon atoms may be bonded to fewer than four oxygen atoms, and voids may exist in the structure. There are vestiges of a crystal lattice at short range, but the geometric regularity is not complete, and does not persist over large distances.

Exercise 22.1

a. Without trying to represent the correct three-dimensional structure, sketch a section of a network of Si and O atoms in which every silicon atom is bonded to four oxygen atoms and every O atom is bonded to two Si atoms.

***b.** What kind of hybrid orbitals on the silicon atoms and on the oxygen atoms would be used to construct localized molecular orbitals to represent the bonding in crystalline silicon dioxide?

Crystal Lattices

Crystals are solid phases with a lattices consisting of repetitive geometric arrays of identical units or atoms, molecules, or ions. The **basis** of a crystal is the smallest set of atoms, ions, or molecules with fixed bond distances and angles and with identical orientation and molecular environment that repeats again and again to make up the crystal. For example, the basis of the sodium chloride crystal consists of one sodium ion and one chloride ion with a fixed interionic distance and a fixed orientation. The crystal could be reproduced by stacking the replicas of the basis with the same orientation. The basis is not necessarily the same as the formula unit of the substance. For example, the basis of a carbon dioxide crystal contains four molecules. Even though the molecules all have the same bond distances and angles, the four molecules have different orientations and environments.

The crystal lattice is a set of points generated by placing a **lattice point** at the same location in each basis. Usually a point at the center of an atom or ion is chosen, but any point will do. Each lattice point must reside in the same kind of atom or ion. The crystal lattice is not the same as the crystal, which is a real piece of matter. The crystal lattice can be divided into identical **unit cells**. The unit cell is the smallest region in space that can reproduce the lattice by translations in three directions. That is to say, the lattice is reproduced by stacking replicas of the unit cell in straight rows, files, and columns, with no spaces between them. The contents of the unit cell must have the same stoichiometry as the whole crystal, and must have the same symmetry properties as the entire lattice. A unit cell is always bounded by planes such that the planes on the opposite sides of the unit cell are parallel to each other.

Figure 22.1 shows the unit cell of the sodium chloride lattice. This unit cell is a cube with side equal to 5.63×10^{-10} m. It contains four sodium ions: 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. It also contains four chloride ions: a one-fourth share of the 12 ions at the centers of the edges, plus the chloride ion at the center of the cell. It contains four basis units. 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. In some lattices, these axes are not perpendicular to each other.

There are seven different **crystal systems**, or unit cell shapes, which are listed in Table 22.1. The unit cells are depicted in Figure 22.2 with the lattice points indicated. The hexagonal unit cell can be cut into three parallelepiped units cells, one of which is shown. Some of the crystal systems correspond to more than one kind of lattice. A **primitive lattice** (denoted by P) is one in which lattice points occur only at the corners of the unit cell. It is also called a **simple lattice**. A unit cell of a primitive lattice contains one basis unit (one eighth of the basis unit 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 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. A **base-centered** lattice or **end-centered** lattice (denoted by C) is one in which there is a lattice point at the center of only one pair of opposite faces as well as at the corners. The table and figure show the 14 possible lattices, which are called **Bravais**

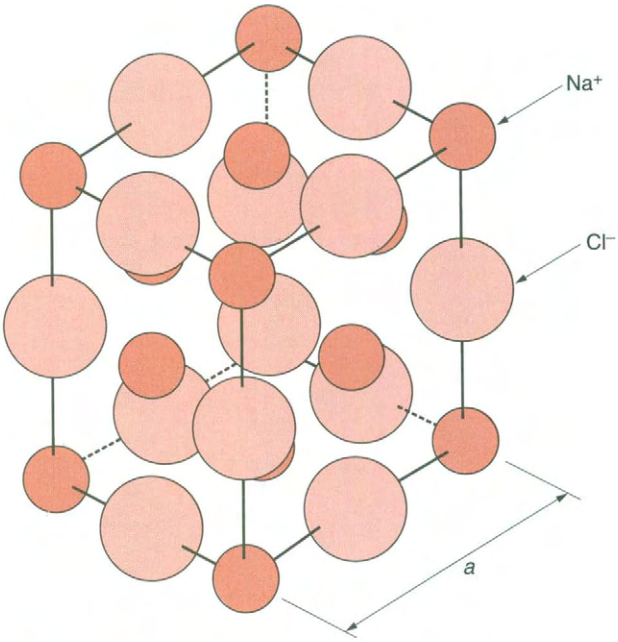
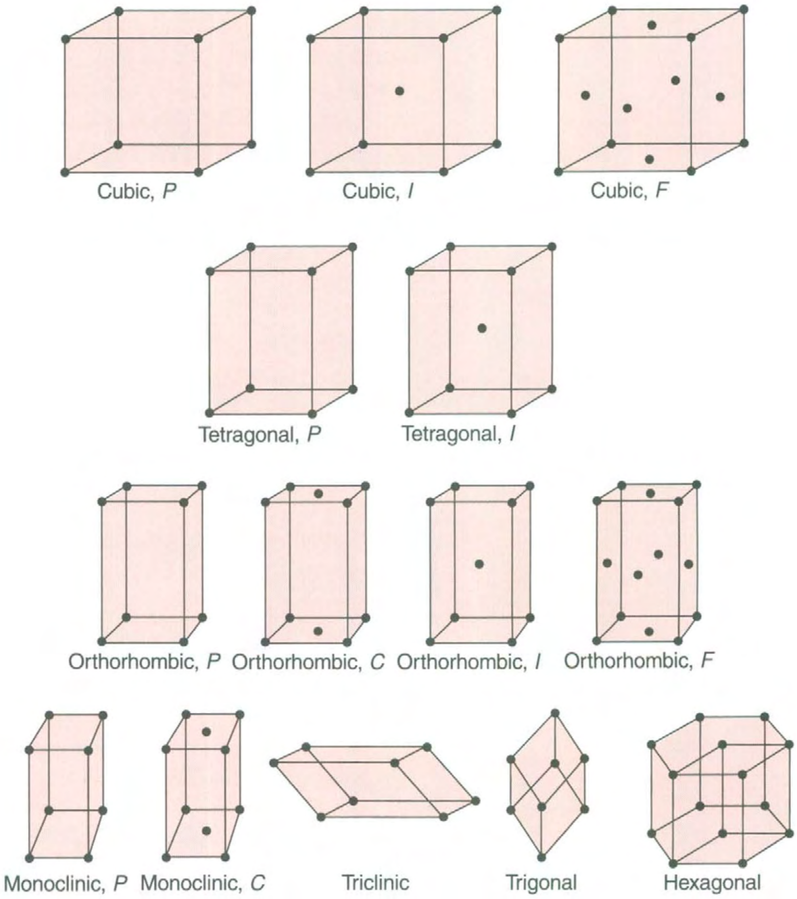


Figure 22.1. The Sodium Chloride Unit Cell. The sodium chloride lattice consists of a face-centered cubic lattice of sodium ions (the small spheres in the figure) and another face-centered cubic lattice of chloride ions ion a position shifted by a distance $a/2$ relative to the sodium ion lattice.

Table 22.1 Crystal Systems and Lattices

System	Defining Conditions	Bravais Lattices
Cubic	$a = b = c$ $90° = \alpha = \beta = \gamma$	P, I, F
Tetragonal	$a = b \neq c$ $90° = \alpha = \beta = \gamma$	P, I
Orthorhombic	$a \neq b \neq c$ $90° = \alpha = \beta = \gamma$	P, C, I, F
Monoclinic	$a \neq b \neq c$ $90° = \alpha = \gamma \neq \beta$	P, C
Triclinic	$a \neq b \neq c$ $\alpha \neq \beta \neq \gamma$	P
Trigonal (rhombohedral)	$a = b = c$ $90° \neq \alpha = \beta = \gamma < 120°$	P
Hexagonal	$a = b \neq c$ $90° = \alpha = \beta, \gamma = 120°$	P



Cubic, *P* Cubic, *I* Cubic, *F*

Tetragonal, *P* Tetragonal, *I*

Orthorhombic, *P* Orthorhombic, *C* Orthorhombic, *I* Orthorhombic, *F*

Monoclinic, *P* Monoclinic, *C* Triclinic Trigonal Hexagonal

Figure 22.2. The Unit Cells of the 14 Bravais Lattices. These are all of the space-filling unit cells. The designations are as follows: *P* means primitive (no lattice points except at the corners of the unit cell); *I* (for innenzentriert) means body-centered; *F* means face-centered; and *C* means end-centered.

lattices. The sodium chloride lattice is a face-centered cubic lattice. In Figure 22.1, the lattice points are at the centers of the sodium ions. If the center of the chloride ions had been chosen, there would be another lattice of exactly the same properties, with the corner of the unit cell for one lattice at the center of the unit cell or at the center of an edge of the unit cell of the other lattice.

*Exercise 22.2

For each of the 14 Bravais lattices, list the number of basis units in the unit cell.

The location of a point within a unit cell is specified by three fractions, which indicate the distances from the origin in the directions of the three axes. We generally take the origin at the lower left rear corner of the unit cell. The fractions are listed in *xyz* order. If the first fraction is $\frac{1}{2}$, it means a distance of $a/2$ along the a axis, and if the second fraction is $\frac{1}{4}$, it means a distance of $b/4$ along the b axis, etc. The center of a unit cell is denoted by $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.

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 22.3. If one layer of spheres is laid down in a plane another layer can be placed on it, as shown in Figure 22.3a (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 22.3b. 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 22.3c.

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. (It is also called the "filling fraction" or the "packing efficiency.") The nearest-neighbor distance and the number of nearest neighbors is also identical. However, the neighbors 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, while 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.

Exercise 22.3

a. From the formula for the volume of a sphere and the fact that the diagonal of the face of the unit cell is equal to four times the sphere radius, show that the packing fraction for the fcc close-packed lattice is equal to 0.74.

***b.** 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

Since X-rays are electromagnetic radiation with wavelengths of the same general size as crystal lattice spacings, crystals can act as diffraction gratings for X-rays. Study of the

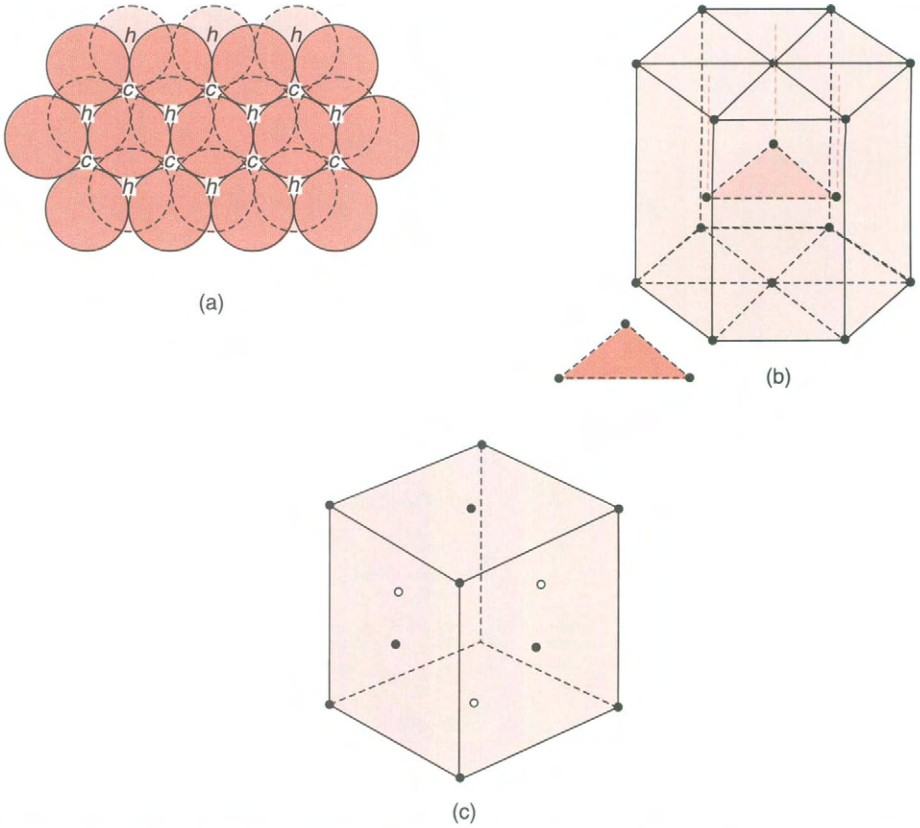


Figure 22.3. Closest Packing of Spheres. (a) **Layers of spheres.** This figure shows two layers of spheres with the second layer resting in hollows of the first layer. The third layer can be placed in either of two positions. The positions labeled *h* give the hexagonal close-packed lattice, and the positions labeled *c* give the cubic close-packed lattice. (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 22.7a 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.

angles and intensities of diffracted X-ray beams can allow unit cell dimensions and positions of atoms within the unit cells to be calculated. In order 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. The planes in which we are interested intersect with one or more of the axes within a unit cell. We consider any 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. These planes can contain repeating patterns of lattice points.

The set of 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 often denoted by putting the negative sign above the digit, as in $(11\bar{1})$. Figure 22.4 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.

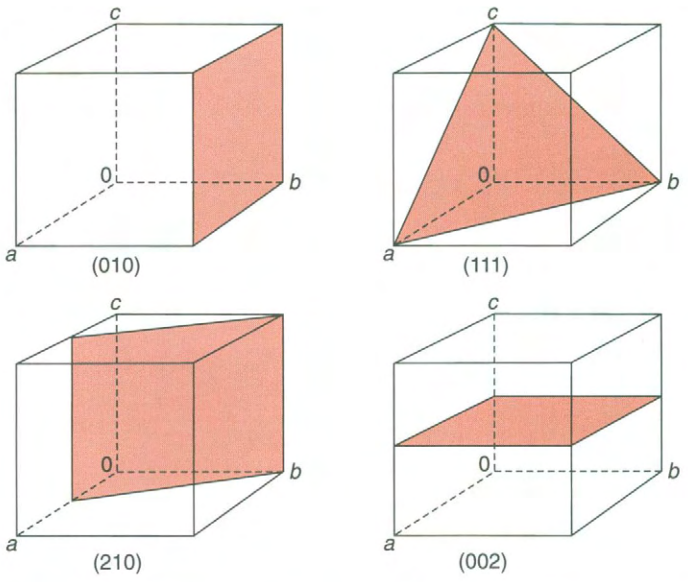


Figure 22.4. Some Planes and Their Miller Indices. All of these planes intersect the edges of the unit cell at points that are distances a/h, b/k and c/l from the origin where h, k, and l are integers (the Miller indices).

Figure 22.5 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 is an atom to act as a scattering center at each lattice point. Each atom 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 is that the extra distance traveled by the wave diffracted from the second layer is an integral number of wavelengths. Trigonometry gives the condition:

$$n\lambda = 2d\ \sin(\theta) \tag{22.1-1}$$

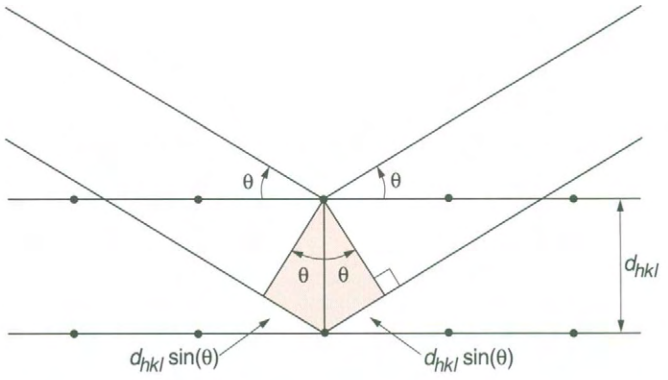


Figure 22.5. Diagram Showing the Bragg Condition for X-Ray Diffraction by a Crystal Lattice. The path lengths of the two rays must differ by an integral number of wavelengths.

The Bragg equation is named after Sir William Henry Bragg and his son William Lawrence Bragg, who received the 1915 Nobel Prize in physics for their studies in X-ray diffraction.

where θ is the angle between the plane and the direction of the radiation. Equation (22.1-1) is called the **Bragg equation**.

At first glance, it would 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 22.4

By drawing a replica of Figure 22.5 and drawing incident and diffracted rays from other pairs of atoms, show that if the two angles labeled θ in Figure 22.5 are equal, all of the diffracted beams interfere constructively if the Bragg condition is satisfied.

It is not necessary that a plane have lattice points directly across from corresponding lattice points in a parallel plane to diffract electrons. Any planes specified by Miller indices can diffract X-rays, so we specify the Miller indices of the plane in Eq. (22.1-1)

$$n\lambda = 2d_{hkl}\ \sin(\theta) \tag{22.1-2}$$

This equation is the same as

$$\lambda = 2d_{nh,nk,nl}\ \sin(\theta) \tag{22.1-3}$$

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 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.

The simplest kind of X-ray diffraction experiment is carried out with a finely powdered sample of the crystalline material placed in a small container in an X-ray beam. Since there are very many small crystals with many different orientations, an impinging 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 plate or film 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.

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[1] M. J. Buerger, *Contemporary Crystallography*, McGraw-Hill, New York, 1970, Chapter 5.

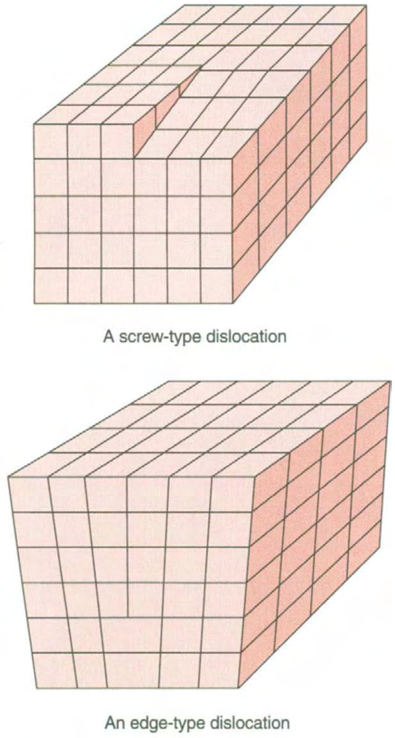

Figure 22.6. Some Crystal Defects (Schematic). In addition to the step defect pictured in Figure 13.3, these types of defects are the most common simple types of crystal defects.

We have discussed the diffraction of X-rays up to now as though each atom in the crystal lattice were a point from which the X-rays are scattered. In fact, the scattering takes place over the entire unit cell, and electrons scatter X-rays much more strongly than do nuclei. The scattering from the different parts of the unit cell interferes constructively and destructively in ways that are determined from 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 well as determination of the unit cell size and shape. This is a complicated process, which we cannot describe in detail. The first such structure determinations were done before the advent of computers, with many hours of hand calculation. Present-day calculations are done almost automatically by sophisticated computer programs, using intensity data taken with automated computer-driven diffractometers.

When a crystal grows, it adds more and more basis units in each of three directions. The crystal will have the same shape as the unit cell if unit cells are added at the same rate in each direction. However, crystals can exhibit various **habits**, which are shapes corresponding to different growth rates in the three lattice axis directions. For example, a cubic lattice could give rise to a crystal that is rectangular but not cubic. Furthermore, the faces of the crystal do not have to be the (001), (010), and (100) planes that correspond to the faces of the unit cell. Other planes, such as the (111) plane, can form boundaries of the crystal.

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 22.6 and in Figure 13.3. The presence of defects often increases the catalytic activity.

22.2 Crystal Vibrations

In Section 22.1 we discussed crystal lattices as though the atoms of the crystal were permanently fixed at various locations in the unit cell. These positions are actually equilibrium positions about which the atoms vibrate. 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. Sound waves in a crystal correspond to organized collective vibrations, but all kinds of vibrations occur at any nonzero temperature. Crystal vibrations are difficult to study exactly since the potential energy of a crystal is a complicated function of all of the atoms' coordinates. However, there are simple model systems that represent the vibrations of a crystal in an approximate way.

The Einstein Crystal Model

This model system corresponds to the assumption that all of the vibrational normal modes of a crystal have the same frequency, the value of which can be chosen to give the best fit to experimental data. It is further assumed that each normal mode vibrates like a hamonic oscillator, as was assumed in Chapter 19 for molecular vibrations. The

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[2] D. W. Goodman, *Annu. Rev. Phys. Chem.*, **37**, 425 (1986).

Einstein model is usually used to represent a crystal made up of atoms, such as solidified inert gas, a metal, or a covalent crystal like diamond. In one version of the model, it is assumed that the potential energy of each atom depends only on the displacement of that atom from its equilibrium position. Each atom vibrates independently in three perpendicular directions as though all of the other atoms in the crystal were stationary. A second version recognizes that each normal mode involves many atoms but assigns the same frequency to all normal modes. The results are the same for both treatments.

If we assume that the entire crystal is not translating or rotating and if we assume the electronic state to be the ground state, the total energy of the crystal is the vibrational energy and is given by

$$E_{\text{vib}} = N\mathcal{V}_0 + \sum_{i=1}^{3N-6} h\nu_i v_i \approx N\mathcal{V}_0 + \sum_{i=1}^{3N} h\nu v_i \tag{22.2-1}$$

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 energy of the crystal in its ground vibrational state is represented by $N\mathcal{V}_0$, so that $\mathcal{V}_0$ is the ground-state energy per atom. In the approximate equation, we have assumed that all normal modes have the same frequency and have ignored the difference between $3N - 6$ and $3N$, since N is a large number.

The vibrational partition function for the entire crystal is a sum over all values of the quantum numbers:

$$\mathcal{Z}_{\text{vib}} = \sum_{v_1 \geq 0} \sum_{v_2 \geq 0} \cdots \sum_{v_{3N} \geq 0} \exp\left(\frac{-N\mathcal{V}_0 - \sum_{i=1}^{3N} h\nu v_i}{k_{\text{B}}T}\right) \tag{22.2-2}$$

This expression can be factored with one factor for each normal mode and a factor for the constant term in the energy expression:

$$\begin{aligned} \mathcal{Z}_{\text{vib}} &= \exp\left(\frac{-N\mathcal{V}_0}{k_{\text{B}}T}\right) \prod_{i=1}^{3N} \left(\sum_{v_i=0}^{\infty} e^{-h\nu v_i/k_{\text{B}}T}\right) \\ &= \exp\left(\frac{-N\mathcal{V}_0}{k_{\text{B}}T}\right) \left(\sum_{v=0}^{\infty} e^{-h\nu v/k_{\text{B}}T}\right)^{3N} = \exp\left(\frac{-N\mathcal{V}_0}{k_{\text{B}}T}\right) z^{3N} \end{aligned} \tag{22.2-3}$$

where we recognize that after summation all of the factors in the product are equal to z, which is the partition function for one vibrational mode. There is no correction for indistinguishability, since each normal mode is distinguishable from the others, and there is no need to divide by $N!$.

The partition function z is the same as that in Eq. (21.4-20):

$$z = \sum_{v=0}^{\infty} e^{-h\nu v/k_{\text{B}}T} = \frac{1}{1 - e^{-h\nu/k_{\text{B}}T}} \tag{22.2-4}$$

with the result

$$\mathcal{Z}_{\text{vib}} = \exp\left(\frac{-N\mathcal{V}_0}{k_{\text{B}}T}\right) \left(\frac{1}{1 - e^{-h\nu/k_{\text{B}}T}}\right)^{3N} \tag{22.2-5}$$

We use a capital $\mathcal{Z}$ for the partition function since it is a partition function for the entire crystal (a canonical partition function).

We can now write formulas for the thermodynamic functions of the Einstein model of a crystal using the equations containing the logarithm of the canonical partition function, Eq. (21.8-35):

$$\begin{aligned}\ln(\mathcal{Z}_{\text{vib}}) &= -\frac{N\mathcal{V}_0}{k_BT} + 3N\ \ln(z) = -\frac{N\mathcal{V}_0}{k_BT} + 3N\ \ln\left(\frac{1}{1-e^{-h\nu/k_BT}}\right)\\ &= -\frac{N\mathcal{V}_0}{k_BT} - 3N\ \ln(1-e^{-h\nu/k_BT})\end{aligned} \tag{22.2-6}$$

$$\begin{aligned}U &= k_BT^2\left(\frac{\partial\ln(\mathcal{Z})}{\partial T}\right)_V = N\mathcal{V}_0 + 3Nk_BT^2\left(\frac{\partial\ \ln(z)}{\partial T}\right)_V\\ &= N\mathcal{V}_0 + \frac{3Nh\nu}{e^{h\nu/k_BT}-1}\end{aligned} \tag{22.2-7a}$$

$$C_V = \left(\frac{\partial U}{\partial T}\right)_{V,N} = 3Nk_B\left(\frac{h\nu}{k_BT}\right)^2\frac{e^{h\nu/k_BT}}{(e^{h\nu/k_BT}-1)^2} \tag{22.2-7b}$$

$$\begin{aligned}S &= \frac{U}{T} + k_B\ \ln(z) = \frac{N\mathcal{V}_0}{T} + \frac{3Nh\nu}{e^{h\nu/k_BT}-1} - \frac{N\mathcal{V}_0}{k_BT} + 3Nk_B\ \ln(z)\\ &= \frac{3Nh\nu}{e^{h\nu/k_BT}-1} - 3Nk_BT\ \ln(1-e^{-h\nu/k_BT})\end{aligned} \tag{22.2-7c}$$

$$A = -k_BT\ \ln(z) = N\mathcal{V}_0 - 3Nk_BT\ \ln(1-e^{-h\nu/k_BT}) \tag{22.2-7d}$$

$$P = k_BT\left(\frac{\partial\ \ln z)}{\partial V}\right)_T = Nk_BT\left(\frac{\ln(z)}{\partial V}\right)_T \tag{22.2-7e}$$

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{T,V} \approx A_N - A_{N-1} = \mathcal{V}_0 + 3k_BT\ \ln(1-e^{-h\nu/k_BT}) \tag{22.2-7f}$$

We use the chemical potential per molecule as in Chapter 21, not the chemical potential per mole. We have replaced a derivative by a finite difference and have recognized that A_N contains $N\mathcal{V}_0$ while A_{N-1} contains $(N-1)\mathcal{V}_0$.

There is a difficulty with the pressure of the Einstein crystal model. For a one-component system, G is given by Euler's theorem as:

$$\begin{aligned}G &= N\mu = N\mathcal{V}_0 - 3Nk_BT\ \ln(z)\\ &= N\mathcal{V}_0 + 3Nk_BT\ \ln(1-e^{-h\nu/k_BT})\end{aligned} \tag{22.2-7g}$$

so that $G = A$, and PV is predicted to vanish, since G equals $A + PV$. Furthermore, the model does not include any simple way to evaluate the derivative in Eq. (22.2-7e) for the pressure. This result is a shortcoming of a crude model, but for a crystal the value of PV is small compared with G and A, and the numerical effect of this shortcoming is not important.

There is no simple theoretical way to evaluate ν, the assumed frequency of the normal modes in the Einstein theory. Its value is usually determined by fitting the heat capacity formula to experimental data. The formulas for the thermodynamic functions can be restated in terms of the parameter

$$\Theta_E = \frac{h\nu}{k_B} \quad \text{(definition)} \tag{22.2-8}$$

which has the dimensions of temperature, and which is called the **Einstein temperature** or the **characteristic temperature**. Figure 22.7 shows the heat capacity of diamond as a function of temperature as well as the heat capacity of the Einstein

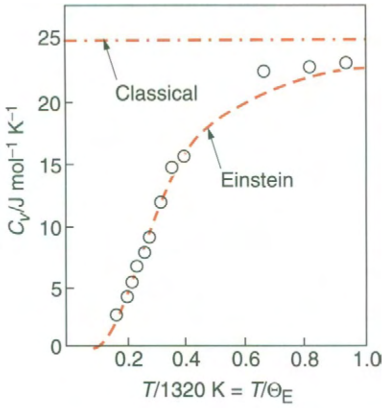

Figure 22.7. The Heat Capacity of Diamond Fit to the Einstein Crystal Model Result. The horizontal line corresponds to the classical result. From J. S. Blakemore, *Solid State Physics*, 2d ed., W. B. Saunders, Philadelphia, 1974, p. 121.

crystal model with an Einstein temperature of 1320 K, which gives the best fit to these experimental data.

Exercise 22.5

a. Express the thermodynamic functions of an Einstein crystal in terms of the Einstein temperature.
***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 $N\mathscr{V}_0$.
***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 $N\mathscr{V}_0$.
e. Calculate the molar entropy of a diamond crystal at 298.15 K and at 500.0 K.

In the limit of high temperature,

$$\lim_{T\to\infty} C_V = 3Nk_{\mathrm{B}} \tag{22.2-9}$$

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 it does not apply well to diamond at room temperature (see Problem 22.48).

Exercise 22.6

a. Show that Eq. (22.2-9) is correct.
b. Calculate the molar heat capacity of a diamond crystal at 298.15 K, at 500.0 K, and at 1320 K.

The Debye Crystal Model

This model is a physically motivated improvement over the Einstein crystal model, which assumes a single vibrational frequency. Real crystals have vibrational normal modes of many different frequencies. Debye assumed that the vibrational normal modes could be approximately represented by sound waves that are standing waves with zero amplitude at the surfaces of the crystal. The quanta of energy of these sound waves are called **phonons**. Consider a cubic sample of the solid with side L. The amplitide of a standing sound wave that vanishes at the boundaries of the cube is the same function of position as the wave function of a particle in a three-dimensional box:

$$(\text{Amplitude}) = \sin\left(\frac{s_x \pi x}{L}\right) \sin\left(\frac{s_y \pi y}{L}\right) \sin\left(\frac{s_z \pi y}{L}\right) \tag{22.2-10}$$

where s_x, s_y, and s_z are positive integers that play the same role as n_x, n_y, and n_z in the particle wave function. We let

$$s^2 = s_x^2 + s_y^2 + s_z^2 \tag{22.2-11}$$

The wavelength is given by

$$\lambda = \frac{2L}{s} \tag{22.2-12}$$

and the frequency of the wave is given by

$$\nu = \frac{c}{\lambda} = \frac{cs}{2L} \tag{22.2-13}$$

where c is the speed of propagation of the waves in the solid (the speed of sound in the solid, assumed to be a constant although different for each substance).

There is a different wave for each set of integers s_x, s_y, s_z. For fairly large values of the integers, the number of sets of integers such that s lie between s and $s + ds$ is approximately equal to

$$[\text{Number of waves in } (s, s + ds)] = \frac{\pi s^2}{2}\, ds \tag{22.2-14}$$

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 waves. The result in Eq. (22.2-14) must be multiplied by a factor of 3 since in a given direction in a continuous solid there can be 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 to 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.

Exercise 22.7

Show that Eq. (22.2-14) is correct by constructing a 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, corresponding to the requirement that all of the integers are positive.

Equations (22.2-13) and (22.2-14) can be combined:

$$\begin{aligned}(\text{Number of waves in } ds) &= \frac{3\pi}{2}\left(\frac{2L\nu}{c}\right)^2 ds \\ &= \frac{3\pi}{2}\left(\frac{2L\nu}{c}\right)^2 \frac{2L}{c}\, d\nu = 12\pi \frac{V}{c^3} \nu^2\, d\nu = g(\nu)\, d\nu \end{aligned} \tag{22.2-15}$$

The function $g(\nu)$ is called the **frequency distribution**.

In a crystal of N atoms the total number of vibrational modes is equal to $3N - 6$, approximately equal to $3N$ since N is large. All possible frequencies cannot be included, since this would give infinitely many normal modes. Debye chose a maximum frequency ν_D such that he had the correct number of modes:

$$3N = \int_0^{\nu_D} g(\nu)\, d\nu = \frac{12\pi V}{c^3}\int_0^{\nu_D} \nu^2\, d\nu = \frac{4\pi V \nu^3}{c^3} \tag{22.2-16}$$

$$\nu_D^3 = \frac{3Nc^3}{4\pi V} \tag{22.2-17}$$

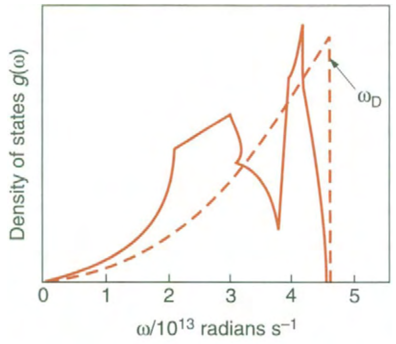

Figure 22.8. The Debye Distribution of Frequencies, with the Experimental Distribution of Frequencies for Copper. The distribution is shown as a function of $\omega = 2\pi\nu$. The experimental distribution is obviously complicated enough that a theory to reproduce such a distribution would likely be difficult to produce. From J. S. Blakemore, *Solid State Physics*, 2d ed. W. B. Saunders, Philadelphia, 1974, p. 126.

Debye's frequency distribution is shown in Figure 22.8 along with the experimental distribution of frequencies for copper. The **Debye temperature**, Θ_D, is a parameter with the dimensions of temperature. It is defined by

$$\Theta_D = \frac{h\nu_D}{k_B} \quad \text{(definition)} \tag{22.2-18}$$

The appropriate value of Θ_{D} for a given crystal is usually chosen by fitting heat capacity data to the Debye formula in Eq. (22.2-21).

The logarithm of the partition function of the Debye model of a crystal is given by the analogue of Eq. (22.2-6) where we must integrate over the normal modes:

$$\ln(\mathcal{Z}) = -\frac{N\mathcal{V}_0}{k_{\mathrm{B}}T} - \int_0^{\nu_{\mathrm{D}}} (1 - e^{-h\nu/k_{\mathrm{B}}T})g(\nu)\,d\nu \tag{22.2-19}$$

The vibrational energy in the Debye model of a crystal is given by the analogue of Eq. (22.2-7a):

$$\begin{aligned} U &= N\mathcal{V}_0 + \int_0^{\nu_{\mathrm{D}}} \frac{h\nu}{e^{h\nu/k_{\mathrm{B}}T} - 1} g(\nu)\,d\nu = N\mathcal{V}_0 + \frac{9N}{\nu_{\mathrm{D}}^3}\int_0^{\nu_D} \frac{h\nu^3}{e^{h\nu/k_{\mathrm{B}}T} - 1}\,d\nu \\ &= N\mathcal{V}_0 + \frac{9Nk_{\mathrm{B}}T}{u_{\mathrm{D}}^3}\int_0^{u_D} \frac{u^3}{e^u - 1}\,du \end{aligned} \tag{22.2-20}$$

where $u = h\nu/k_{\mathrm{B}}T$ and $u_{\mathrm{D}} = h\nu_{\mathrm{D}}/k_{\mathrm{B}}T = \Theta_{\mathrm{D}}/T$. The integral in Eq. (22.2-20) cannot be evaluated in closed form, but it can be evaluated numerically.

The heat capacity is given by

$$C_V = \frac{9Nk_{\mathrm{B}}}{\nu_{\mathrm{D}}^3}\int_0^{\nu_{\mathrm{D}}} \left(\frac{h\nu}{k_{\mathrm{B}}T}\right)^2 \frac{e^{h\nu/k_{\mathrm{B}}T}\nu^2}{e^{h\nu/k_{\mathrm{B}}T} - 1}\,d\nu \equiv 3Nk_{\mathrm{B}}D(\Theta_{\mathrm{D}}/T) \tag{22.2-21}$$

which defines the **Debye function**, D, which depends on the ratio Θ_{D}/T. Tables of values of this function are available[3] and a computer program can easily be written to evaluate the integral.

Formulas for the other thermodynamic functions can be obtained as integrals over the frequencies, analogous to sums over the normal modes of polyatomic molecule. The Helmholt energy is given by

$$\begin{aligned} A &= N\mathcal{V}_0 - k_{\mathrm{B}}T\int_0^{\nu_{\mathrm{D}}} \ln\left(\frac{1}{1 - e^{-h\nu/k_{\mathrm{B}}T}}\right)g(\nu)\,d\nu \\ &= N\mathcal{V}_0 + k_{\mathrm{B}}T\int_0^{\nu_{\mathrm{D}}} \ln(1 - e^{-h\nu/k_{\mathrm{B}}T})g(\nu)\,d\nu \end{aligned} \tag{22.2-22}$$

Exercise 22.8

a. Verify Eq. (22.2-21).

b. Write a formula for the vibrational entropy of the Debye model of a crystal.

The Debye function generally fits experimental data on the heat capacity of atomic solids quite well if an optimum choice of Θ_{D} is chosen. Figure 22.9 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 22.9

Show that the energy expression in Eq. (22.2-20) reduces to $U = 3Nk_{\mathrm{B}}T$ for high temperatures, so that $C_V = 3Nk_{\mathrm{B}}$. Use the fact that for high temperatures, e^u can be approximated by $1 + u$.

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[3] N. Davidson, *Statistical Mechanics*, McGraw-Hill, New York, 1962, p. 359.

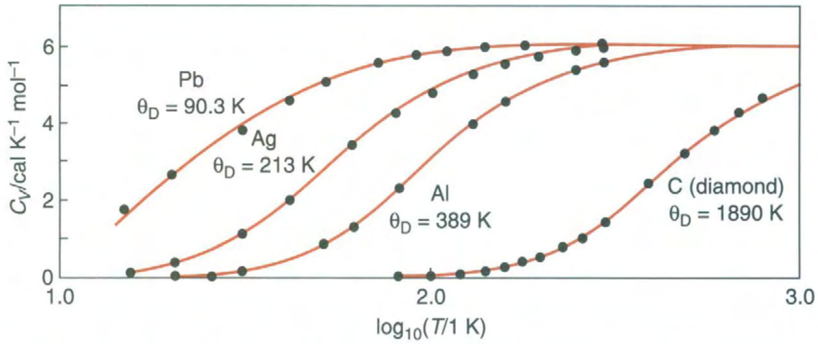

Figure 22.9. The Heat Capacity of Several Elements as a Function of Temperature, with Debye Curves. The value of the Debye temperature is chosen to give the best fit for each substance. From G. N. Lewis and M. Randall, *Chemical Thermodynamics*, 2d ed., rev. by K. S. Pitzer and L. Brewer, McGraw-Hill, New York, 1961, p. 56.

The Debye temperature of diamond is equal to 1890 K, while its Einstein temperature is 1320 K. Since the Einstein temperature ought to be equal to some kind of average frequency in the Debye model, these values are reasonable. Modifications to the Debye theory have been devised that use a temperature-dependent Debye temperature and give improved agreement with experiment.[4]

*Exercise 22.10

Obtain a formula for an average Debye frequency,

$$\langle \nu \rangle = \frac{\displaystyle\int_0^{\nu_D} \nu g(\nu)\, d\nu}{\displaystyle\int_0^{\nu_D} g(\nu)\, d\nu}$$

Compare the average Debye frequency for diamond with the Einstein frequency for diamond.

For small temperatures (T smaller than $\Theta_D/10$), ν_D is large, 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

$$U = \frac{3\pi^4 Nk_B T^4}{5\Theta_D^3} \tag{22.2-23}$$

For small values of the temperature, the heat capacity is

$$C_V = \frac{12\pi^4}{5}\frac{Nk_B T^3}{\Theta_D} \tag{22.2-24}$$

Heat capacities are hard to measure at low temperatures, and data below 15 K are quite rare. Equation (22.2-24) is commonly used as a substitute for experimental data between 0 K and 15 K in calculating third-law entropies. (See Section 4.5.) In metals, there is also a contribution to the heat capacity from the electronic motion (see Section 22.3).

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[4] See J. S. Blakemore, *Solid State Physics*, 2d ed., W. B. Saunders, Philadelphia, 1974, pp. 128ff.

Exercise 22.11

Verify Eq. (22.2-23).

22.3 The Electronic Structure of Crystalline Solids

Molecular crystals can to a first approximation be pictured as separate molecules held together by intermolecular forces such as London dispersion forces or hydrogen bonds. Ionic crystals can be thought of as separate ions held together by electrostatic (Coulomb) forces. The electronic wave function of the crystal can be crudely approximated as a product of wave functions of individual molecules, which are similar to those of the same molecules in the gas phase. Similarly, the electronic wave function of an ionic crystal can be crudely approximated as a product of the wave functions of the ions, which are much the same as those of the separated ions. Covalently bonded crystals, including metals, can be thought of as giant molecules. An approximate description of the electronic structure of these crystals can include localized and delocalized covalent bonding similar to that described in Chapter 18.

EXAMPLE 22.1

Describe the bonding in a gold crystal of N atoms.

Solution

A gold atom in its ground state has one electron in the $6s$ orbital and 78 electrons in filled subshells. For a first approximation to the wave function of the crystal, we construct a wave function that is a product of one-electron wave functions (orbitals). We use the atomic orbitals of the filled subshells as nonbonding orbitals. The $6s$ orbitals from the N atoms can be made into N different LCAO molecular orbitals, which can be delocalized and extend over large regions of the crystal or even over the entire crystal. These LCAO-MOs will have slightly different energies from each other.

Each one of the N space orbitals can combine either with the α spin function or the β spin function, giving $2N$ spin orbitals from N gold atoms. At low temperature, the N spin orbitals of lowest energy will be occupied. That is, $N/2$ space orbitals will be occupied by pairs of electrons with opposite spins. The occupied orbitals will have fewer nodes than the unoccupied orbitals, and will have more bonding character than antibonding character. The crystal is therefore held together very strongly, as illustrated by the fact that gold melts at a high temperature (1063°C).

Exercise 22.12

Explain in simple terms why mercury, which has one more electron per atom than gold, melts at a low temperature (−38.4°C).

The crude description of the bonding in crystalline gold of Example 22.1 is somewhat analogous to a description of the bonding in C_2, for which the electron configuration is given in Table 18.2. There is a double bond corresponding to the two occupied bonding orbitals. The $2p_x$ and $2p_y$ orbitals also form antibonding orbitals, the $\pi_g^*2p_x$ and $\pi_g^*2p_y$ orbitals, which remain vacant in the molecule. The bond strength in the molecule comes from greater occupation of bonding orbitals than of antibonding orbitals. Similarly, in the delocalized π bonding of benzene the six π electrons occupy the three lowest-energy delocalized π space orbitals, leaving the other (primarily antibonding) orbitals vacant. The occupied molecular orbitals have more bonding character than antibonding character, contributing to the stability of the molecule. In a gold crystal we also have twice as many orbitals as are needed to accommodate the valence electrons, allowing orbitals with bonding character to be occupied and orbitals with antibonding character to be left vacant.

The Band Theory of Solid Electronic Structure

In a crystal of N atoms, N atomic orbitals of equal energy form N delocalized molecular orbitals of different orbital energies. These energies are confined to a fairly narrow range, as were the π orbital energies of benzene. This range is called a **band**. If we include all of the orbitals, there is a band from the $1s$ orbitals, another band from the $2s$ orbitals, a third band from the $2p$ orbitals, etc. In many cases these bands will not overlap, leaving a **band gap** between two adjacent bands. Figure 22.10 shows the X-ray photoelectron spectrum of a gold foil, in which several of the bands can be seen, as well as the $1s$ band from a carbon impurity. The subscript on each band label is the value of j, the quantum number for the total angular momentum for the electrons.

If a band is created from orbitals that are filled in the ground state of the separated atoms, there are as many electrons to fill the band as there are spin orbitals in the band, so that the band is completely filled in the ground state. If the highest occupied band in a crystal is completely filled, an electron can move from one orbital to another in the

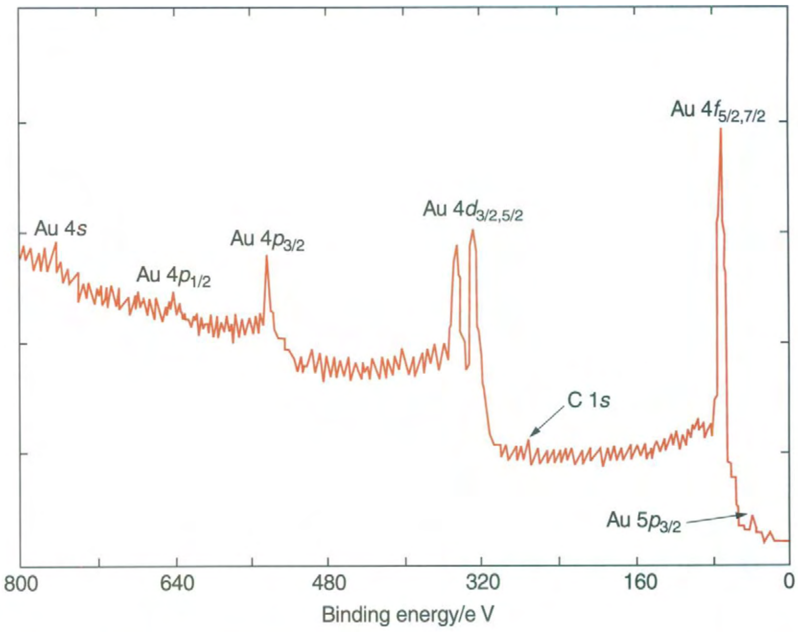

Figure 22.10. X-Ray Photoelectron Spectrum of Gold. Each peak is labeled with the subshell and the value of J, the quantum number for the total angular momentum. (Courtesy of Dr. Kevin Ogle.)

band only if another electron vacates the second orbital. If there is no way to create a vacancy the crystal will not conduct electricity (it will be an insulator). If a band is created from orbitals that are partly filled in the separated atoms, as in the 6*s* band of gold in Example 22.1, the resulting band is only partly filled. There will be a number of vacant orbitals for electrons to move into and the crystal will be an electrical conductor.

If the highest occupied band contains only a few electrons, there will be many unoccupied orbitals but only a few movable electrons, and the crystal will be a semiconductor with a fairly large resistance. If the highest occupied band is nearly filled, there will be many movable electrons but only a few unoccupied orbitals for the electrons to move into, and this crystal will also be a semiconductor. Semiconductors with only a few electrons in the highest band are called n-type semiconductors. Those with only a few vacant orbitals ("holes") are called p-type semiconductors. The designation "p" stands for "positive," since the positive holes are considered to be moving, and the designation "n" stands for "negative," since electrons are considered to be moving. Figure 22.11 schematically depicts the band occupations in insulators, conductors, and semiconductors.

The behavior of semiconductors is strongly temperature dependent. Electrons are fermions, and the probability distributions of noninteracting fermions and bosons are given in Section 21.1. From Eq. (21.2-21), the probability of finding a fermion in state i with energy ε_i is

$$\frac{N_i}{g_i} = f(\varepsilon_i) = \frac{1}{e^{-\alpha+\beta\varepsilon_i} + 1} \tag{22.3-1}$$

where g_i is the degeneracy of the level. Although this equation applies to noninteracting particles, we assume that it applies approximately to the behavior of electrons in a crystal.

We have established that $\beta = 1/k_{\mathrm{B}}T$. From our discussion of noninteracting particles in the case of dilute occupation, Eq. (21.3-2) gives

$$\alpha = \ln(N/z) \tag{22.3-2}$$

where z is the molecular function. Equation (21.5-17) gives

$$\mu = -k_{\mathrm{B}}T\ \ln(z/N) \tag{22.3-3}$$

so that

$$\alpha = \mu/k_{\mathrm{B}}T \tag{22.3-4}$$

where μ is the chemical potential. It is not permissible to use the molecular partition function for fermions or bosons if the dilute occupation case cannot be used. However, α must be the same parameter for all cases, so that Eq. (22.3-4) can be used for noninteracting fermions or bosons even if dilute occupation does not apply. The distribution for noninteracting fermions now becomes

$$f(\varepsilon_i) = \frac{1}{e^{(\varepsilon_i-\mu)/k_{\mathrm{B}}T} + 1} \tag{22.3-5}$$

and we ignore the interactions between electrons and assume that we can use this equation for electrons in a crystal.

The value of 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 up to the Fermi level are fully occupied and those above the Fermi level are vacant. As the temperature is increased,

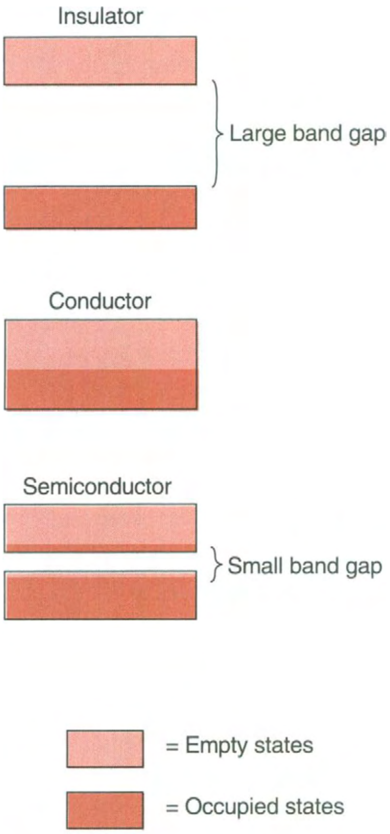

Figure 22.11. Bands of Orbital Energies in a Hypothetical Insulator, Conductor, and Semiconductor. The top figure, for an insulator, shows the band gap, which is large compared with $k_{\mathrm{B}}T$. The middle figure, for a conductor, shows a partly filled band, so that there is no band gap. The bottom figure, for a semiconductor, shows a band gap that is not large compared with $k_{\mathrm{B}}T$.

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 changes from approximately unity to nearly zero is approximately equal to k_BT. Figure 22.12 shows the fermion probability distribution for 0 K and for two nonzero temperatures.

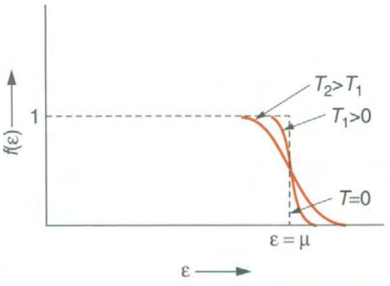

Figure 22.12. The Fermion Probability Distribution. At $T = 0$, the electron states are completely filled up to the Fermi level, and completely empty above the Fermi level. At higher temperatures, some of the states below the Fermi level are empty and some of those above the Fermi level are occupied.

If the Fermi level lies within a band, the crystal will be a conductor. If the Fermi level lies at the top of a band or between two bands, the crystal will either be an insulator or a semiconductor. If the band gap to the next higher band is small, then at ordinary 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 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, the highest occupied band will be completely filled, and the crystal will be an insulator.

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 in both crystals can be approximated as localized bonding molecular orbitals made from two sp^3 hybrid orbitals on adjacent atoms. The vacant antibonding molecular orbitals lie somewhat higher in energy.

In silicon, there is a band made from the $3d$ orbitals. The band gap between the bonding orbitals and the $3d$ band is small enough so that silicon is a semiconductor at room temperature. Diamond is an insulator because there is no $2d$ subshell. The lowest vacant band of diamond is the $3s$ band, which has a large band gap from the bonding orbitals. Figure 22.13 shows an approximate energy level diagram. At 0 K, no electrons in the silicon crystal could occupy orbitals in the $3d$ band and silicon would be an insulator like diamond. In some applications, silicon is "doped" with small amounts of other substances. For example, if aluminum atoms are introduced into the lattice and replace silicon atoms, there are "holes" in the available orbitals since aluminum has 13 electrons while silicon has 14. This makes the doped silicon into a p-type semiconductor that would conduct electricity even at 0 K.

Nickel is ferromagnetic (it can be permanently magnetized).[5] Figure 22.14 shows the $4s$ and $3d$ bands for both nickel and copper. In both elements, the two bands overlap in energy (with no band gap) since the $3d$ and $4s$ orbitals in the isolated atoms are nearly at the same energy. However, the $4s$ band covers a wider range of energy. In copper, which has one $4s$ electron and ten $3d$ electrons in the isolated atom, the Fermi level is at the middle of the $4s$ band. The $4s$ band is 50% occupied and the $3d$ band is fully occupied. In nickel, which has two $4s$ electrons and eight $3d$ electrons, the Fermi level is lower, and lies below the top of the $3d$ band. The spin-up states of the $3d$ 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 $3d$ band and an average of 0.54 electron per atom in the $4s$ 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, as shown in part (c) of the figure.

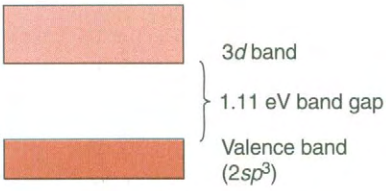

Figure 22.13. The Electron Bands of Silicon (Schematic). The band gap, 1.11 eV, is roughly 43 times as large as k_BT at room temperature. Although silicon is a semiconductor, it must be "doped" by addition of impurities, making either holes or extra electrons, to conduct very much electricity.

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[5] N. B. Hannay, *Solid-State Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1967, p. 38.

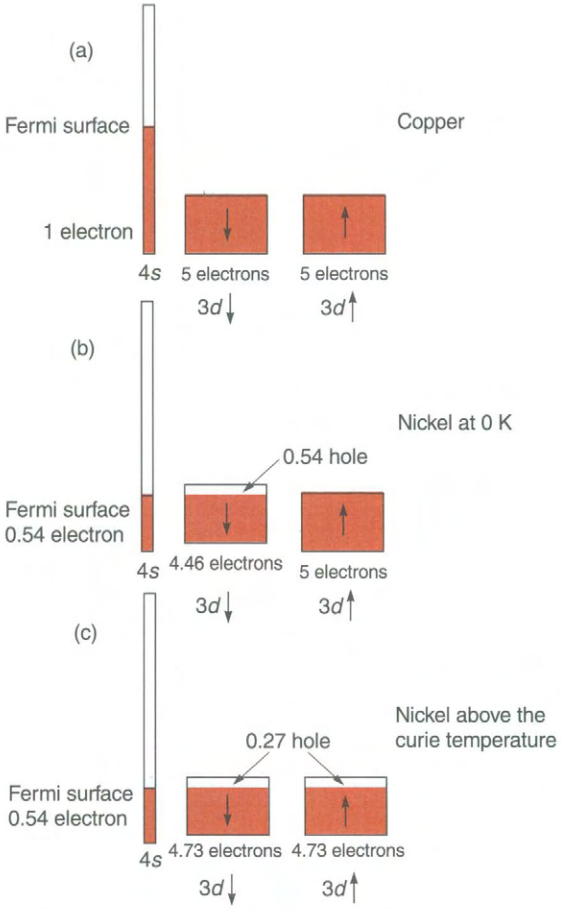

Figure 22.14. The 4*s* and 3*d* Bands of Nickel and Copper. The vertical axis in each diagram represents the electronic energy. The fact that the 3*d*-spin-up electrons in nickel have a slightly lower energy than the 3*d*-spin-down electrons gives an excess of spin-up electrons, which can align in domains to make nickel ferromagnetic. From N. B. Hannay, *Solid-State Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1967, p. 38.

The Free-Electron Theory

This simple theory describes approximately the electron states within the occupied bands. The electrons are represented as a gas of noninteracting fermions. This approximation is similar to the free-electron approximation of Eq. (18.7-16), in which the delocalized π orbitals for a conjugated chain of carbon atoms were represented by one-dimensional particle-in-a-box wave functions. We represent the orbitals for the mobile electrons in our crystal by free-particle wave functions, representing traveling waves as in Section 14.5:

$$\psi = e^{i\mathbf{k}\cdot\mathbf{r}} = e^{i(k_x x + k_y y + k_z z)} \tag{22.3-6}$$

where the vector **k** is called the **wave vector**.

Consider a cubic region with dimensions L by L by L that is part of a very large crystal. We impose "periodic boundary conditions"

$$\psi(x+L, y, z) = \psi(x, y, z) \tag{22.3-7}$$

with similar equations for y and z. To satisfy this condition,

$$k_x = \frac{2\pi n_x}{L}, \qquad k_y = \frac{2\pi n_y}{L}, \qquad k_x = \frac{2\pi n_z}{L} \tag{22.3-8}$$

where n_x, n_y, and n_z are integers. The situation is similar to that of a particle in a three-dimensional box, and similar to the Debye crystal model, except that the integers are now not required to be positive.

The vector **k** that has components k_x, k_y, and k_z is called the **wave vector**. The kinetic energy of a wave is determined by this vector:

$$\varepsilon_k = \frac{\hbar^2 k^2}{2m} = \frac{\hbar^2}{2m}(k_x^2 + k_y^2 + k_z^2) \tag{22.3-9}$$

The number of sets of integers in the range dn is similar to that shown in Eq. (22.2-14):

$$[\text{Number of sets in } (n, n + dn)] = 4\pi n^2\, dn \tag{22.3-10}$$

This number is 8 times as large as that given by Eq. (22.2-14) to account for the possibilities that negative integers can occur. There are two possible spin states for each electron, so we double this expression to get the number of states. Using Eq. (22.3-8), we obtain for the number of states in the range dk,

$$(\text{Number of states in } dk) = g(k)\, dk = \frac{L^3 k^2}{\pi^2}\, dk$$

Using Eq. (22.3-9),

$$(\text{Number of states in } d\varepsilon) = \frac{L^3\sqrt{2}m^{3/2}}{\pi^2\hbar^3}\varepsilon^{1/2}\, d\varepsilon \tag{22.3-11a}$$

$$\begin{pmatrix}\text{Number of states in} \\ d\varepsilon \text{ per unit volume}\end{pmatrix} = g(\varepsilon)\, d\varepsilon = \frac{\sqrt{2}m^{3/2}}{\pi^2\hbar^3}\varepsilon^{1/2}\, d\varepsilon \tag{22.3-11b}$$

This degeneracy is depicted in Figure 22.15. At 0 K, electrons will occupy the available states from the state of lowest energy up to the Fermi level. This occupation is shown by the shaded area in Figure 22.15. At nonzero temperatures the occupation of states is given by Eq. (22.3-5), and the occupation of the levels correspond to a curve similar to the curve in the figure.

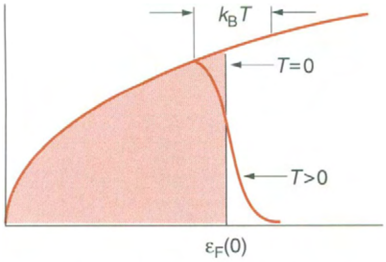

Figure 22.15. The Degeneracy of Energy Levels in the Free-Electron Theory. The monotonically rising curve is the degeneracy. The vertical cutoff gives the degeneracy times the fermion state distribution at 0 K. That is, it gives the distribution in terms of levels. The curve labeled $T > 0$ K is the product of the degeneracy and the fermion state distribution for a nonzero temperature. From N. B. Hannay, *Solid State Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1967, p. 26.

The number of electrons per unit volume is

$$n = \int_0^\infty g(\varepsilon) f(\varepsilon)\, d\varepsilon \tag{22.3-12}$$

where $f(\varepsilon)$ is the fermion probability distribution of Eq. (22.3-5). 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 without error:

$$n = \frac{\sqrt{2}m^{3/2}}{\pi^2\hbar^3}\int_0^{\mu_0} \varepsilon^{1/2}\, d\varepsilon = \frac{1}{3\pi^2}\left(\frac{2m\mu_0}{\hbar^2}\right)^{3/2} \tag{22.3-13}$$

The Fermi level at 0 K is

$$\mu_0 = \varepsilon_{F0} = (3\pi^2 n)^{2/3}\frac{\hbar^2}{2m} \tag{22.3-14}$$

A typical metal has a density of mobile electrons approximately equal to 10^{28} m^{-3}, corresponding to a value of the Fermi level equal to several electronvolts.

*Exercise 22.13

a. Find the value of the constant A when Eq. (22.3-14) is written in the form $\varepsilon_{\mathrm{F0}} = An^{2/3}$.

b. The density of copper is 8960 kg m^{-3}. Find the density of mobile electrons, assuming one electron from each atom, and find the zero-temperature value of the Fermi level in joules and in electron volts.

The Fermi level for nonzero temperature is approximately[6]

$$\mu = \varepsilon_{\mathrm{F}} = \varepsilon_{\mathrm{F0}}\left(1 - \frac{(\pi k_{\mathrm{B}} T)^2}{12\varepsilon_{\mathrm{F0}}^2}\right) \tag{22.3-15}$$

For fairly low temperatures, this formula gives roughly the same value for the Fermi level as Eq. (22.3-14).

The energy per unit volume of the free-electron gas at 0 K is

$$U_0 = \int_0^{\varepsilon_{\mathrm{F0}}} \varepsilon g(\varepsilon)\, d\varepsilon = \frac{1}{5\pi^2}\left(\frac{2m}{\hbar^2}\right)\varepsilon_{\mathrm{F0}}^{5/2} = \frac{3n\varepsilon_{\mathrm{F0}}}{5} \tag{22.3-16}$$

The energy at a nonzero temperature is approximately[7]

$$U = U_0 + \frac{n\pi^2 k_{\mathrm{B}}^2 T^2}{4\varepsilon_{\mathrm{F}}} \tag{22.3-17}$$

if $T \ll \varepsilon_{\mathrm{F}}/k_{\mathrm{B}}$. Equation (22.3-17) leads to a formula for the electronic contribution to the heat capacity per unit volume

$$C_{\mathrm{elec}} = \frac{\pi^2 n k_{\mathrm{B}} T}{2\varepsilon_{\mathrm{F}}} \tag{22.3-18}$$

We obtain a formula for the molar heat capacity by replacing n by the number of mobile electrons per mole.

If the electron gas obeyed classical mechanics, the heat capacity would be $3k_{\mathrm{B}}/2$ per electron, so that

$$C_{\mathrm{elec}} = \frac{\pi^2 T}{3\varepsilon_{\mathrm{F}}} C_{\mathrm{class}} \tag{22.3-19}$$

Although the classical heat capacity is independent of T, the quantum-mechanical heat capacity is proportional to T. 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. (22.3-19). 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.

*Exercise 22.14

a. Find the electronic contribution to the heat capacity of copper at 15 K, using the same assumptions and data as in Exercise 22.13.

b. Find the ratio of the electronic contribution to the classical prediction of the electronic contribution.

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[6] Blakemore, *op. cit.*, p. 176 (Note 4).

[7] Blakemore, *op. cit.*, p. 176 (Note 4).

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 15 K.

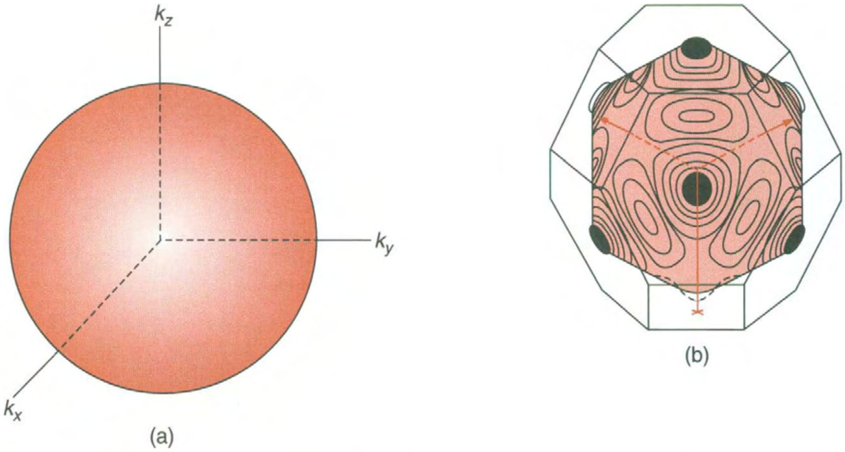

Figure 22.16. The Fermi Surface. (a) **The Fermi surface in the free-electron theory.** This surface is a sphere in the space of the wave vectors denoted by **k**. (b) **The Fermi surface of copper.** This surface is a distorted sphere. It is shown imbedded in a polyhedron whose surfaces coincide with the dark areas of the Fermi surface. From G. E. Smith, in *The Fermi Surface*, ed. W. A. Harrison and M. B. Webb, Wiley, New York, 1960.

The simple free-electron theory has been modified by Bloch.[8] The uniform potential energy function of the free-electron theory is replaced by a potential function which is periodic with the same period as the crystal lattice. The wave function is like that shown in Eq. (22.3-6) except for the presence of another factor u, called the Bloch function:

$$\psi = e^{i\mathbf{k}\cdot\mathbf{x}}u(\mathbf{x}) \tag{22.3-20}$$

The energy levels are found to lie in bands, similar to the bands of the LCAO molecular orbitals discussed above. Each band is said to correspond to a **Brillouin zone**. The Fermi level is sometimes depicted as a surface in a space in which k_x, k_y, and k_z are plotted on the axes. For the free-electron theory, all states below the Fermi surface are contained within a sphere, as schematically depicted in Figure 22.16a. For the Bloch theory, the Fermi surface is not spherical, as shown in Figure 22.16b for copper.

22.4 The Structure of Liquids

When a solid melts to form a liquid, a considerable change in properties takes place with a small change in temperature. The rigidity of the solid suddenly disappears. The molar volume usually increases slightly by 5–15%, although it decreases by about 8% in the case of water. The isothermal compressibility increases by a few percent in some cases and by a factor of 2–3 in others. The thermal conductivity drops, but diffusion coefficients greatly increase. The solid's lattice structure, which extends over long

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[8] F. Bloch, *Z. Physik*, **52**, 555 (1928). See Hannay, *op. cit.*, pp. 27ff (Note 5), or Blakemore, *op. cit.*, pp. 204ff (Note 4).

distances compared with molecular dimensions, suddenly collapses. Vestiges of this structure exist in the liquid, but only at short distances. For example, in most atomic solids, each atom has 12 nearest neighbors. When the solid melts, the average nearest-neighbor distance changes only slightly, but the average number of nearest neighbors decreases. In liquid argon at the melting temperature, the average nearest-neighbor distance is only 1% larger than in the solid at the same temperature, but the average number of nearest neighbors drops from 12 to a value between 10 and 11. The lower density of the liquid is due to the presence of voids around molecules, and "hole theories" of liquids have been devised to explain the properties of liquids on this basis.[9] The void among nearest-neighbor molecules does not necessarily represent one missing molecule with all others in the same locations as in the solid. Instead, 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, etc., the long-range order of the solid is absent.

There are three common approaches to the theoretical study of liquids. The first approach is by fundamental classical statistical mechanics. When this approach is used, the liquid is usually treated as though it were a very dense nonideal gas. The second approach is by the use of approximate model systems. When this approach is used, the liquid is usually treated as though it were a somewhat disordered solid. The third approach is through numerical simulation, in which computer programs calculate liquid properties from the velocities and positions of a collection of molecules.

The Fundamental Statistical Mechanical Approach to Liquid Structure

We consider the simplest model system, a one-component liquid of N atoms that obey classical mechanics and do not exhibit electronic excitation. The equilibrium probability density of classical statistical mechanics is given by Eq. (21.9-2):

$$f(p, q) = \frac{1}{\mathcal{Z}_{\mathrm{cl}}} e^{-[\mathcal{K}(p)+\mathcal{V}(q)]/k_{\mathrm{B}}T} \tag{22.4-1}$$

where $\mathcal{K}$ and $\mathcal{V}$ are the kinetic energy and potential energy of the entire system and where p and q are abbreviations for the momenta and coordinates of all of the molecules. We assume that the potential energy is pairwise additive and depends only on the distances between pairs of particles:

$$\mathcal{V} = \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} u(r_{ij}) \tag{22.4-2}$$

where r_{ij} is the distance between atom number i and atom number j. This assumption means that the contribution of a pair of molecules to the potential energy is unchanged if a third molecule moves close to them. It is apparently a good approximation for dense gases, and a fairly good approximation for simple liquids.

Equation (21.9-5) gives the classical canonical partition function for our system:

$$\mathcal{Z}_{\mathrm{cl}} = (2\pi m k_{\mathrm{B}} T)^{3N/2} \int e^{-\mathcal{V}(q)/k_{\mathrm{B}}T}\, dq \tag{22.4-3}$$

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[9] H. Eyring and M. S. Jhon, *Significant Liquid Structures*, Wiley, New York, 1969.

From Eq. (21.9-25), the ensemble average energy of the liquid is

$$U = \langle E \rangle = k_B T^2 \left(\frac{\partial \ln(\mathcal{Z}_{\rm cl})}{\partial T} \right)_V = \frac{3Nk_B T^2}{2} \frac{d \ln(2\pi m k_B T)}{dT} + \frac{1}{\zeta} \int \mathcal{V} e^{-\mathcal{V}/k_B T}\, dq$$
$$= \frac{3}{2} N k_B T + \langle \mathcal{V} \rangle \tag{22.4-4}$$

Exercise 22.15

Verify Eq. (22.4-4).

The ensemble average potential energy cannot be computed exactly. We can write

$$\langle \mathcal{V} \rangle = \frac{1}{\zeta} \sum_{i=1}^{N-1} \sum_{j=i+1}^{N} \int u(r_{ij}) e^{-\mathcal{V}/k_B T}\, dq \tag{22.4-5}$$

where we have exchanged the order of summation and integration. Every pair of particles in our system is just like every other pair, so that all of the $N(N-1)/2$ terms in the sum of Eq. (22.4-2) will be equal after integration. Therefore,

$$\langle \mathcal{V} \rangle = \frac{N(N-1)}{2} \frac{1}{\zeta} \int u(r_{12}) e^{-\mathcal{V}/k_B T}\, dq \tag{22.4-6}$$

The integration in Eq. (22.4-6) is over all of the coordinates of the N particles. We can divide up the integrations

$$\int u(r_{12}) e^{-\mathcal{V}/k_B T}\, dq = \int d^3\mathbf{r}_1\, d^3\mathbf{r}_2\, u(r_{12}) \int e^{-\mathcal{V}/k_B T}\, dq_{N-2} \tag{22.4-7}$$

where $\int \cdots dq_{N-2}$ represents the integration over the coordinates of all particles except numbers 1 and 2. This much of the integration would be the same if we were averaging any quantity that depends only on the coordinates of two particles at a time, so it is useful to define the **two-body reduced coordinate distribution function**:

$$n^{(2)}(\mathbf{r}_1, \mathbf{r}_2) = n^{(2)}(1,2) = \frac{1}{\zeta} \int e^{-\mathcal{V}/k_B T}\, dq_{N-2} \tag{22.4-8}$$

The one-particle reduced coordinate distribution function is defined similarly, with integration over the coordinates of $N-1$ particles. It is independent of position in an equilibrium fluid system:

$$n^{(1)}(1) = \frac{1}{V} \quad \text{(general liquid or gas system)} \tag{22.4-9}$$

The probability that particle 1 is in a volume element $d^3\mathbf{r}_1$ and that particle 2 is simultaneously in a volume element $d^3\mathbf{r}_2$, irrespective of where the other $N-2$ particles are, is

$$\text{(Probability)} = n^{(2)}(1,2)\, d^3\mathbf{r}_1\, d^3\mathbf{r}_2 \tag{22.4-10}$$

In a dilute gas the intermolecular forces can be neglected and the two-body distribution function is

$$n^{(2)} = \frac{1}{V^2} \quad \text{(dilute gas)} \tag{22.4-11}$$

In an equilibrium system in which the potential energy function u depends only on the distance between the particles, $n^{(2)}$ depends only on r_{12}, the distance between particles 1 and 2.

The **radial distribution function**, or **pair correlation function**, $g(r)$, is defined by

$$g(r_{12}) = \frac{n^{(2)}(1,2)}{n^{(1)}(1)n^{(1)}(2)} = \frac{n^{(2)}(1,2)}{V^2} \tag{22.4-12}$$

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, discussed in Chapter 16.

The pressure can be expressed in terms of the radial distribution function[10]

$$P = \frac{Nk_BT}{V}\left[1 - \frac{N}{Vk_BT}\int r\left(\frac{du}{dr}\right)g(r)\,d^3\mathbf{r}\right] \tag{22.4-13}$$

Exercise 22.16

Show that Eq. (22.4-13) gives the correct pressure of an ideal gas.

The radial distribution function, $g(r)$, is the probability of finding a second molecule at distance r from a given molecule divided by the probability of finding a molecule far from the given molecule. In an ideal gas, $g(r)$ is equal to unity for all distances and the positions of the particles are uncorrelated. In a monatomic nonideal gas or in a monatomic liquid, $g(r)$ vanishes at $r = 0$ due to the short-range repulsions between molecules and approaches unity at large values of r. At intermediate distances in a liquid there are several maxima representing shells of neighboring molecules.

If one averages over all directions, the radial distribution function can be defined for a solid. In a solid, the radial distribution function has large "blips" at distances equal to distances between lattice points, and vanishes for other distances. Figure 22.17 shows the radial distribution function for liquid and solid mercury. The vestiges of the solid structure in the liquid can be seen in the layers of neighbors at very nearly the distances between pairs of lattice points.

We will not discuss them, but there are a number of theories that are used to calculate approximate radial distribution functions for liquids.[11] Some of the theories involve integral equations satisfied by approximate radial distribution functions. Others are "perturbation" theories somewhat like quantum-mechanical perturbation theory (see Section 17.2). 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.

The radial distribution function can be determined experimentally by neutron diffraction or X-ray diffraction. When moving at speeds near their thermal average speed, neutrons are scattered in much the same way as X-rays, since they exhibit deBroglie wavelengths roughly equal to intermolecular spacings in liquids. Neutron diffraction is more commonly used to determine radial distribution functions in liquids than is X-ray diffraction, since X-rays are scattered primarily by electrons while neutrons are scattered primarily by nuclei.

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[10] P. A. Egelstaff, *An Introduction to the Liquid State*, Academic Press, New York, 1967, p. 20.

[11] H. L. Friedman, *A Course in Statistical Mechanics*, Prentice-Hall, Englewood Cliffs, NJ, 1985, Ch. 7, 8 and 9. D. A. McQuarrie, *Statistical Mechanics*, Harper & Row, New York, 1976, Chs. 13 and 14.

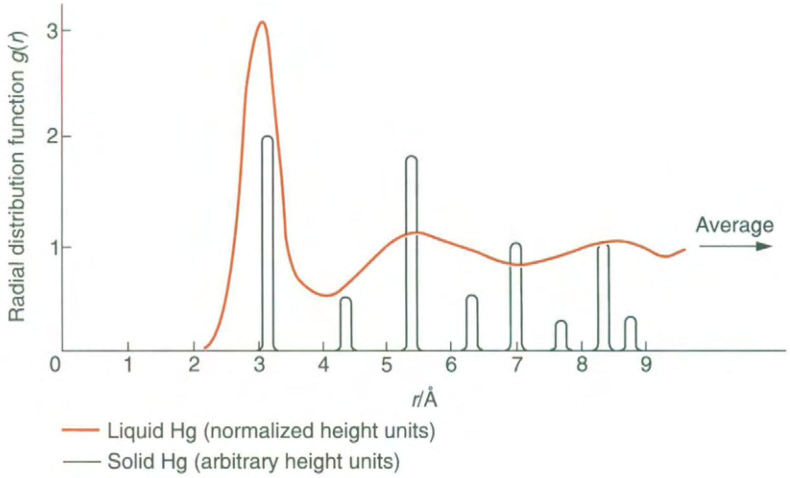

Figure 22.17. The Radial Distribution Function of Solid and Liquid Mercury. Since the solid has a lattice structure, the positions of neighboring atoms give narrow "blips" in the radial distribution function. In the liquid, the disorder that is present makes the function into a smooth curve, which shows vestiges of the crystal lattice. From D. Tabor, *Gases, Liquids and Solids*, 2d ed., Cambridge University Press, Cambridge, 1979, p. 197.

***Exercise 22.17**

a. Find the speed of a neutron such that its deBroglie wavelength is equal to 2.00×10^{-10} m.

b. Find the temperature such that the root-mean-square speed of thermally equilibrated neutrons is equal to the speed of part (a), using Eq. (10.3-9). Neutrons that have been equilibrated near room temperature are called **thermal neutrons**.

Solidlike Model Approaches to Liquid Structure

There are several model theories that treat a liquid like a disordered solid. These model theories are sometimes called "quasi-lattice" theories of liquids. In the **cell model**[12] each atom of a fluid of atoms is assumed to be confined in a cell whose walls are made up of its nearest neighbors. In the simple cell model, this cell is approximated as a spherical cavity, inside which the potential energy of the moving atom is constant. Since each atom moves independently in this simple model, the classical canonical partition function can be written as a product of molecular partition functions. Each atom moves in a small cell instead of in the entire volume of the system, so that the canonical partition function is

$$\mathcal{Z}_{\mathrm{cl}} = (2\pi m k_{\mathrm{B}} T)^{3N/2} (V_{\mathrm{f}} e^{-u_0/k_{\mathrm{B}}T})^N \qquad (22.4\text{-}14)$$

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 a cell. We assume that the atoms in the solid at 0 K are hard spheres in contact with each other. The centers of nearest-neighbor atoms are at a distance d from each other, where d is twice the radius of the atoms (their

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[12] T. L. Hill, *Statistical Thermodynamics*, Addison-Wesley, Reading, MA, 1960, Ch. 16. H. Eyring and M. S. Jhon, *op. cit.*, Ch. 2 (Note 9).

diameter). At nonzero temperature, the thermal expansion of the lattice moves the nearest neighbors to an average distance b that is larger than d. The center of the atom can now move about in a small region at the center of the cell, approximated as a sphere with radius equal to $b - d$.

The free volume is

$$V_{\mathrm{f}} = \tfrac{4}{3}\pi(b-d)^3 \qquad (22.4\text{-}15)$$

so that the partition function and thermodynamic variables can be found by combining Eqs. (22.4-14) and (22.4-15). If we assume a close-packed lattice, the distance b can be expressed in terms of the molar volume.

Exercise 22.18

In a face centered cubic close-packed lattice, the unit cell dimension is equal to $\sqrt{2}b$, and there are four atoms in a unit cell. Show that

$$b^3 = \frac{\sqrt{2}V_{\mathrm{m}}}{N_{\mathrm{Av}}} \qquad (22.4\text{-}16)$$

where V_{m} is the molar volume and N_{Av} is Avogadro's number.

Using Eq. (22.4-16), the classical canonical partition function of an atomic liquid of N atoms is

$$\mathcal{Z}_{\mathrm{cl}} = (2\pi m k_{\mathrm{B}}T)^{3N/2}\left\{\frac{4}{3}\pi\left[\left(\frac{\sqrt{2}V_{\mathrm{m}}}{N_{\mathrm{Av}}}\right)^{1/3} - \left(\frac{\sqrt{2}V_{\mathrm{m,s}}}{N_{\mathrm{Av}}}\right)^{1/3}\right]^3 e^{-u_0/k_{\mathrm{B}}T}\right\}^N \qquad (22.4\text{-}17)$$

where $V_{\mathrm{m,s}}$ is the molar volume of the solid at 0 K. The pressure can be calculated from Eq. (21.8-35b) using this partition function:

$$P = k_{\mathrm{B}}T\left(\frac{\partial \ln(\mathcal{Z})}{\partial V}\right)_T = \frac{Nk_{\mathrm{B}}T}{V}\frac{1}{1-(V_{\mathrm{m,s}}/V_{\mathrm{m}})^{1/3}} \qquad (22.4\text{-}18)$$

Exercise 22.19

Carry out the differentiation to obtain Eq. (22.4-18).

The simple cell theory result for the pressure given in Eq. (22.4-18) 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[13] developed an improved version of the cell model, in which they explicitly summed up the potential energy contributions for the nearest neighbors, operating better results.

There is a problem with all quasi-lattice theories of the liquid state. In calculating the entropy and any entropy-related thermodynamic variables such as the Gibbs energy, etc., we must make the semiclassical correction to the partition function of Eq. (21.9-19). If we really were discussing a crystal, we would divide by h^{3N}, where h is

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[13] J. E. Lennard-Jones and A. F. Devonshire, *Proc. Roy. Soc. (London)*, **A163**, 53 (1937) and **A165**, 1 (1938).

Planck's constant. There would be no corection for the indistinguishability of the particles, since the lattice sites are distinguishable. If we were discussing a gas, as in Section 22.4, we would divide by $N!$ as well as by h^{3N}, as in Eq. (21.9-19). Our present model is an intermediate case. There is insufficient order to claim that the quasi-lattice sites are distinguishable, but our model is still not so completely disordered as a gas. The simplest procedure is to treat the system like a gas and divide by $N!$, making a contribution to the entropy that is called the **communal entropy**. There has been some discussion of whether this procedure is reasonable, but in view of the crudity of the cell model and in view of the fact that nearly all current research concentrates on the fundamental statistical mechanical approach rather than on quasi-lattice approaches, this discussion is not very important.

Exercise 22.20

Write expressions for the energy and entropy of the simple cell model, including correction for the communal entropy.

Numerical Simulations of Liquid Structure

With the advent of fast computers numerical simulations of liquid structure have become practicable. There are two principal types of simulation, the Monte Carlo method and the molecular dynamics method. 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.[14] It is a modification of the original Monte Carlo method, which is used to evaluate integrals by randomly choosing points within the interval of integration. The integrand is evaluated at these points, and summing these values with equal weight gives an approximation to the integral.

In the Monte Carlo method a system of several hundred or a few thousand molecules is considered. Such a system is of course much smaller than a macroscopic liquid sample, but the error so introduced can be estimated. A sample set of coordinate states for all of the molecules is generated, and the average of mechanical quantities (energy, pressure, etc.) is taken over all of these states. These states are generated as follows: An initial coordinate state of the system is assigned in some way. A random number generator is used to pick a number, b, between -1 and 1. The 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 that is equal to $\exp(-\Delta\mathcal{V}/k_{\mathrm{B}}T)$. 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 added to the sum that is producing the average value. It was shown by Metropolis and

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[14] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, *J. Chem. Phys.*, **21**, 1087 (1953).

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 side of the cube.

The second simulation technique is **molecular dynamics**. In this technique, which was pioneered by Alder,[15] the classical equations of motion of all of the particles of a system of several hundred particles are numerically integrated by a computer program. The method is somewhat similar to the Monte Carlo method, except that the displacements of the particles are determined by numerically simulating the classical equations of motion for a time step of about 1 fs (one femtosecond). Periodic boundary conditions are applied as in the Monte Carlo method. The equations of motion are followed for a period of time that is short on macroscopic time scale, perhaps a fraction of a second. However, even this much calculation can use a large amount of computer time. The first molecular dynamics calculations were done on systems of hard spheres, but the method has been applied to systems having intermolecular forces represented by the square-well and Lennard-Jones potential energy functions.

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 direct information on transport properties.[16] 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.

22.5 Polymer Formation and Conformation

Polymer molecules are often called **macromolecules**. The word polymer comes from *poly*, meaning many, and *meros*, meaning parts. Polymer molecules are formed from smaller molecules (monomers) that react to form covalently bonded chains or networks. There are many synthetic polymers such as polyethylene, nylon, polyesters, etc. Synthetic polymers are found in almost all manufactured products, and polymer chemistry is probably the most important area of industrial chemistry. There are also many naturally occurring polymers, including natural rubber, proteins, starches, celluloses, and nucleic acids. As with all substances, the properties of polymers are determined by their molecular structures, and the properties of synthetic polymers can often be tailored to specific applications.

The simplest polymers have linear chainlike molecules. These materials are called **thermoplastic** substances because the material gradually softens as the temperature is raised. Other polymers have networks instead of chains. Some of these are made up of long chains with short chains (cross links) fastening two or more chains together, and others are three-dimensional networks that are bonded in much the same way in all three dimensions. Network polymers are sometimes called **thermosetting** substances, because they are commonly cross-linked at elevated temperatures. They usually do not soften when they are heated after polymerization.

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[15] B. J. Alder and T. E. Wainwright, *J. Chem. Phys.*, **31**, 459 (1959).

[16] See W. G. Hoover, *Annu. Rev. Phys. Chem.*, **34**, 103 (1983) for a review of work in this field.

Synthetic polymers are also classified by the type of reaction that forms them. The two major classes are **condensation polymers** and **addition polymers**. When a monomer unit is added to a condensation polymer chain there is another product (often water) besides the lengthened chain. In an addition polymer there is no other product, so that the polymer has the same empirical formula as the monomer. 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.[17] Consider the formation of a polyester from a diacid,, HOOC–X–COOH, and a dialcohol, HO–Y–OH, where X and Y represent two hydrocarbon chains. The first step in the polymerization is

$$\mathrm{HOOC{-}X{-}COOH + HO{-}Y{-}OH \rightarrow HOOC{-}X{-}COO{-}Y{-}OH + H_2O}$$

The resulting dimer has one carboxyl group and one hydroxyl group, so it is available for reaction with further monomer units. The next step can be the reaction with a diacid or a dialcohol. Two chains of any length can also bond together to from a longer chain. In any event, a long chain with the repeating unit –OOC–X–COO–Y– is eventually formed, which has a carboxyl group at one end and a hydroxyl group at the other.

To simplify the solution of the rate differential equations for the polymerization reactions, we assume that the rate coefficients for all condensation reactions have the same value. This approximation is commonly justified by the assertion that the reaction is not diffusion-limited and 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. We begin with a stoichiometric mixture that has equal concentrations of diacid and dialcohol, and simplify the problem by using a single dependent variable, c, 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 is 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. We assume that the water is removed as it is formed, so that each time a condensation reaction occurs, one free carboxyl group disappears, and the number of molecules decreases by unity, so that as c changes it remains equal to the concentration of free (unesterified) carboxyl groups, and also to the concentration of free hydroxyl groups.

If the polyesterification reaction is carried out with an acid catalyst, we assume that the reaction is first order in the diacid (or other molecule with a carboxyl group), first order in the dialcohol (or other molecule with a hydroxyl group), and first order in the catalyst. We assume that the back reaction and the uncatalyzed reaction can be neglected. The forward rate differential equation is

$$\frac{dc}{dt} = -k_{\mathrm{f}}[\mathrm{H}^+]c^2 = -k'c^2 \qquad (22.5\text{-}1)$$

where

$$k' = k_{\mathrm{f}}[\mathrm{H}^+] \qquad (22.5\text{-}2)$$

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[17] See H. R. Allcock and F. W. Lampe, *Contemporary Polymer Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1981, pp. 245ff, or C. Tanford, *Physical Chemistry of Macromolecules*, Wiley, New York, 1961, pp. 588ff for the standard treatments of both types of polymerization.

Since the catalyst is not consumed, [H$^+$] is a constant. Equation (22.5-1) is the same as Eq. (12.2-8). Equation (12.2-11) gives its solution:

$$\frac{1}{c} = \frac{1}{c_0} + k't \tag{22.5-3}$$

We define the variable p, the fraction of carboxyl groups that have reacted:

$$p = 1 - \frac{c}{c_0} \tag{22.5-4}$$

Equation (22.5-3) can be written

$$p = \frac{k'c_0t}{1 + k'c_0t} \tag{22.5-5}$$

which is equivalent to

$$\frac{1}{1-p} = 1 + k'c_0t \tag{22.5-6}$$

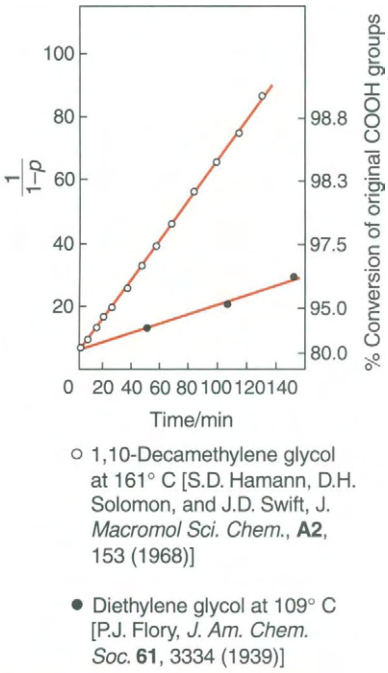

Figure 22.18. Polyesterificaiton of Adipic Acid with Two Polyalcohols, catalyzed with *p*-Toluene Sulfonic Acid. The left axis shows the value of $1/(1-p)$ where p is the fraction of carboxyl groups that have reacted. The right axis is labeled with the percent of original carboxyl groups that have reacted. From H. R. Allcock and F. W. Lampe, *Contemporary Polymer Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1981, p. 254.

Exercise 22.21

Verify Eqs. (22.5-5) and (22.5-6).

The **degree of polymerization**, x, is defined as the number of monomer units in a molecule. In the present example, if x is even there are $x/2$ diacid molecules and $x/2$ dialcohol molecules combined in the polymer molecule. If x is odd, there is an extra diacid or an extra dialcohol. The **number-average degree of polymerization** is called $\bar{x}_n$, and is given by

$$\bar{x}_n = \frac{c_0}{c} = \frac{1}{1-p} \tag{22.5-7}$$

This value is a mean value with each molecule given equal weight. Equation (22.5-3) can be expressed in terms of $\bar{x}_n$:

$$\bar{x}_n = 1 + k'c_0t \tag{22.5-8}$$

Equation (22.5-8) agrees with experiment fairly well for the later stages of polymerization, although not so well for the early stages. Figure 22.18 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 is

$$M_x = \frac{x}{2}M_r + 18\ \text{amu} = xM_0 + 18\ \text{amu} \approx xM_0 \tag{22.5-9}$$

where M_r is the mass of the repeating unit of the polymer and M_0 is equal to $M_r/2$. The 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 (22.5-9) 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 molecules with degree of polymerization equal to x and let X_x be the **number fraction** of molecules with this degree of polymerization:

$$X_x = \frac{N_x}{N} \tag{22.5-10}$$

where N is the total number of molecules. The **number-average molecular mass** is the mean molecular mass with each molecule given equal importance in the averaging process:

$$\bar{M}_n = \frac{1}{N}\sum_{x=1}^{\infty} N_x M_x = \sum_{x=1}^{\infty} X_x M_x \tag{22.5-11}$$

where the sum is over all values of x and where we have used an infinite upper limit for the sum, which introduces a negligible error. The number-average molecular mass is equal to the total mass divided by the total number of molecules.

A formula for $\bar{M}_n$ can be derived from statistical reasoning.[18] We assume that all rate coefficients are equal and 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

$$\text{Probability of } x = p^{x-1}(1 - p) \tag{22.5-12}$$

The number-average molecular mass can now be written

$$\bar{M}_n = \sum_{x=1}^{\infty} X_x x M_0 = M_0(1 - p)\sum_{x=1}^{\infty} x p^{x-1} \tag{22.5-13}$$

where a term equal to 18 amu has been omitted and where we again use an infinite upper limit for the sum. This sum can be found in tables,[19] giving

$$\bar{M}_n = \frac{M_0}{1 - p} \tag{22.5-14}$$

From Eq. (22.5-6) and (22.5-14), we can write an equation for the time dependence of $\bar{M}_n$:

$$\bar{M}_n = M_0(1 + c_0 k' t) \tag{22.5-15}$$

where we continue to neglect 18 amu compared with $\bar{M}_n$. For fairly large values of the time,

$$1 + c_0 k' t \approx c_0 k' t$$

giving

$$\bar{M}_n = M_0 c_0 k' t \tag{22.5-16}$$

This relation can also be obtained using reaction kinetics.[20]

The time dependence of the number fraction of any degree of polymerization can be obtained by substituting Eq. (22.5-5) into Eq. (22.5-12).

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[18] Allcock and Lampe, *op. cit.* (Note 17).

[19] See for example H. B. Dwight, *Tables of Integrals and Other Mathematical Data*, 4th ed., Macmillan, New York, 1961, p. 8.

[20] Tanford, *op. cit.* (Note 17).

*Exercise 22.22

Obtain an expression for the time dependence of X_x.

The **mass fraction** of molecules with degree of polymerization x is

$$W_x = \frac{\text{mass of molecules of degree of polymerization } x}{\text{mass of all molecules}} = \frac{N_x M_x}{\sum_{x=1}^{\infty} N_x M_x} \tag{22.5-17}$$

The **mass-average molecular mass** (often called the "weight-average molecular weight") is defined by

$$\bar{M}_{\mathrm{w}} = \sum_{x=1}^{\infty} W_x M_x = \frac{\sum_{x=1}^{\infty} N_x M_x^2}{\sum_{x=1}^{\infty} N_x M_x} \tag{22.5-18}$$

The required sum can be found in tables,[21] giving

$$\bar{M}_{\mathrm{w}} = (1-p)^2 M_0 \sum_{x=1}^{\infty} x^2 p^{x-1} = M_0 \frac{1+p}{1-p} \tag{22.5-19}$$

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 in the mass average. In our case, 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 $\bar{M}_n$ in Eq. (22.5-15). Figure 22.19a shows the distribution of mass in a polyester, according to Eq. (22.5-12) and Figure 22.19b shows the evolution in time of several mass fractions during a condensation polymerization.

Exercise 22.23

Show that

$$\bar{M}_{\mathrm{w}} = M_0(1 + 2k' c_0 t) \tag{22.5-20}$$

Polymer Conformation

A typical polymer molecule is relatively flexible since most single covalent bonds are able to rotate even if the bond angles are fixed. It can therefore adopt any one of a large number of possible conformations. The principal elementary 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.

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[21] Dwight, *op. cit.*, (Note 19).

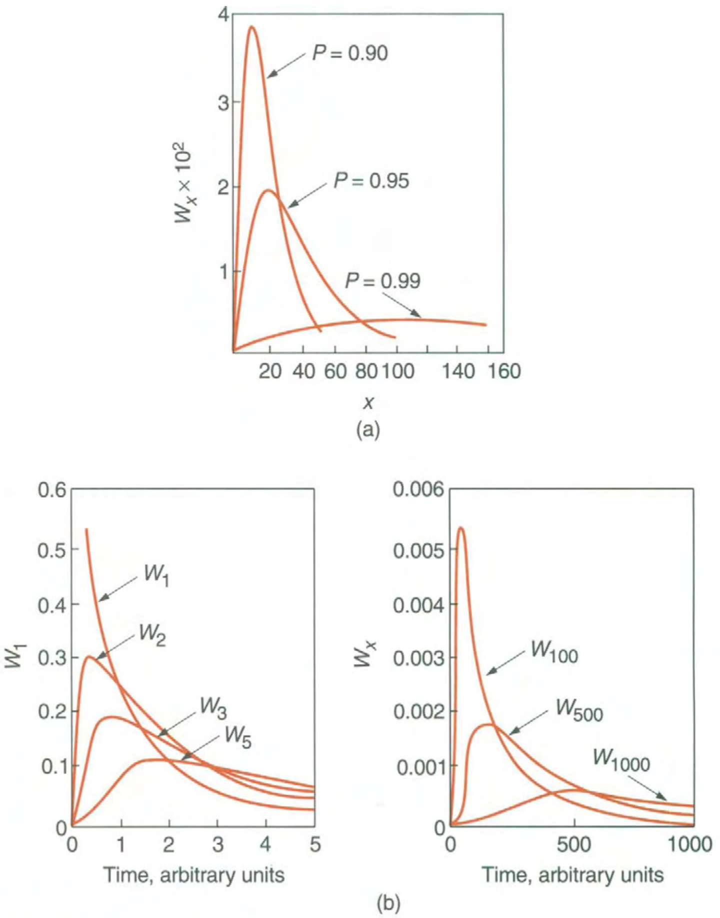

Figure 22.19. A Condensation Polymerization. (a) **Distribution by mass in amu for conversions of 90%, 95%, and 99%.** The horizonal axis is labeled with x, the degree of polymerization, or the number of monomer units in the polymer molecule. The vertical axis is labeled with the mass fraction of molecules with x monomer units. From H. R. Allcock and F. W. Lampe, *Contemporary Polymer Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1981, p. 261. (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. From C. Tanford, *Physical Chemistry of Macromolecules*, Wiley, New York, 1961, p. 595.

We approximate a polymer molecule by a **freely joined chain**, which is a set of links of fixed length a fastened together end-to-end in a chain such that each joint can rotate into any position whatsoever, even folding one link back onto the previous link. To simplify the problem even further, let us 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 $p(n+1, x, y, z)$. This probability will give us our distribution of end-to-end distances for a chain of $n+1$ links. 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

$$p(n+1, x, y, z) = \tfrac{1}{6}[p(n, x+a, y, z) + p(n, x-a, y, z) + p(n, x, y+a, z) + p(n, x, y-a, z) + p(n, x, y, z+a) + p(n, x, y, z-a)] \qquad (22.5\text{-}21)$$

Equation (22.5-21) is a difference equation that can be solved.[22] We apply the condition that the beginning of the chain is known to be at the origin:

$$p(0, x, y, z) = \begin{cases} 1 & \text{if } x = 0,\ y = 0 \text{ and } z = 0 \\ 0 & \text{otherwise} \end{cases} \qquad (22.5\text{-}22)$$

The difference equation will maintain the normalization

$$\sum_{x=-\infty}^{\infty} \sum_{y=-\infty}^{\infty} \sum_{z=-\infty}^{\infty} p(n, x, y, z) = 1 \qquad (22.5\text{-}23)$$

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 now omit the limits on the sum and write

$$p(n+1, x) = \sum_y \sum_z p(n+1, x, y, z) \qquad (22.5\text{-}24)$$

which is the probability that the end of link number $n+1$ is at x, irrespective of the y and z values. Equation (22.5-21) is now summed over all values of y and z to give

$$p(n+1, x) = \tfrac{1}{6}[p(n, x+a) + 4p(n, x) + p(n, x-a)] \qquad (22.5\text{-}25)$$

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.

The principal variable that characterizes the distribution of end-to-end distances is the mean of the square of the distance, called the **second moment** of the distribution, equal to the variance or the square of the standard deviation of the distribution. The x component of this quantity for link number $n+1$ is given by Eq. (22.5-25):

$$\begin{aligned} \langle x^2 \rangle_{n+1} &= \sum_x x^2 p(n+1, x) \\ &= \frac{1}{6}\sum_x x^2 p(n, x+a) + \frac{2}{3}\sum_x x^2 p(n, x) + \frac{1}{6}\sum_x x^2 p(n, x-a) \end{aligned} \qquad (22.5\text{-}26)$$

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

$$\begin{aligned} \langle x^2 \rangle_{n+1} = &\frac{1}{6}\sum_{x'} (x'^2 - 2ax' + a^2) p(n, x') + \frac{2}{3}\langle x^2 \rangle_n \\ &+ \frac{1}{6}\sum_{x''} (x''^2 + 2ax'' + a^2) p(n, x'') \end{aligned} \qquad (22.5\text{-}27)$$

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[22] F. T. Wall, *Chemical Thermodynamics*, 2d ed., W. H. Freeman, San Francisco, 1974, pp. 341ff.

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:

$$\langle x^2\rangle_{n+1} = \left(\frac{2}{3}+\frac{2}{6}\right)\langle x^2\rangle_n + \frac{2}{3}a^2\sum_x p(n,x) = \langle x^2\rangle_n + \frac{a^2}{3} \tag{22.5-28}$$

where we have used the fact that the distribution is normalized as in Eq. (22.5-23). Equation (22.5-28) is a recursion relation, somewhat analogous to the recursion relation used in the solution of the Schrödinger equation for the harmonic oscillator. If the value for $n = 0$ is known the value of $n = 1$ can be calculated, and from this the value for $n = 2$ can be calculated, and so on. From the initial condition in Eq. (22.5-22),

$$\langle x^2\rangle_0 = 0 \tag{22.5-29}$$

so that

$$\langle x^2\rangle_1 = \frac{a^2}{3} \tag{22.5-30}$$

Each iteration of Eq. (22.5-28) adds a term $a^2/3$, so that

$$\langle x^2\rangle_n = \frac{na^2}{3} \tag{22.5-31}$$

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

$$\langle r^2\rangle_n = \langle x^2\rangle_n + \langle y^2\rangle_n + \langle z^2\rangle_n = na^2 \tag{22.5-32}$$

and the root-mean-square distance is

$$r_{\mathrm{rms}} = \langle r^2\rangle^{1/2} = n^{1/2}a \tag{22.5-33}$$

As expected, this distance is proportional to the length of a link. However, it is proportional to the square root of the number of links in the polymer chain, not to the number of links. This behavior arises physically 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.

The discussion that we have followed for the end-to-end distance in a freely jointed chain is analogous to a **random walk** or **random flight** problem, in which the time t plays the same role as n, the number of links. It is applied to various model systems, including a model for diffusion in a liquid in which a diffusing molecule is assumed to jump a distance equal to a at regular intervals in time. The analysis of this model leads to an equation that is the same as Eq. (11.2-16).

In order to solve for the full distribution of end-to-end lengths, as a function of time, we approximate Eq. (22.5-21) by a differential equation.[23] We expand the function p in

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[23] Wall, *op. cit.*; pp 341ff (Note 22).

four different Taylor series in n, x, y, and z, treating n as though it could take on nonintegral values:

$$p(n+1, x, y, z) = p(n, x, y, z) + \frac{\partial p}{\partial n} + \cdots \tag{22.5-34a}$$

$$p(n, x \pm a, y, z) = p(n, x, y, z) \pm \frac{\partial p}{\partial x} a + \frac{1}{2}\frac{\partial^2 p}{\partial x^2} a^2 \pm \cdots \tag{22.5-34b}$$

with equations like Eq. (22.5-34b) for y and z. These series are substituted into Eq. (22.5-21). The lowest-order terms that do not cancel are kept, and the higher-order terms are discarded:

$$\frac{\partial p}{\partial n} = \frac{a^2}{6}\left(\frac{\partial^2 p}{\partial x^2} + \frac{\partial^2 p}{\partial y^2} + \frac{\partial^2 p}{\partial z^2}\right) \tag{22.5-35}$$

Equation (22.5-35) 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. Compare this equation with Fick's second law of diffusion, Eq. (11.2-13).

We transform the equation to spherical polar coordinates, in which p becomes 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 $p = p(n, r)$.

$$\frac{\partial p}{\partial n} = \frac{a^2}{6r^2}\frac{\partial}{\partial r}\left(r^2 \frac{\partial p}{\partial r}\right) \tag{22.5-36}$$

The solution to Eq. (22.5-36) is[24]

$$p(n, r) = \left(\frac{3}{2\pi a^2}\right)^{3/2} e^{-3r^2/2na^2} \tag{22.5-37}$$

where the constant provides for normalization:

$$\int_0^\infty p(n, r) 4\pi r^2 \, dr = 1 \tag{22.5-38}$$

Compare Eq. (22.5-37) to the diffusion equation of Eq. (11.2-16), which can be derived from a one-dimensional random walk.

Exercise 22.24

a. Carry out the substitution of the Taylor series into Eq. (22.5-21) to obtain Eq. (22.5-35).
b. Verify that the function of Eq. (22.5-37) satisfies Eq. (22.5-36).
c. Verify that the function of Eq. (22.5-37) 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 the two parts of a polymer chain or of two different polymer chains cannot occupy the same location at the same time. In addition, the effect of intermolecular

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[24] Wall, *op. cit.*, pp. 341ff (Note 22).

attractions on the conformation can be considerable. Any of the books on polymer chemistry contain discussions of more elaborate theories than the simple freely jointed chain theory.

Most biological macromolecules have far more regular molecular conformations than do synthetic polymers. Proteins, which are condensation polymers of amino acids, can form intramolecular hydrogen bonds that generally 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**.

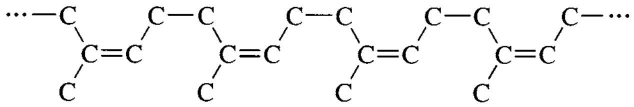
Nucleic acids are polymers of five-carbon sugars (either ribose or deoxyribose), phosphoric acid residues, and certain ring-containing molecules called nitrogen-containing bases. Deoxyribonucleic acid (DNA) is held in a double helix of two chains by hydrogen bonds between certain pairs of bases: cytosine (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.

22.6

Rubber Elasticity

Hermann Staudinger, 1881–1965, was a German chemist who received the 1953 Nobel prize in chemistry for his pioneering work in the chemistry of macromolecules.

Rubber is a naturally occurring polymer, first used as pencil erasers (this use is the origin of the name). Rubber was shown by Staudinger to be macromolecular in nature. It is an addition polymer of isoprene (2-methyl-1,3-butadiene). Since each molecule of the monomer has two double bonds, there remains one double bond per monomer. Natural rubber has the *cis* configuration at all of these bonds. A portion of the structural formula for a rubber molecule is (hydrogens have been omitted):



Prior to 1955, various kinds of synthetic rubber were invented, but were found to be inferior to natural rubber for making automobile tires and most other rubber items. 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 product that is identical to natural rubber, and automobile tires made of synthetic rubber are now common.

Charles Goodyear, 1800–1860, was an American inventor whose patent was widely infringed upon, and who died in debt.

In 1839, after 10 years of trial-and-error experimentation in his kitchen, Goodyear invented the **vulcanization** process in which sulfur is reacted with natural rubber. From natural rubber, a soft, sticky, and semi-fluid thermoplastic, a more nearly solid and elastic product is obtained. 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. In the vulcanization process, the sulfur reacts with double bonds in two adjacent chains, forming short chains of sulfur atoms between the polymer chains. 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.

The Thermodynamics of Rubber

A piece of vulcanized rubber is not a simple system in the thermodynamic sense since work other than compression work ($P\,dV$ work) can be done on it. When it is stretched reversibly, work is done on it:

$$dw = -P\,dV + f\,dL \tag{22.6-1}$$

where L is the length of the piece of rubber and f is the **tension force**.

It is found experimentally that the stretching of rubber approximately displays three properties: (1) the volume remains constant; (2) the tension force is proportional to the absolute temperature; (3) the energy is independent of the length at constant temperature. An **ideal rubber** is defined to be one that exactly conforms to these three properties. Since the volume is constant, the first term on the right-hand side of Eq. (22.6-1) vanishes and the first law of thermodynamics for reversible processes in a closed system made of ideal rubber is

$$dU = T\,dS + f\,dL \tag{22.6-2}$$

We define an enthalpylike variable, K

$$K = U - fL \quad \text{(definition)} \tag{22.6-3}$$

The Helmholtz energy is defined in the standard way:

$$A = U - TS \quad \text{(definition)} \tag{22.6-4}$$

We denote the analogue to the Gibbs energy by J:

$$J = K - TS = U - fL - TS \quad \text{(definition)} \tag{22.6-5}$$

Just as in Chapter 5, we can write differential expressions:

$$dK = T\,dS - L\,df \tag{22.6-6a}$$

$$dA = -S\,dT + f\,dL \tag{22.6-6b}$$

$$dJ = -S\,dT - L\,df \tag{22.6-6c}$$

and can write Maxwell relations from these. For example, we will need the Maxwell relation that can be obtained from Eq. (22.6-6b):

$$\left(\frac{\partial S}{\partial L}\right)_T = -\left(\frac{\partial f}{\partial T}\right)_L \tag{22.6-7}$$

This Maxwell relation is analogous to the Maxwell relations in Section 5.2.

*Exercise 22.25

Write the other three Maxwell relations from Eqs. (22.6-2) (22.6-6a), and (22.6-6c).

Using Eqs. (22.6-2) and (22.6-7), we can derive a thermodynamic equation of state that is analogous to Eq. (5.5-1):

$$\left(\frac{\partial U}{\partial L}\right)_T = T\left(\frac{\partial S}{\partial L}\right)_T + f = -T\left(\frac{\partial f}{\partial T}\right)_L + f \tag{22.6-8}$$

We can now show that property (3) of an ideal rubber follows from property (2). If f is proportional to T we can write

$$f = T\varphi(L) \tag{22.6-9}$$

where φ is some function of L but is independent of T. We now have

$$T\left(\frac{\partial f}{\partial T}\right)_L = T\varphi = f \tag{22.6-10}$$

so that

$$\left(\frac{\partial U}{\partial L}\right)_T = -f + f = 0 \tag{22.6-11}$$

Equation (22.6-11) 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, heat flows out and the energy remains constant. (This behavior is easily observed by stretching a rubber band in contact with the upper lip.) Stretching the rubber band at constant temperature must decrease its entropy. This fact seems reasonable from a molecular point of view since the polymer molecules will be more nearly parallel and more nearly ordered in the stretched state than in the relaxed state. From Eqs. (22.6-8) and (22.6-11) we can derive a relation for this decrease in entropy:

$$f = -T\left(\frac{\partial S}{\partial L}\right)_T \tag{22.6-12}$$

A Molecular Theory of Rubber Elasticity

We represent an ideal rubber by a model system that has the following properties:[25] (1) The equilibrium system is rectangular piece of rubber made up of a set of polymer molecules with an equilibrium distribution of end-to-end lengths given by the freely-jointed chain formula of Eq. (22.5-37). (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 $\mathbf{r}_i = (x_i, y_i, z_i)$. After an elongation in the x direction that preserves the original volume, the end-to-end vector of these molecules will be (x_i', y_i', z_i'):

$$x_i' = \alpha x_i, \qquad y_i' = \frac{y_i}{\alpha^{1/2}}, \qquad z_i' = \frac{z_i}{\alpha^{1/2}} \tag{22.6-13}$$

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 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. (4.4-1):

$$S_{\text{st}} = k_B \ln(\Omega) + \text{const} \tag{22.6-14}$$

where Ω is the thermodynamic probability or the number of system mechanical states that are compatible with the thermodynamic state of the system. To use this formula, we

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[25] Wall, *op. cit.*, Ch. 16 (Note 22); P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953, pp 464ff.

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. The probability is then multiplied by the number of ways to divide the set of polymer molecules into the specified subsets:

$$P' = N! \prod_i \frac{1}{N_i!} p(n, x_i', y_i', z_i')^{N_i} \tag{22.6-15}$$

where the factor $N!/\prod_i N_i!$ is the number of ways to divide the N chains into the required subsets. Using Stirling's approximation,

$$\begin{aligned} \ln(P') &= N\ \ln(N) - N + \sum_i [N_i\ \ln(p_i') - N_i\ \ln(N_i) + N_i] \\ &= \sum_i N_i\ \ln(p_i' N/N_i) \end{aligned} \tag{22.6-16}$$

where we have abbreviated $p(n, x_i', y_i', z_i')$ by p_i'. We now write this equation for the equilibrium distribution:

$$\ln(P) = \sum_i N_i\ \ln(p_i N/N_i) \tag{22.6-17}$$

Since P is proportional to Ω we can write a formula for the entropy change:

$$\begin{aligned} \Delta S &= S(\text{stretched}) - S(\text{equilibrium}) = k[\ln(P') - \ln(P)] \\ &= k_B \sum_i N_i\ \ln(p_i'/p_i) = Nk_B \sum_i p_i\ \ln(p_i'/p_i) \end{aligned} \tag{22.6-18}$$

where we have used the fact that $p_i = N_i/N$, since the randomly selected cross-linked chains obey the equilibrium distribution.

If we can consider x, y, and z to range continuously to an adequate approximation, we can replace the sum by an integral:

$$\Delta S = Nk_B \int p\ \ln(p'/p)\, dx\, dy\, dz \tag{22.6-19}$$

where the integral is over all values of x, y, and z. From Eq. (22.5-37),

$$\ln(p'/p) = \frac{3}{2na^2}\left[-x^2(\alpha^2 - 1) - (y^2 + z^2)\left(\frac{1}{\alpha} - 1\right)\right] \tag{22.6-20}$$

When Eq. (22.6-20) is substituted into Eq. (22.6-19),

$$\begin{aligned} \Delta S &= \frac{3Nk_B}{2na^2}\left[-\langle x^2\rangle_n(\alpha^2 - 1) - (\langle y^2\rangle_n + \langle z^2\rangle_n)\left(\frac{1}{\alpha} - 1\right)\right] \\ &= -\frac{Nk_B}{2}\left(\alpha^2 + \frac{2}{\alpha} - 3\right) \end{aligned} \tag{22.6-21}$$

where we have used Eq. (22.5-31) 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. (22.6-21) and (22.6-12), we can write an equation of state for ideal rubber:

$$f = -T\left(\frac{\partial S}{\partial L}\right)_T = -\frac{T}{L_0}\left(\frac{\partial S}{\partial \alpha}\right)_T = \frac{Nk_B T}{L_0}\left(\alpha - \frac{1}{\alpha^2}\right) \tag{22.6-22}$$

This equation of state agrees fairly well with experiment for values of α up to 3 or 4.[26]

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[26] Wall, *op. cit.*, p. 348 (Note 22).

EXAMPLE 22.2

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.

$$dw = f\,dL = \frac{Nk_BT}{L}\left(\alpha - \frac{1}{\alpha^2}\right)dL = Nk_BT\left(\alpha - \frac{1}{\alpha^2}\right)d\alpha$$

$$w = Nk_BT\int_1^{\alpha'}\left(\alpha - \frac{1}{\alpha^2}\right)d\alpha = \frac{Nk_BT}{2}\left(\alpha'^2 + \frac{2}{\alpha'} - 3\right)$$

***Exercise 22.26**

a. Write the formula for the heat transferred in the isothermal elongation of a piece of ideal rubber.

b. For a piece of ideal rubber that is large enough that 1.00×10^{-6} mol of cross-linked polymer chains occur in it, find the value of q and w for stretching it to 3.00 times its original length at 298.15 K.

22.7 Polymers in Solution

Polymers such as polyvinyl alcohol can be somewhat soluble in water, and other polymers can dissolve in nonpolar solvents. The conformation of polymer molecules in solution is similar to that of the pure polymers except that there is an additional effect due to intermolecular forces between polymer molecules and solvent molecules and between solvent molecules. 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. Polar polymer molecules will tend to form tight balls in nonpolar solvents, but can attract water molecules and can swell in aqueous solution. Similarly, nonpolar polymers can swell in nonpolar solvents (try placing a rubber object in benzene).

Just as for a pure polymer, we use the mean-square end-to-end distance as a measure of the conformation of the polymer molecules. The **expansion coefficient** α is defined such that

$$\langle r^2 \rangle = \alpha^2 \langle r^2 \rangle_0 \qquad (22.7\text{-}1)$$

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 in the solution. Do not confuse this expansion coefficient with the degree of elongation in the previous section or with the coefficient of thermal expansion defined in Chapter 2. A solvent in which polymer molecules adopt on the average the same conformation as in the pure polymer is called a **theta solvent**. In a theta solvent, $\alpha = 1$. In a poor solvent for the particular polymer, α will be smaller than unity, and in a good solvent, which 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 a rigid sphere of that size. Einstein solved the hydrodynamic equations for flow around a hard sphere in a viscous fluid. If the total volume of the spheres in a dilute suspension is denoted by v and the volume of the entire suspension is denoted by V, his result is that the viscosity of the suspension is given by[27]

$$\eta = \eta_0\left(1 + \frac{5}{2}\phi\right) \tag{22.7-2}$$

where η_0 is the viscosity of the pure solvent and ϕ is the volume fraction of the spheres in the suspension:

$$\phi = \frac{v}{V} \tag{22.7-3}$$

Equation (22.7-2) can be written in the form

$$\eta_{\mathrm{sp}} = \frac{\eta}{\eta_0} - 1 = \eta_r - 1 = \frac{5}{2}\phi \tag{22.7-4}$$

where η_{sp} is called the **specific viscosity** and η_{r} is called the **relative viscosity**. Since the volume of a set of spherical particles is proportional to the number of the spheres, the specific viscosity of a dilute suspension of spheres is proportional to the concentration of the spheres. We define the **intrinsic viscosity**, $[\eta]$, also called the **limiting viscosity number**.

$$[\eta] = \lim_{c\to 0}\left(\frac{1}{c}\eta_{\mathrm{sp}}\right) = \lim_{c\to 0}\left[\frac{1}{c}\left(\frac{\eta}{\eta_0} - 1\right)\right] \tag{22.7-5}$$

where c is the concentration of the polymer, expressed as mass per unit volume (usually grams per deciliter). For a dilute suspension of hard spheres of the same size, the specific viscosity divided by c is independent of the concentration:

$$[\eta] = \frac{1}{c}\eta_{\mathrm{sp}} = \frac{5}{2}\frac{1}{c}\frac{v}{V} = \frac{5}{2}\frac{1}{M}\frac{4}{3}\pi r^3 \tag{22.7-6}$$

where M and r are the mass and the radius of one of the spheres.

Exercise 22.27

Verify Eq. (22.7-6).

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. Therefore, the volume of the sphere is proportional to $M^{3/2}$ and the intrinsic viscosity is proportional to $M^{1/2}$:

$$[\eta] = K'M^{1/2} \tag{22.7-7}$$

where K' depends on temperature and on the identities of the solvent and polymer, but not on M. Equation (22.7-7) is called the **Mark–Houwink equation**. It is considered to

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[27] A. Einstein, *Ann. Physik.* **19**, 289 (1906).

be valid for a polymer in a theta solvent. For other solvents we can write a modified version of the Mark–Houwink equation:

$$[\eta] = KM^a \tag{22.7-8}$$

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, and found that for aqueous solutions at 25°C,[28]

$$[\eta] = (2.0 \times 10^{-4}\ \mathrm{dL\ g^{-1}})(M/1\ \mathrm{amu})^{0.76} \tag{22.7-9}$$

For a typical polydisperse sample of a single polymer, one can apply Eq. (22.7-8) to each molecular mass that is present, multiply each equation by W_i, the mass fraction for molecular mass M_i, and sum the equations over all possible molecular masses. Recognizing that the intrinsic viscosity is a sum of all contributions (since it applies to infinite dilution) and that K has the same value for all molecules of a given polymer, we can write

$$[\eta] = K \sum_i W_i M_i^a \tag{22.7-10}$$

where the sum is over different molecular masses. We define the **viscosity-average molecular mass**:

$$\bar{M}_v = \left(\sum_i W_i M_i^a\right)^{1/a} \tag{22.7-11}$$

Combining Eq. (22.7-10) and Eq. (22.7-11) gives

$$[\eta] = K\bar{M}_v^a \tag{22.7-12}$$

The viscosity-average molecular mass is not defined in the same way as the number-average and mass-average molecular weights, being more like a geometric mean than an arithmetic mean. However, it can be shown that if $a = 1$ the viscosity-average molecular mass is the same as the mass-average molecular mass. It can also be shown that the viscosity-average molecular mass is the same as the number-average molecular mass if $a = -1$. It is conceivable that $a = 1$, but not that $a = -1$. The viscosity-average molecular mass is more nearly equal to the mass-average value than to the number-average value.

Exercise 22.28

Using the fact that the mass fractions sum to unity, show that the viscosity-average molecular mass is the same as the mass-average molecular mass in the case that $a = 1$.

Summary of the Chapter

In this chapter, we have studied the structure of solids and liquids. Many solids are crystalline, with molecular units arranged in a regular three-dimensional lattice. We have discussed the principal types of solid lattices.

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[28] P. J. Flory and F. S. Leutner, *J. Polymer. Sci.*, **5**, 267 (1950).

There are two principal theories for the vibrations of lattices of atoms, the Einstein and the Debye theories. In the Einstein model, each atom is assumed to vibrate independently of the other atoms, with all atoms vibrating with the same frequency. In the Debye model, the lattice is assumed to vibrate with the same distribution of frequencies as would a structureless solid. In each theory, the principal result is a formula for the heat capacity of the solid lattice. In each case, the high-temperature limit of the formula conforms to the law of Dulong and Petit.

The electronic structure of solids was discussed through the band theory, in which the electrons are assumed to occupy delocalized orbitals that comprise bands of energy levels. The differences between conductors, semiconductors, and insulators were discussed in terms of the band theory.

The structure of liquids is more difficult to discuss than is the structure of solids, since 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 another molecule at a given distance from a molecule.

The kinetics of the formation of condensation polymers was discussed. An approximation solution of the rate law was presented, and distributions of molecular mass were discussed. The conformation of a simple polymer model, a freely jointed chain, was also presented. Rubber elasticity was discussed at the same level of approximation.

PROBLEMS

Problems for Section 22.1

***22.29.** Without looking up any properties, classify the following solids into the four classes of Section 22.1. Rearrange the list in order of increasing melting temperature without looking up any data.

diamond, neon, copper, cesium nitrate, sodium, krypton

22.30. Without looking up any properties, classify the following solids into the four classes of Section 22.1. Rearrange the list in order of increasing melting temperature without looking up any data.

carbon dioxide, argon, xenon, sodium chloride, quartz, silicon

22.31. Explain why a single crystal has a greater mechanical strength than a polycrystalline sample of the same material.

22.32. 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.

***22.33.** Gallium crystallizes in a primitive cubic lattice. Its density is 5.92 g cm^{-3}. Find the unit cell dimension.

22.34. What is the basis for a crystal of argon (fcc cubic lattice)? What is the number of atoms per unit cell? What is the number of bases per unit cell?

***22.35.** The CsCl crystal has a cubic unit cell with a cesium ion at each corner and a chloride ion at the center. To which Bravais lattice does it belong? How many bases are there in a unit cell? The density of CsCl is 3988 kg m^{-3}. Find the unit cell dimension.

22.36. 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 radius of a barium atom.

c. Calculate the molar volume of solid barium and the volume of empty space in 1.00 mol of barium.

22.37. Iron forms a body-centered crystal with unit cell dimension equal to 2.861×10^{-10} m. Calculate the density of iron.

22.38. **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 $\theta = 36.5^\circ$, find the wavelength of the X-rays.

c. Find the density of molybdenum carbide.

***22.39.** **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.

22.40. **a.** The stretching of a uniform bar due to a tensile force is described by **Young's modulus**, E, defined by

$$E = \frac{\text{stress}}{\text{strain}} = \frac{F/A}{\Delta L/L}$$

where F is the magnitude of the tensile force, A is the cross-sectional 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}.

***21.41.** The value of Young's modulus for iron is 2.8×10^7 lb in^{-2}. Make reasonable assumptions and estimate the force constant for an Fe–Fe bond. See the previous problem.

Problems for Section 22.2

22.42. The value of Θ_E that fits the Einstein crystal model heat-capacity formula to aluminum data 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?

22.43. The value of Θ_E that fits the Einstein crystal model heat-capacity formula to diamond data is 1320 K.

***a.** What is the vibrational frequency corresponding to this value of the parameter?

b. Draw a 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?

22.44. Derive a formula for the vapor pressure of an Einstein crystal, treating the sublimation reaction as a chemical reaction. Take the potential energy of the gas to equal zero, and call the energy of an atom of the crystal in its ground vibrational state $-u_0$ (a constant).

22.45. **a.** Write a computer program to evaluate the Debye function, using Simpson's rule.[29]

b. Use this program to evaluate the heat capacity of aluminum at several temperatures, using the Debye temperature of 428 K. Draw a rough graph of the heat capacity of aluminum as a function of temperature.

22.46. 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 $\nu = 3.94 \times 10^{12}$ s^{-1} (one-half of the Debye frequency for germanium).

c. If a table of the Debye function as available,[30] find the ratio of your result to the Debye result for several values of T.

Problems for Section 22.3

22.47. Make an accurate graph of the fermion distribution, Eq. (22.3-5), using ε/k_BT as the independent variable and assuming (a) that $T = \mu/10k_B$, (b) that $T = \mu/k_B$, and (c) that $T = 10\mu/k_B$.

22.48. Evaluate the Fermi level for copper at 298 K using Eq. (22.3-15). Find the percent error of using Eq. (22.3-14).

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[29] S. I. Grossman, *Calculus*, 3d ed., Academic Press, Orlando, FL, 1984, pp. 518ff, or any standard calculus text.

[30] Davidson, *op. cit.*, p. 359.

22.49. ***a.** Evalute the Fermi level for silver at 298 K using Eq. (22.3-15). State any assumptions.

b. Find the electronic contribution to the heat capacity of silver at 15.00 K and at 298.15 K.

22.50. 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.

22.51. 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).

22.52. 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.

Problems for Section 22.4

***22.53.** The density of ice at 0°C is equal to 0.917 g mL^{-1}, and that of liquid water is equal to 1.000 g 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.

22.54. Show that the pressure of a system of hard spheres can be obtained from the value of the radial distribution function at only one value of r. What value is it?

***22.55.** At 1.00 atm and 84 K, the normal melting temperature, the density of solid argon is 1.82 g mL^{-1} and that of liquid argon is 1.40 g/mL^{-1}. Find the pressure according to the cell model result, Eq. (22.4-18), for these two systems at these two temperatures and compare it with the correct value, 1.00 atm.

Problems for Section 22.5

22.56. The sum in Eq. (22.5-13) is similar to the geometric progression of Eq. (21.4-19). Show that the result used in Eq. (22.5-14) can be obtained by differentiating the sum

$$S = \sum_{n=0}^{\infty} p^x$$

with respect to p.

***22.57.** 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.

22.58. 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%	5,000 amu
25.00%	15,000 amu
60.00%	25,000 amu
5.00%	35,000 amu

22.59. The hydroxy acid $HO{-}(CH_2)_5{-}CO_2H$ forms a polyester by condensation polymerization.

a. Show that the same equations apply as used in Section 22.5 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 have been esterified.

***c.** Find the number-average molecular mass for part (b).

***d.** Find the average degree of polymerization.

22.60. The amino acid 7-aminoheptanoic acid forms a polyamide (nylon) in *m*-cresol solution, with the second-order rate coefficients:[31]

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.

22.61. 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:

$$\frac{dc}{dt} = k_f c^3$$

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[31] Zhubanov *et al.*, *Izv. Akad. Nauk. SSR Ser. Khim.*, **17**, 69 (1967), cited in Allcock and Lampe, *op. cit.*, p. 268 (Note 17).

22.62. Show that Eq. (22.5-30) is compatible with the fact that a "chain" of one link is rigid.

***22.63.** 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, and (b) 10,000 links.

22.64. 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) 1,000 links, and (b) 100,000 links.

22.65. 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. (22.5-33).

Problems for Section 22.6

22.66. **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.

22.67. **a.** Write equations for q and w for each step of a Carnot cycle using a piece of ideal rubber instead of a working fluid.

b. Write an expression for the efficiency of a Carnot engine using a piece of ideal rubber instead of a working fluid.

Problems for Section 22.7

22.68. 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 unit.)

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 g L^{-1}, using the Einstein equation, Eq. (22.7-2).

c. Find the viscosity at 20°C of the solution of part (a) using Eq. (22.7-9) and assuming that the limiting value of the specific viscosity can be used at this concentration.

***22.69.** Find the viscosity-average molecular mass of the polyvinyl alcohol sample of Problem 22.57.

22.70. Find the viscosity-average molecular mass of the polyvinyl alcohol sample of Problem 22.58.

General Problem

***22.71.** 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. The properties of gases arise primarily from the molecular kinetic energy while the properties of liquids and solids arise primarily from the molecular potential energy.

d. The stretching of a rubber band can be treated thermodynamically just like the stretching of a coil spring.

e. The Einstein temperature of a crystal is generally smaller than the Debye temperature of the same crystal.

f. 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.

g. All solids obey the law of Dulong and Petit at sufficiently high temperature.

h. 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.

i. The heat capacity of a nonconductor is approximately proportional to T^3 at sufficiently low temperature.

23

Some Additional Theories of Nonequilibrium Processes

OBJECTIVES

After studying this chapter, a student should:

1. understand the basic ideas of the RRK theory of unimolecular reactions;
2. understand the collisional activation of unimolecular reactions;
3. understand the molecular basis of transport processes in liquids;
4. understand the principles of nonequilibrium electrode processes;
5. understand the assumptions behind the Drude theory of electrical conduction and be able to solve simple exercises related to it.

PRINCIPAL FACTS AND IDEAS

1. Several theories of unimolecular reaction rates exist.
2. Very few reactions have been thoroughly studied on the molecular level.
3. Transport processes in liquids can be discussed in terms of the activated complex theory.
4. Nonequilibrium electrochemistry can be studied with the same theories as other chemical reactions.
5. Electrical conductivity in solids is described by the Drude theory.

23.1 Theories of Unimolecular Chemical Reactions

Unimolecular reactions are fairly rare, and many reactions once thought to be unimolecular actually occur by multistep mechanisms that produce first order kinetics. Three reactions accepted as unimolecular are[1]

$$Br_2 \rightarrow 2Br$$
$$SO_2Cl_2 \rightarrow SO_2 + Cl_2$$
$$\text{cyclo-}C_3H_6 \rightarrow CH_3CH{=}CH_2$$

In addition, the *cis–trans* isomerization at a C=C double bond appears to be unimolecular.

The Lindemann–Christiansen mechanism discussed in Section 13.3 apparently applies to most unimolecular reactions. For the unimolecular reaction of a substance C, this mechanism is given in Eq. (13.4-13):

$$(1) \qquad C + M \rightleftharpoons C^* + M \tag{23.1-1a}$$
$$(2) \qquad C^* \rightarrow \text{products} \tag{23.1-1b}$$

where C* stands for a molecule of C that is excited or activated by an inelastic collision with a molecule of the substance M. (The first C molecule could also collide with another molecule of C). From Eq. (13.4-18),

$$\frac{d[C]}{dt} = -k_{\text{uni}}[C] \tag{23.1-2}$$

where

$$k_{\text{uni}} = \frac{k_1k_2[M]}{k_2 + k_1'[M]} = \frac{k_2k_1}{\dfrac{k_2}{[M]} + k_1'} \tag{23.1-3}$$

This quantity k_{uni} is not a constant since it depends on [M], but in the limit of large concentration of M, k_{uni} becomes nearly constant and the reaction is first order. This is the assumption that was used in Chapter 13 in the analysis of reaction mechanisms.

The Activated Complex Theory of Unimolecular Reactions

The activated complex theory can be applied to a unimolecular reaction in the limit of large concentration (the region in which the reaction is first order). As an example unimolecular reaction, consider a *cis–trans* isomerization at a carbon–carbon double bond. The reaction is a 180° internal rotation of the atoms at one end of the double bond relative to those at the other end. In the orbital approximation the overlap between the unhybridized *p* orbitals from which we construct the π bonding orbital is at a maximum in the planar conformation (either *cis* or *trans*). Upon a rotation of 90°, the overlap between the *p* orbitals on the two carbon atoms vanishes, and the carbon–carbon bond becomes a single bond instead of a double bond. The molecule is in a transition state with an activation energy roughly equal to the difference between the C–C single bond energy and the C=C double bond energy.

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[1] K. J. Laidler, *Chemical Kinetics*, 3d ed., Harper and Row, New York, 1987, p. 151.

Application of the activated complex theory to the unimolecular process gives an expression analogous to Eq. (21.7-11) for the rate constant:

$$k = \frac{k_{\mathrm{B}}T}{h} e^{-\Delta\varepsilon_0^{\ddagger}/k_{\mathrm{B}}T} \frac{z^{\ddagger}}{z_{\mathrm{r}}} \tag{23.1-4}$$

where $_{\mathrm{r}}$ is the partition function of the reactant and $z^{\ddagger}$ is the partition function of the transition state without the factor for the reaction coordinate. Since the activated complex and the reactant molecule have the same atoms and nearly the same chemical bonding, all factors in the partition function might nearly cancel except for the factor of the "missing" vibrational normal mode. Since vibrational partition functions near room temperature are generally nearly equal to unity, the ratio $z^{\ddagger}/z_{\mathrm{r}}$ will nearly equal unity in those cases in which the activated complex resembles the reactant molecule. In this case, the preexponential factor in the rate constant is roughly equal to $k_{\mathrm{B}}T/h$, which at room temperature is approximately equal to $6 \times 10^{12}\ \mathrm{s}^{-1}$. In other cases, the activated complex is "looser" than the reactant molecule, having lower vibrational frequencies and larger moments of inertia, and in this case the preexponential factor is larger than $6 \times 10^{12}\ \mathrm{s}^{-1}$, since $z^{\ddagger}$ is then larger than z_{r}.

***Exercise 23.1**

Estimate the rate constant and the half-life of a *cis–trans* isomerization at 300 K. State any assumptions.

Other Theories of Unimolecular Reactions

Modern theories of unimolecular reactions are generally based on a theory due to Rice, Ramsperger, and Kassel,[2] which predated the activated complex theory. It begins with the Lindemann–Christiansen mechanism, discussed in Chapter 13 and summarized at the beginning of this chapter. Once a molecule becomes activated by an inelastic collision, even though it has enough energy to dissociate or to isomerize, this process does not occur immediately. If it did, the process would be an elementary bimolecular process and would be second order. One picture of what happens is that an inelastic collision excites some or all of the vibrational normal modes of the reactant molecule. This excited vibration goes on for a time, during which the normal modes exchange energy or change their relative phases until a vibrational amplitude of a specific bond becomes so large that the molecule reacts. This is sometimes referred to as "energy storage." It is assumed that the energy of a particular vibrational normal mode must have at least a threshold energy $\varepsilon_0{}^*$ in order to react. That is, if a molecule undergoes a strong collision such that its vibrational energy after the collision is equal to ε^*, then there is a chance for reaction to occur if ε^* is at least as large as $\varepsilon_0{}^*$ and if that energy can become concentrated in the reactive normal mode before deactivation occurs by another collision.

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[2] O. K. Rice and H. C. Ramsperger, *J. Am. Chem. Soc.*, **49**, 1616 (1927); **50**, 617 (1928); L. S. Kassel, *J. Phys. Chem.*, **32**, 225 (1928). See K. J. Laidler, *op. cit.*, pp. 150 ff, (Note 1) for a clear discussion.

The expression for the rate constant in the Lindemann–Christiansen mechanism is modified by assuming a different rate constant for each value of ε^*,

$$dk_{\text{uni}} = \frac{k_2(\varepsilon^*)f(\varepsilon^*)}{1+\dfrac{k_2(\varepsilon^*)}{k_1'[\mathrm{M}]}}\,d\varepsilon^* \tag{23.1-5}$$

and writing the total rate constant as the integral over all values of ε^* that are at least as large as $\varepsilon_0{}^*$:

$$k_{\text{uni}} = \int_{\varepsilon_0^*}^{\infty} dk_{\text{uni}} = \int_{\varepsilon_0^*}^{\infty} \frac{k_2(\varepsilon^*)f(\varepsilon^*)}{1+\dfrac{k_2(\varepsilon^*)}{k_1'[\mathrm{M}]}}\,d\varepsilon^* \tag{23.1-6}$$

where we have replaced the quotient k_1/k_1' by $f(\varepsilon^*)$. This quantity is the equilibrium constant for step 1, and it is taken as equal to the Boltzmann probability for energy ε^*. When this is expressed as a function of ε^*, the result for s vibrational normal modes is[3]

$$f(\varepsilon^*)\,d\varepsilon^* = \frac{1}{(s-1)!}\left(\frac{\varepsilon^*}{k_\mathrm{B}T}\right)^{s-1}\frac{1}{k_\mathrm{B}T}e^{-\varepsilon^*/k_\mathrm{B}T}\,d\varepsilon^* \tag{23.1-7}$$

The rate constant k_2 is the rate constant for the vibrational energy of excitation to accumulate in the reactive degree of freedom and for the reaction to occur. Rice, Ramsperger, and Kassel used the approximation that all of the vibrational degrees of freedom have the same frequency, so that their quanta of energy are of the same size. Consider a molecule with s vibrational normal modes. The number of ways to distribute j quanta of energy among s oscillators, with no restriction on the number of quanta in each oscillator, is

$$w = \frac{(j+s-1)!}{j!(s-1)!} \tag{23.1-8}$$

and the number of ways to have m quanta in one oscillator if there are $j-m$ quanta in the other oscillators is

$$w' = \frac{(j-m+s-1)!}{(j-m)!(s-1)!} \tag{23.1-9}$$

The probability of having m quanta in one oscillator if there are j quanta in all s oscillators is the ratio of these quantities:

$$r = \frac{w'}{w} = \frac{(j-m+s-1)!j!}{(j-m)!(j+s-1)!} \tag{23.1-10}$$

where we denote the ratio by the letter r.

If we apply Stirling's approximation in the form

$$n! = \left(\frac{n}{e}\right)^n \tag{23.1-11}$$

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[3] K. J. Laidler, *op. cit.*, pp. 77, 159 (Note 1).

the factors of e cancel. If we then make the assumption that $j - m \gg s - 1$, we get the result

$$r = \left(\frac{j-m}{j}\right)^{s-1} = \left(\frac{\varepsilon^* - \varepsilon_0^*}{\varepsilon^*}\right)^{s-1} \tag{23.1-12}$$

where we have used the fact that the number of quanta is proportional to the vibrational energy. The rate constant k_2 is now written in the form

$$k_2 = k^\ddagger\left(1 - \frac{\varepsilon_0^*}{\varepsilon^*}\right)^{s-1} \tag{23.1-13}$$

where $k^\ddagger$ is the rate constant for "free passage" over the "dividing surface" that marks the locations on the potential energy surface beyond which reaction is certain.

When Eq. (23.1-13) is substituted into Eq. (23.1-7), the result is

$$k_{\text{uni}} = \frac{k^\ddagger e^{-\varepsilon_0^*/k_\text{B}T}}{(s-1)!}\int_0^\infty \frac{x^{s-1}e^{-x}}{1 + \dfrac{k^\ddagger}{k_1'[\text{M}]}\left(\dfrac{x}{x+b}\right)^{s-1}}\,dx \tag{23.1-14}$$

where the substitution

$$x = \frac{\varepsilon^* - \varepsilon_0^*}{k_\text{B}T} \tag{23.1-15}$$

has been made.

In the limit of high pressure (large values of [M]), the rate constant approaches the limit:

$$\lim_{c\longrightarrow\infty} k_{\text{uni}} = k^\ddagger e^{-\varepsilon_0^*/k_\text{B}T} \tag{23.1-16}$$

Exercise 23.2

Verify Eq. (23.1-16).

In the original RRK theory, $k^\ddagger$ was considered to be a constant. However, the results of numerical calculations with Eq. (23.1-14) did not always agree well with experiment, often giving a value for the preexponential factor that was too small. However, if the high-pressure limit is made to agree with the activated complex result, Eq. (23.1-4), then

$$k^\ddagger = \frac{k_\text{B}T}{h}\frac{z^\ddagger}{z_\text{r}} \tag{23.1-17}$$

This allows for large preexponential factors in the case that the activated complex is "looser" than the reactant.

The RRK theory has been modernized by Marcus.[4] The resulting theory is called the RRKM theory, and this theory is the principal modern theory of unimolecular reactions.

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[4] R. Marcus, *J. Chem. Phys.*, **20**, 359 (1952).

23.2 The Molecular Case History of a Chemical Reaction

A reaction that has been thoroughly studied is[5]

$$F + H_2 \rightarrow H + HF \qquad (23.2\text{-}1)$$

Figure 23.1a shows the potential energy along the reaction coordinate, based on a semiempirical London–Eyring–Polanyi–Sato (LEPS) calculation. The molar energy change of the reaction from ground state to ground state is $\Delta E_0 = -29.2\ \text{kcal mol}^{-1}$ ($-122\ \text{kJ mol}^{-1}$). The height of the energy barrier (E_b) is small, $0.9\ \text{kcal mol}^{-1}$ ($4\ \text{kJ mol}^{-1}$), while the zero-point energies of the H_2 and HF are fairly large, respectively equal to $6.2\ \text{kcal mol}^{-1}$ and $5.85\ \text{kcal mol}^{-1}$ ($26\ \text{kJ mol}^{-1}$ and $24.5\ \text{kJ mol}^{-1}$). The zero-point energy of the activated complex is $6.9\ \text{kcal mol}^{-1}$ ($29\ \text{kJ mol}^{-1}$), so that the molar activation energy $\Delta E_0^{\ddagger}$ is equal to $1.6\ \text{kcal mol}^{-1}$ ($6.7\ \text{kJ mol}^{-1}$). 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." The reaction is sufficiently exoergic that the first four vibrational states of the product HF can be populated, as shown in Figure 23.1b.

Levine and Bernstein review the experimental and theoretical study of this reaction up to the time of publication of their book. The first investigation was a chemical 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, giving a surface in fairly good agreement with the LEPS surface from which Figure 23.1 was drawn. There followed 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.[6]

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[5] R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity*, Oxford University Press, New York, 1987, pp. 306ff, 396ff.

[6] 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. Letters*, **157**, 491 (1989).

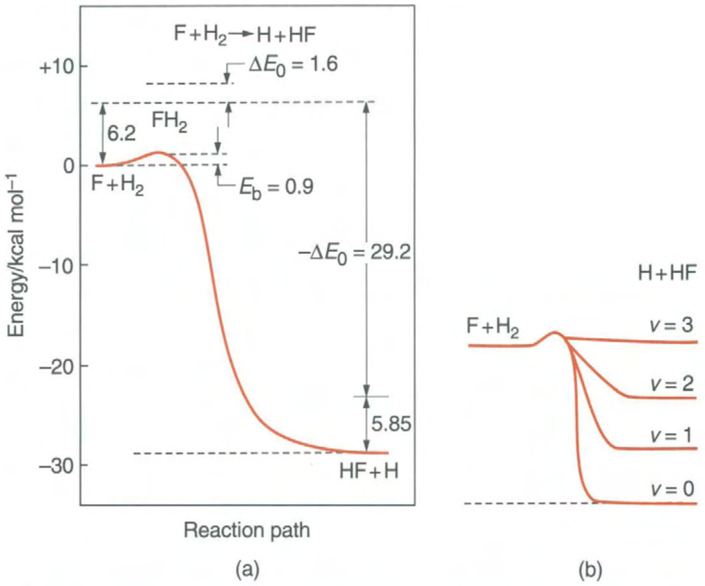

Figure 23.1. The Potential Energy on the Reaction Coordinate for Collinear FH_2. This figure is analogous to Figure 21.5c. The activation energy for the forward reaction is rather small. Figure 21.5b shows the surface for various final vibrational states. From R. D. Levine and R. B. Bernstein, *Molecular Reaction Dynamics and Chemical Reactivity*, Oxford University Press, New York, 1987, p. 127.

Several different potential energy surfaces were used in these calculations, but only states of zero angular momentum were included. Better agreement with experiment was attained. Further research is focused on finding better potential energy surfaces. A recent calculation gave a barrier height of 0.089 eV, corresponding to $8.6\,\mathrm{kJ\,mol^{-1}}$.[7] Gimenez *et al.* carried out a detailed comparison between their three-dimensional quantum-mechanical calculations, and found good agreement with experiment.[8] Aoiz and co-workers carried out a quasi-classical trajectory study and found significant discrepancies between recent experimental results and the theory.[9] Persky and Kornweitz published a critical review of the experimental data on this reaction.[10] 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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[7] G. E. Scuseria, *J. Chem. Phys.*, **95**, 7426 (1991).

[8] X. Gimenez, J. M. Lucas, A. Aguilar, and A. Lagana, *J. Phys. Chem.*, **97**, 8578 (1993).

[9] F. J. Aoiz, L. Banares, V. J. Herrero, V. S. Rabanos, K. Stark, and H.-J. Werner, *J. Chem. Phys.*, **102**, 9248 (1995).

[10] A. Persky and H. Kornweitz, *Int. J. Chem. Kinetics*, **29**, 67 (1997).

23.3 Theories of Transport Processes in Fluid Systems

Chapter 11 presented an elementary kinetic theory of transport processes in gases, based on formulas for collision rates and mean free paths. The activated complex theory of Eyring and Polanyi was applied to chemical reactions in Chapter 21. We now apply the same theory to diffusion, illustrating the fact that physical and chemical processes are not fundamentally different from each other from a theoretical point of view. We assume a quasi-lattice model system that resembles a disordered crystal, much as in the cage model described in Chapters 10, 11, and 13. We assume that fluctuating vacancies occur in the liquid, and 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 23.2. This potential energy maximum is analogous to the maximum along the reaction coordinate for a chemical reaction. We treat the coordinate representing motion into the vacancy as a reaction coordinate and treat the transition state of high potential energy as an activated complex. In the thermodynamic formulation of the activated complex theory, the rate constant is given by

$$k = \frac{k_{\mathrm{B}}T}{h} e^{-\Delta G^{\ddagger\circ}/RT} \tag{23.3-1}$$

where $\Delta G^{\ddagger\circ}$ is the Gibbs energy change per mole to form the activated complex in its standard state, not including motion along the reaction coordinate.

Assume a two-component liquid system in which the concentrations depend on the vertical coordinate z, with a larger concentration of component 2 at the bottom of the system. We assume that component 2 is fairly dilute, so that most of its neighbors are molecules of component 1. Consider a vacancy at height $z = z'$. On the average, there

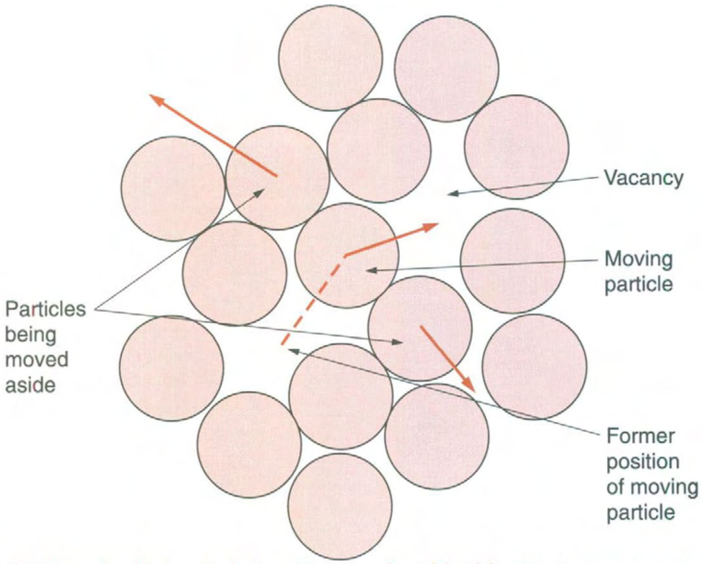

Figure 23.2. Motion of a Molecule into a Vacancy in a Liquid. This figure attempts to illustrate the position of maximum potential energy of a molecule moving from one shell of neighbors to another.

will be 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

$$\mathrm{Rate}_{\mathrm{b}} = kc_2(z' - a) \tag{23.3-2}$$

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 distance a will presumably be roughly equal to the nearest-neighbor distance, since some of the displacements are not parallel to the z axis but since the magnitude of some of the displacements will be greater than the nearest-neighbor distance. The rate at which molecules move into the vacancy from above is equal to

$$\mathrm{Rate}_{\mathrm{a}} = kc_2(z' + a) \tag{23.3-3}$$

We assume that the molecules coming from above on the average have the same z component and the same rate constant as those coming from below.

The net contribution to the diffusion flux is

$$J_{2z} = k[c_2(z' - a) - c_2(z' + a)]a \tag{23.3-4}$$

Let us write $c_2(z' + a)$ as a Taylor series around the point $z' - a$:

$$c_2(z' + a) = c_2(z' - a) + \frac{\partial c_2}{\partial z}(2a) + \cdots \tag{23.3-5}$$

where the derivative is evaluated at $z = z' - a$. If we neglect the terms not shown in Eq. (23.3-5), Eq. (23.3-4) becomes

$$J_{2z} = -\frac{k_{\mathrm{B}}T}{h}(2a^2)e^{-\Delta G^{\ddagger\circ}/RT}\left(\frac{\partial c_2}{\partial z}\right) \tag{23.3-6}$$

Comparison with Fick's law, Eq. (11.2-4), gives an expression for the diffusion coefficient,

$$D = 2\frac{k_{\mathrm{B}}T}{h}a^2 e^{-\Delta G^{\ddagger\circ}/RT} \tag{23.3-7}$$

EXAMPLE 23.1

Many liquids with molecules of ordinary size have diffusion coefficients approximately equal to $10^{-9}\ \mathrm{m^2\ s^{-1}}$. Assume that a is equal to 1×10^{-10} m and estimate the value of $\Delta G^{\ddagger\circ}$ for $T = 300$ K.

Solution

$$\begin{aligned}\Delta G^{\ddagger\circ} &= -RT\ \ln\left(\frac{Dh}{2a^2k_{\mathrm{B}}T}\right)\\ &= -(8.3\ \mathrm{J\ K^{-1}\ mol^{-1}})(300\ \mathrm{K})\ \ln\left(\frac{(10^{-9}\ \mathrm{m^2\ s^{-1}})(6.6 \times 10^{-34}\ \mathrm{J\ s})}{2(10^{-10}\ \mathrm{m})^2(1.4 \times 10^{-23}\ \mathrm{J\ K^{-1}})(300\ \mathrm{K})}\right)\\ &= 1 \times 10^4\ \mathrm{J\ mol^{-1}} = 10\ \mathrm{kJ\ mol^{-1}}\end{aligned}$$

This value is reasonable, being about one-fourth of a typical energy change of vaporization. (It is always a good idea to decide whether an answer to a numerical calculation has a reasonable size.)

The diffusion coefficient is sometimes written in the Arrhenius form, analogous to Eq. (13.3-1):

$$D = A_{\mathrm{d}} e^{-\Delta E_{\mathrm{ad}}/RT} \tag{23.3-8}$$

where E_{ad} is the activation energy and A_{d} is the preexponential factor for the diffusion process. To compare Eq. (23.3-7) with this equation, we recognize 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,

$$D = 2\frac{k_{\mathrm{B}}T}{h} a^2 e^{-\Delta S^{\ddagger\circ}/R} e^{-\Delta U^{\ddagger\circ}/RT} \tag{23.3-9}$$

and if we identify $\Delta U^{\ddagger\circ}$ with E_{a},

$$A_{\mathrm{d}} = 2\frac{k_{\mathrm{B}}T}{h} a^2 e^{-\Delta S^{\ddagger\circ}/R} \tag{23.3-10}$$

This preexponential factor is temperature-dependent, but its temperature dependence is much weaker than that of the exponential factor.

*Exercise 23.3

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.

a. Find the value of the apparent energy of activation.
b. Estimate the value of $\Delta S^{\ddagger}$, 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 molecules of different species, have been considered.[11] This exchange would correspond to a very high activation energy unless there were a vacancy adjacent to the pair of molecules, in which case the activation energy could be small enough that 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. Other processes could correspond to one molecule dragging another along with it. 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:

$$\mathbf{J}_i = -\sum_{j=1}^{c} D_{ij} \nabla c_j \tag{23.3-11}$$

In the theory of nonequilibrium thermodynamics, such cross-effects are systematically studied, and thermodynamic theorems relating the cross-coefficients are proved.[12]

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[11] R. G. Mortimer and N. H. Clark, *Ind. Eng. Chem. Fundam.*, **10**, 604 (1971).

[12] S. R. DeGroot and P. Mazur, *Nonequilibrium Thermodynamics*, North Holland, Amsterdam, 1962.

Viscosity

In viscous (shearing) flow in a liquid, one layer of molecules flows at a greater speed than an adjacent layer. If we use a moving coordinate system, one layer of molecules can be considered stationary, with the adjacent layer moving relative to it. In the simple model theory of transport processes, 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. (23.3-1). By Eq. (11.2-20), the viscosity is inversely proportional to the rate of shear, so that a formula of the Arrhenius type is

$$\eta = A_{\eta} e^{+E_{\mathrm{a}\eta}/RT} \qquad (23.3\text{-}12)$$

where $E_{\mathrm{a}\eta}$ is an activation energy and A_{η} is a preexponential factor for viscous flow. This activation energy should nearly equal that for diffusion in the same liquid.

Exercise 23.4

The viscosity of carbon tetrachloride at 20°C is equal to $9.69 \times 10^{-4}\ \mathrm{kg\ m^{-1}\ s^{-1}}$, and is equal to $6.51 \times 10^{-4}\ \mathrm{kg\ m^{-1}\ s^{-1}}$ at 50°C. Calculate the Arrhenius activation energy for viscosity, and compare it with the value for the activation energy for diffusion in Exercise 23.3a. Try to explain any difference in the activation energies.

There are various other theories of transport coefficients in liquids. In an approach that was pioneered by Kubo and by Green, formulas for transport coefficients are derived that contain time-correlation functions. For example, the coefficient of self-diffusion is given by[13]

$$D = \frac{1}{3}\int_0^{\infty} \langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle dt \qquad (23.3\text{-}13)$$

where $\mathbf{v}$ is the velocity of a molecule, and where $\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle$ is the **time-correlation function** of the velocity. Time-correlation functions are ensemble averages of a quantity evaluated at time 0 and the same quantity or a different quantity evaluated at time t. At $t = 0$, the time-correlation function in Eq. (23.3-13) is equal to the average of the square of the velocity, which in a classical system is $3k_{\mathrm{B}}T/m$. As time passes, the time-correlation function approaches zero, representing the decay of the correlation of the velocity of a molecule with its initial velocity. In a system of free noninteracting particles, the velocities would not change and the time-correlation function would remain constant. The decay of the time-correlation function allows the integral in Eq. (23.3-13) to converge. Frequency-dependent transport coefficients are given as Fourier transforms of the time-correlation functions instead of as time integrals of the time-correlation functions, which are equivalent to zero-frequency Fourier transforms.

EXAMPLE 23.2

Assume that the velocity–time correlation function of a molecule in a liquid is equal to

$$\langle \mathbf{v}(0)\cdot\mathbf{v}(t)\rangle = \frac{3k_{\mathrm{B}}T}{m} e^{-t/\tau} \qquad (23.3\text{-}14)$$

where τ is a **correlation time**, or a time for correlation of a particle's velocity with its initial velocity to be lost. The self-diffusion coefficient of $\mathrm{CCl_4}$ is equal to $1.30 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$ at 298.15 K. Find the value of τ.

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[13] D. A. McQuarrie, *Statistical Mechanics*, Harper and Row, New York, 1976, pp. 467ff.

Solution

$$D = \frac{k_B T}{m} \int_0^\infty e^{-t/\tau}\, dt = \frac{k_B T \tau}{m}$$

$$\tau = \frac{mD}{k_B T} = \frac{(2.56 \times 10^{-25}\ \text{kg})(1.3 \times 10^{-9}\ \text{m}^2\ \text{s}^{-1})}{(1.38 \times 10^{-23}\ \text{J K}^{-1})(298\ \text{K})} = 8.1 \times 10^{-14}\ \text{s}$$

***Exercise 23.5**

If a carbon tetrachloride molecule is moving with a speed equal to the rms speed of carbon tetrachloride molecules at 298 K, find the distance that it travels in a time equal to the correlation time from Example 23.2. Comment on the size of your answer.

Other transport coefficients are expressed in terms of different time-correlation functions. The exact calculation of a time-correlation function cannot be carried out, since this would involve solution of the equations of motion of the entire system, but a variety of techniques have been developed to obtain approximate results.[14]

23.4 Nonequilibrium Electrochemistry

Chapter 9 presented a discussion of the cell voltage of electrochemical cells at equilibrium. 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 the equilibrium value. This deviation arises from **polarization** of the cell. The extent of polarization for a given current is determined not only by the nature of the reactions but also by the concentrations of the electrolyte solutes, the surface area of the electrodes, stirring in the solution, etc. 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.

Electrolytic Cells near Equilibrium

Figure 23.3 schematically shows a particular electrolytic cell. The two electrodes are made of platinum, and the electrolyte solution is an aqueous HCl solution with unit activity. 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 in the opposite direction.

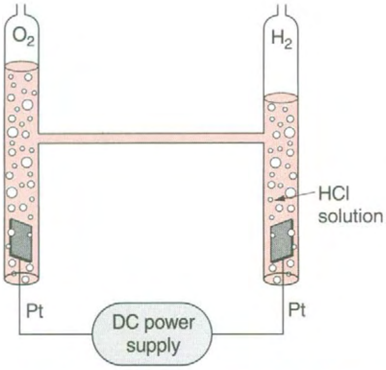

Figure 23.3. An Electrolytic Cell. This is a cell in which water can be electrolyzed by passage of a direct electric current. The volume of H_2 that is formed is twice that of the O_2 that is formed.

EXAMPLE 23.3

Find the voltage required to produce an infinitesimal electrolysis current at 298.15 K in the cell of Figure 23.3. 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.

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[14] D. A. McQuarrie, *op. cit.*, pp. 467ff (Note 13).

Solution

The only possible cathode half-reaction is

$$2\mathrm{H}^+ + 2e^- \rightarrow \mathrm{H}_2(\mathrm{g}) \qquad E^\circ = 0.0000\ \mathrm{V}$$

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:

$$2\mathrm{H}_2\mathrm{O} \rightarrow \mathrm{O}_2(\mathrm{g}) + 4\mathrm{H}^+ + 4e^- \qquad E^\circ = -1.229\ \mathrm{V}$$
$$2\mathrm{Cl}^- \rightarrow \mathrm{Cl}_2(\mathrm{g}) + 2e^- \qquad E^\circ = -1.3583\ \mathrm{V}$$

To produce oxygen at pressure P°, 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. Therefore, water, not chloride ions, will be oxidized at the anode if a voltage slightly larger than 1.229 V is applied to the cell.

If the products and reactants in Example 23.3 were not at unit activity, the Nernst equation would be used to find the voltage required to produce each possible product.

Exercise 23.6

a. Determine what products will be formed if an aqueous solution of sodium chloride with activity on the molality scale equal to 5.000 is electrolyzed with an infinitesimal current, 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.

The Electrical Double Layer

In order to discuss electrochemical cells with finite currents, we must investigate the molecular processes at the surfaces of the 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 phase 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 conductor. Ions and neutral molecules can also be adsorbed on an electrode surface. Adsorbed ions are divided into two classes. If the 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 exactly 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. If they are not specifically adsorbed, 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) with one sign of charge and a more diffuse layer made up of nonspecifically adsorbed ions of the opposite charge, as shown schematically in Figure 23.4a. This structure is called the **electrical double layer**, or sometimes the **diffuse double layer**. The layer of specifically adsorbed ions is called the **compact layer**, the **Helmholtz layer**, or the **Stern layer**. The plane of closest approach of nonspecifically adsorbed ions is sometimes called the **outer Helmholtz plane**, or the **Guoy plane**.

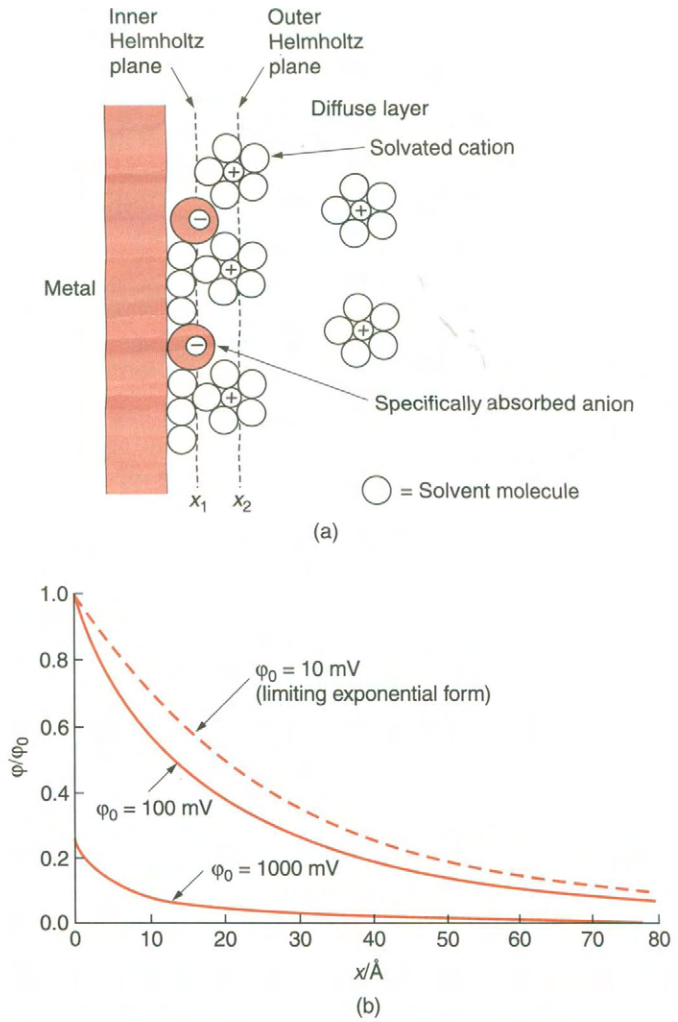

Figure 23.4. The Electrical Double Layer. (a) The structure of the double layer (schematic). The double layer consists of a layer of ions of one sign specifically adsorbed on the electrode surface, and a diffuse layer of hydrated ions of the opposite charge further from the electrode surface. **(b) The electric potential in the diffuse double layer.** From A. J. Bard and L. R. Faulkner, *Electrochemical Methods—Fundamentals and Applications*, Wiley, New York, 1980, pp. 8, 505.

Guoy and Chapman developed a theory of the charge distribution in the diffuse double layer about 10 years before Debye and Hückel developed their theory of ionic solutions, which is quite similar to it.[15] If one neglects nonelectrostatic contributions to the potential energy of an ion of valence z, the concentration of ions in a region of electric potential φ is given by the Boltzmann probability formula, Eq. (1.7-25):

$$c = c_0 e^{-ze\varphi/k_B T} = c_0 e^{-zF\varphi/RT} \tag{23.4-1}$$

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[15] G. Guoy, *J. Phys. (Paris)*, **9**, 457 (1910); D. L. Chapman, *Phil. Mag.*, **25**, 475 (1913).

where c is the concentration of the particular type of ion and c_0 is the concentration at a location where $\varphi = 0$. In the second version of the equation, F is Faraday's constant, equal to $N_{\mathrm{Av}}e = 96{,}485\ \mathrm{C\ mol^{-1}}$.

Guoy and Chapman combined Eq. (23.4-1) with the Poisson equation of electrostatics, and found (by an analysis similar to that of Debye and Hückel) that if the potential as taken equal to zero at large distances, the electric potential in the diffuse double layer is given by

$$\varphi = \varphi_0 e^{-\kappa x} \tag{23.4-2}$$

where φ_0 is the value of the potential at the surface of the electrode. The parameter κ is the same parameter as in the Debye–Hückel theory, given by Eq. (7.4-3):

$$\kappa = e\left(\frac{2N_{\mathrm{Av}}\rho_1 I}{\varepsilon k_{\mathrm{B}} T}\right)^{1/2} \tag{23.4-3}$$

where the symbols are defined in Section 7.4. Figure 23.4b 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 to 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 0.37) of its value at the surface, and is a measure of the effective thickness of the diffuse double layer.

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 carry charges of opposite sign on the two plates. Typical values of the capacitance of the electrical double layer range from 10 to 40 microfarads per square centimeter.[16]

*Exercise 23.7

Find the Debye length for a solution of HCl with a molality of $0.0200\ \mathrm{mol\ kg^{-1}}$.

The **charge density** (charge per unit volume) ρ_c is given by

$$\rho_c = F(z_+c_+ + z_-c_-) \tag{23.4-4}$$

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. (23.4-1), (23.4-2), and (23.4-4).

Exercise 23.8

Write the equation for the charge density in the Guoy–Chapman theory.

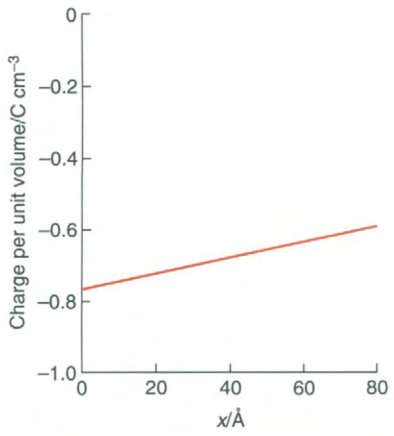

Figure 23.5. The Distribution of Charge in the Diffuse Double Layer. This distribution was calculated with the Guoy–Chapman theory.

Figure 23.5 shows the charge density in an aqueous 1–1 electrolyte solution of molality equal to $0.010\ \mathrm{mol\ kg^{-1}}$ at 298.15 K in the vicinity of a positive electrode with $\varphi_0 = 10\ \mathrm{mV}$, according to the Guoy–Chapman theory. Compare this figure with Figure 7.11 for the charge density near a negative ion in an electrolyte solution.

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[16] A. J. Bard and L. R. Faulkner, *Electrochemical Methods—Fundamentals and Applications*, Wiley, New York, 1980, p. 8.

Rates of Electrode Processes

When any chemical reaction comes to equilibrium, the forward and reverse processes cancel. The chemical reaction at an electrode is a half-reaction, so the forward reaction is an oxidation (anodic) half-reaction and the reverse reaction is a reduction (cathodic) half-reaction (or vice versa). Either of these half-reactions if occurring alone would correspond to a current passing through the electrochemical cell, and the half-reactions can be thought of as producing anodic and cathodic currents that cancel at equilibrium. The **exchange current** is defined as the equilibrium magnitude of each of these currents. The exchange current per unit area is denoted by i_0 and is commonly expressed in $\mathrm{A\ cm^{-2}}$ (amperes per square centimeter). In SI units it is expressed in $\mathrm{A\ m^{-2}}$.

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. However, 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 $0.02\ \mathrm{mol\ L^{-1}}\ \mathrm{Zn^{2+}}$ against a Zn 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.[17] The zinc electrode is said to be a reversible electrode, since it is possible in practice 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

There are three sources of **back e.m.f.** that oppose the passage of a current through an electrolytic cell. 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 the passage of an infinitesimal current, the reversible back e.m.f. is the only contribution to the back e.m.f. For a finite current, there is also a second source of back e.m.f., the "*IR* drop" in the voltage across the electrolyte solution due to its electrical resistance. 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 a measure of the polarization of the electrode.

There are two principal contributions to the overpotential.[18] 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. It exists in at least some systems because the reactive species have to pass through a transition state of high potential energy in order to react at an electrode.

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[17] H. A. Laitinen and W. E. Harris, *Chemical Analysis*, 2d ed., McGraw-Hill, New York, 1975, p. 233.

[18] H. A. Laitinen and W. E. Harris, *op. cit.*, p. 258ff (Note 17).

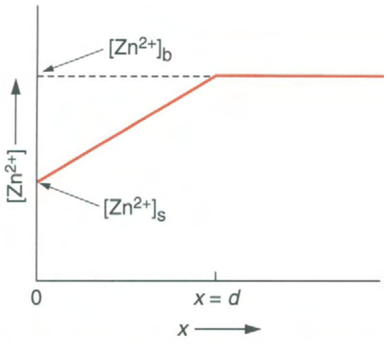

Figure 23.6. The Assumed Concentration Profile in a Boundary Layer near an Electrode. This concentration profile is assumed in order to obtain a relatively simple theory of the rates of electrode processes.

The Concentration Overpotential

If electrolysis (charging) is occurring in a Daniell cell 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 only by diffusion. As an oversimplification, let us assume that the concentration of zinc ions near the zinc electrode is as represented in Figure 23.6, where *d* is the effective thickness of a boundary layer. The value of *d* depends on the shape of the electrodes, the concentration of the solutes, the value of the diffusion coefficient, etc., so we will not attempt to evaluate it directly, but will express it in terms of a limiting current.

For a planar electrode and for the assumed concentration profile of Figure 23.6, Fick's law of diffusion, Eq. (11.2-4), gives the diffusion flux of zinc ions as

$$J_{Zn^{2+}} = D\frac{[Zn^{2+}]_b - [Zn^{2+}]_s}{d} \tag{23.4-5}$$

where D is the diffusion coefficient of Zn^{2+} ions, where $[Zn^{2+}]_b$ is the concentration in the bulk of the solution, and where $[Zn^{2+}]_s$ is the concentration at the surface. The current density j (current per unit area of electrode surface) is

$$j = nFD\frac{[Zn^{2+}]_b - [Zn^{2+}]_s}{d} \tag{23.4-6}$$

where n is the number of electrons reacting per ion ($n = 2$ in the case of Zn^{2+} ions).

As a larger electrolytic current flows, the concentration of zinc ions at the surface becomes smaller as they are reduced more rapidly. The current density approaches a limit for large counter e.m.f., when the surface concentration approaches zero:

$$j_{\text{lim}} = \frac{nFD[Zn^{2+}]_b}{d} \tag{23.4-7}$$

Of course, if the potential is increased enough, water can be reduced to form hydrogen gas, so the limiting value in Eq. (23.4-7) 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/d in Eq. (23.4-7) 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/d is replaced by a weighted sum of D/d and the rate of convection.

If we regard the boundary layer as a concentration cell, the analogue of Eq. (9.3-7) gives the electric potential difference across the boundary layer. This potential difference is the concentration overpotential, denoted by η_{conc}:

$$\eta_{\text{conc}} = \frac{RT}{nF}\ln\left(\frac{[Zn^{2+}]_b}{[Zn^{2+}]_s}\right) = \frac{RT}{nF}\ln\left(1 - \frac{j}{j_{\text{lim}}}\right) \tag{23.4-8}$$

where we have used Eqs. (23.4-6) and (23.4-7). We assume activity coefficients equal to unity and use the concentration description instead of the molality description.

Exercise 23.9

a. Show that Eq. (23.4-8) follows from Eqs. (23.4-6) and (23.4-7).

***b.** 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 and the assumptions that $d = 200\ \mu\text{m}$, that the concentration at the electrode is $0.0100\ \text{mol L}^{-1}$, and that the concentration in the bulk is 0.0200 mol L^{-1}. The diffusion coefficient for Cd^{2+} ions equals 8.7×10^{-10} m^2 s^{-1}.[19]

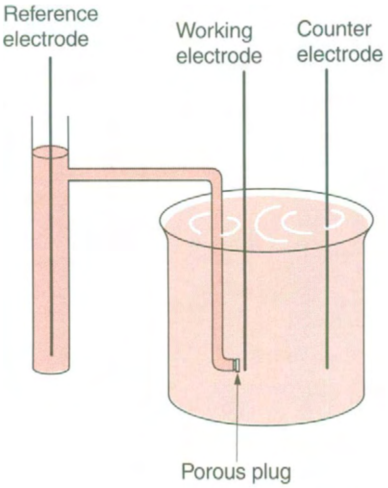

Figure 23.7. An Electrochemical Cell with a Third Electrode. The function of the third electrode (the counter electrode) is to provide a means of passing a current through the cell without passing a current between the reference electrode and the working electrode.

Equation (23.4-8) 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 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 electrode is built with a porous plug at the end, forming a liquid junction. The liquid junction potential is presumably fairly small, and should be very 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 23.7. 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.

The Activation Overpotential

This part of the overpotential is due to chemical processes at the electrode. For example, consider a cation of valence z that can be oxidized by losing n electrons at an inert electrode such as a platinum electrode. An example of such a half-reaction is

$$Fe^{2+} \rightleftharpoons Fe^{3+} + e^-$$

We write the general version of such a half-reaction equation:

$$R^{z+} \rightleftharpoons O^{(z+n)+} + ne^-$$

where R^{z+} stands for the reduced species and $O^{(z+n)+}$ stands for the oxidized species. In the Fe^{2+}/Fe^{3+} half-reaction, $z = 2$ and $n = 1$.

We assume that the progress of the reaction can be represented by a potential energy depending on a reaction coordinate as shown in Figure 23.8a. 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 1×10^8 V m^{-1}.

The maximum in the potential energy is partly due to the increase of the potential energy of the positive ion as it approaches the positive electrode, and partly due to the energy required to remove n electrons from the ion. This increase in potential energy is related to the ionization potential of the ion, but differs in that the electron is not removed into a vacuum but is transferred into the electrode. The decrease of potential energy as the reaction proceeds past the maximum in Figure 23.8a is due to the binding of the electrons into the electrode. This amount of energy is related to the negative of the work function of the electrode material, which is the minimum energy required to remove an electron from the electrode material into a vacuum, but differs since the electrons move into the electrode from ions instead of from a vacuum.

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[19] A. J. Bard and L. R. Faulkner, *op. cit.*, p. 154 (Note 16).

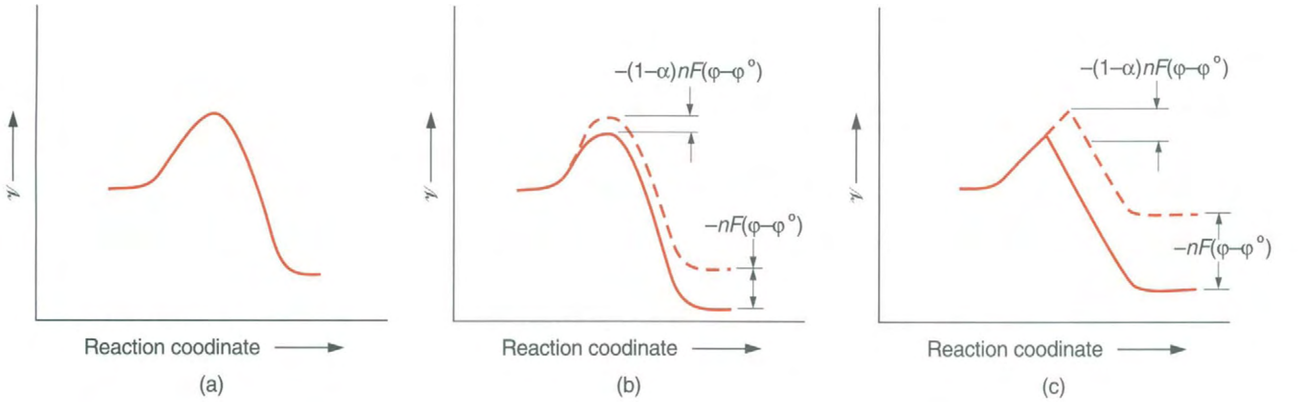

Figure 23.8. The Potential Energy as a Function of a Reaction Coordinate. **(a) Without applied potential.** In this figure, the potential energy is that for the oxidation of a cation by the loss of *n* electrons. The ion must approach the electrode, and the electrons must be removed. **(b) With a negative applied potential.** This figure is for the same process, but with a negative applied potential at the electrode. The applied potential changes the potential energy of the negative electrons in their final state (in the electrode), and changes the height of the maximum in the curve by a smaller amount. **(c) Figure to show the effect of the symmetry factor.** This figure shows an oversimplified analysis to determine the shift in the maximum of the potential energy curve. After A. J. Bard and L. R. Faulkner, *Electrochemical Methods—Fundamentals and Applications*, Wiley, New York, 1980, p. 94.

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 forward (oxidation) half-reaction. The potential energy required to reach the maximum from the right is the activation energy for the reverse (reduction) half-reaction. We write the forward and reverse rate constants for our unimolecular reaction in the "thermodynamic form" analogous to Eq. (21.7-12)

$$k = \frac{k_\mathrm{B}T}{h} e^{\Delta S^{\ddagger\circ}/R} e^{-\Delta H^{\ddagger\circ}/RT} = \frac{k_\mathrm{B}T}{h} e^{\Delta S^{\ddagger\circ}/R} e^{-\Delta U^{\ddagger\circ}/RT} \tag{23.4-9}$$

where we neglect the difference between $\Delta H^\ddagger$ and $\Delta U^\ddagger$. As in Eq. (21.7-18), we identify $\Delta U^\ddagger$ with the Arrhenius activation energy, E_a, and identify the preexponential factor as

$$A = \frac{k_\mathrm{B}T}{h} e^{\Delta S^{\ddagger\circ}/R} \tag{23.4.10}$$

The rate constants of the forward and reverse half-reactions can be written in the Arrhenius form:

$$k_\mathrm{ox} = A_\mathrm{ox} e^{-E_{\mathrm{a(ox)}}/RT} \tag{23.4-11a}$$

$$k_\mathrm{red} = A_\mathrm{red} e^{-E_{\mathrm{a(red)}}/RT} \tag{23.4-11b}$$

If the system is at equilibrium and if each half-reaction is first order in its reactant, we can write for unit area of the electrode

$$\begin{aligned}(\text{Oxidation rate per unit area}) &= k_\mathrm{ox}[\mathrm{R}]_\mathrm{eq} \\ &= (\text{reduction rate per unit area}) = k_\mathrm{red}[\mathrm{O}]_\mathrm{eq}\end{aligned}$$

where [O] is the concentration of the oxidized species ($\mathrm{Fe^{3+}}$ in our example) and [R] is the concentration of the reduced species at the surface of the electrode (we omit the subscript s). At equilibrium at the standard-state voltage, the concentrations are equal and $k_{\text{red}} = k_{\text{ox}}$. We denote this value of the rate constants by k°:

$$k^\circ = A_{\text{ox}} \exp\left(-\frac{E^\circ_{\text{aox}}}{RT}\right) = A_{\text{red}} \exp\left(-\frac{E^\circ_{\text{ared}}}{RT}\right) \tag{23.4-12}$$

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 when $E = E^\circ$) to a new value φ. The potential energy of n moles of electrons in the electrode is changed by an amount equal to $-nF(\varphi - \varphi^\circ)$. 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 23.8b, 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 23.8a.

Figure 23.8c 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, while 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 23.10

Show by sketching graphs similar to Figure 23.8c 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. (23.4-11) do not depend on the electric potential in the electrode, we write

$$\begin{aligned} k_{\text{ox}} &= A_{\text{ox}} \exp\left(-\frac{E_{\text{aox}} - (1-\alpha)nF(\varphi - \varphi^\circ)}{RT}\right) \\ &= k^\circ \exp\left(\frac{(1-\alpha)nF(\varphi - \varphi^\circ)}{RT}\right) \end{aligned} \tag{23.4-13a}$$

Similarly,

$$k_{\text{red}} = k^\circ \exp\left(\frac{-\alpha nF(\varphi - \varphi^\circ)}{RT}\right) \tag{23.4-13b}$$

Let us now investigate the case of equilibrium at a potential not necessarily equal to φ°. The magnitudes of the anodic and cathodic currents per unit area of electrode are given by

$$|j_a| = nFk_{ox}[R] \qquad (23.4\text{-}14a)$$

$$|j_c| = nFk_{red}[O] \qquad (23.4\text{-}14b)$$

At equilibrium, the net current is zero and the surface concentrations are equal to the bulk concentrations, so that

$$nFk^\circ \exp\left(\frac{(1-\alpha)nF(\varphi_{eq}-\varphi^\circ)}{RT}\right)[R]_b = nFk^\circ \exp\left(-\frac{\alpha nF(\varphi_{eq}-\varphi^\circ)}{RT}\right)[O]_b \qquad (23.4\text{-}15)$$

Each side of Eq. (23.4-15) 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 disappears from the equation:

$$\exp\left(\frac{nF(\varphi_{eq}-\varphi^\circ)}{RT}\right) = \frac{[O]_b}{[R]_b} \qquad (23.4\text{-}16)$$

This equation is equivalent to the Nernst equation if the reactants and products at the counter electrodes are at unit activities, which means that our treatment is consistent with equilibrium electrochemical theory.

Exercise 23.11

Carry out the algebraic steps to put Eq. (23.4-16) into the standard form of the Nernst equation.

If both sides of Eq. (23.4-16) are raised to the $-\alpha$ power, we obtain

$$\exp\left(\frac{-\alpha nF(\varphi_{eq}-\varphi^\circ)}{RT}\right) = \left(\frac{[O]_b}{[R]_b}\right)^{-\alpha} \qquad (23.4\text{-}17)$$

When Eq. (23.4-17) is substituted into Eq. (23.4-15), we obtain an expression for the exchange current density, j_0:

$$j_0 = nFk^\circ[R]_b^{1-\alpha}[O]_b^{\alpha} \qquad (23.4\text{-}18)$$

If the voltage is changed from the equilibrium value, the resulting current density is

$$\begin{aligned} j &= j_a - |j_c| \\ &= nFk^\circ \exp\left(\frac{(1-\alpha)nF(\varphi-\varphi^\circ)}{RT}\right)[R] - nFk^\circ \exp\left(-\frac{\alpha nF(\varphi-\varphi^\circ)}{RT}\right)[O] \end{aligned} \qquad (23.4\text{-}19)$$

where we count the current as positive if the electrode half-reaction proceeds in the oxidation direction.

Equation (23.4-19) 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

$$\eta = \varphi - \varphi_{eq} \qquad (23.4\text{-}20)$$

We divide the first time on the right-hand side of Eq. (23.4-19) by the left-hand side of Eq. (23.4-15) and divide the second term by the right-hand side of Eq. (23.4-15) and obtain

$$\frac{j}{j_0} = \frac{[\mathrm{R}]}{[\mathrm{R}]_\mathrm{b}} \exp\left(\frac{(1-\alpha)nF\eta}{RT}\right) - \frac{[\mathrm{O}]}{[\mathrm{O}]_\mathrm{b}} \exp\left(\frac{-\alpha nF\eta}{RT}\right) \tag{23.4-21}$$

Exercise 23.12

Carry out the steps of algebra to obtain Eq. (23.4-21).

Equation (23.4-21) 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 23.9 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. (23.4-21), which is then known as the **Butler–Volmer equation**:

$$\frac{j}{j_0} = \exp\left(\frac{(1-\alpha)nF\eta}{RT}\right) - \exp\left(\frac{-\alpha nF\eta}{RT}\right) \tag{23.4-22}$$

There are two important limiting cases. One is the case of small overpotential, in which case the exponents in Eq. (23.4-21) or Eq. (23.4-22) are small, and the approximation

$$e^x \approx 1 + x$$

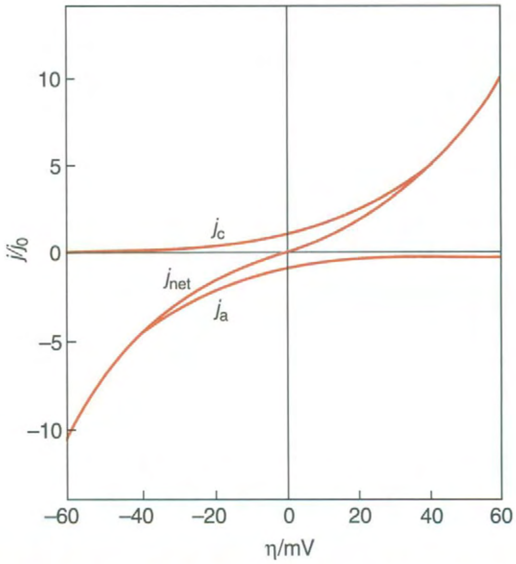

Figure 23.9. The Anodic Current, the Cathodic Current, and the Net Current at an Electrode as a Function of the Overpotential (Schematic). This figure shows how the net current is composed of the two contributions, which cancel at zero overpotential.

can be used. Application of this approximation to the Butler–Volmer equation gives

$$j \approx j_0\left(1 + \frac{(1-\alpha)nF\eta}{RT} - 1 + \frac{\alpha nF\eta}{RT}\right) \approx \frac{j_0 nF\eta}{RT} \qquad (23.4\text{-}23)$$

so that Ohm's law is obeyed. The factor $RT/(j_0nF)$ 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. (23.4-22), is much larger than the first term, and

$$|j| \approx j_0 e^{-\alpha nF\eta/RT} \qquad (23.4\text{-}24)$$

Solving this equation for η gives

$$\eta = \frac{RT}{\alpha nF}\ln(j_0) - \frac{RT}{\alpha nF}\ln(|j|) \qquad (23.4\text{-}25)$$

Equation (23.4-25) is of the form of the **Tafel equation**, an empirical equation of the form

$$|\eta| = a + b\log_{10}(|j|) \qquad (23.4\text{-}26)$$

Exercise 23.13

Derive the version of Eq. (23.4-25) that applies for large positive values of the overpotential.

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[20]

$$(1) \qquad H^+ + e^- + M \rightleftharpoons M\text{-}H \qquad (23.4\text{-}27a)$$

$$(2) \qquad 2M\text{-}H \rightarrow 2M + H_2 \qquad (23.4\text{-}27b)$$

where M denotes the metal of the electrode, and M-H denotes a chemisorbed hydrogen atom. Another possible mechanism is[21]

$$(1) \qquad H^+ + e^- + M \rightleftharpoons M\text{-}H \qquad (23.4\text{-}28a)$$

$$(2) \qquad M\text{-}H + H^+ + e^- \rightarrow M + H_2 \qquad (23.4\text{-}28b)$$

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. (23.4-27) is rate-limiting in both directions,

$$(\text{Forward rate}) = k_1[H^+]_G(1-\theta) \qquad (23.4\text{-}29)$$

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

$$[H^+]_G = [H^+]_b e^{-F\varphi_1/RT} \qquad (23.4\text{-}30)$$

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[20] K. J. Laidler, *J. Chem. Educ.*, **47**, 600 (1970).

[21] K. J. Laidler, *op. cit.* (Note 20).

where $[\mathrm{H}^+]_\mathrm{b}$ 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. (23.4-13a) for the rate constant,

$$j_0 = F(1-\alpha)[\mathrm{H}^+]_\mathrm{b} \exp\left(\frac{-F\varphi_1}{RT}\right) k^\circ \exp\left(\frac{(1-\alpha)nF(\varphi-\varphi^\circ)}{RT}\right) \tag{23.4-31}$$

With the expression in Eq. (23.4-31) for the exchange current, the Butler–Volmer equation, Eq. (23.4-22), and Eqs. (23.4-23) through (23.4-25) can be used, since it is of the same form for a reduction as for an oxidation half-reaction.

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[22]

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.

23.5 Electrical Conductivity in Solids

The Drude model system[23] represents the conduction of electrical currents in metallic conductors. The system consists of conduction electrons and positively charged "cores," which are the ions produced if the conduction electrons are removed from the atoms of the crystal. The electrons are assumed to obey classical mechanics, which is obviously a bad approximation for the motion of one electron, but which might be a usable approximation for the average motion of many electrons.

Since electrons are fermions, it is necessary to assume dilute occupation, so that most of the available electron states are vacant. At zero temperatures, all states of non-interacting fermions with energies up to the Fermi level are occupied and none with energies above the Fermi level are occupied, as discussed in Section 22.4. The Drude model must assume a high temperature in order for dilute occupation to be achieved.

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[22] W. C. Gardiner, Jr., *Rates and Mechanisms of Chemical Reactions*, W. A. Benjamin, New York, 1969, p. 197.

[23] See J. S. Blakemore, *Solid State Physics*, 2d ed., W. B. Saunders, Philadelphia, 1974, pp. 158ff, and D. Tabor, *Gases, Liquids and Solids*, 2d ed., Cambridge University Press, Cambridge, UK, 1979, pp. 188ff.

As the electrons move about in the crystal, they will interact with the nuclei. An accurate description of this interaction would treat the electrons quantum-mechanically and would include diffraction effects. However, the Drude model assumes that this interaction can be described adequately as a sequence of classical collisions with the nuclei. We define

$$\text{(Collision probability per unit time)} = \frac{1}{\tau} \tag{23.5-1}$$

The quantity $1/\tau$ is like a first-order rate constant, and the rate of collisions per unit volume is the number of electrons per unit volume times $1/\tau$, so that by analogy with the first-order chemical kinetics result,

$$n(t) = n(0)e^{-t/\tau} \tag{23.5-2}$$

where $n(t)$ is the number of electrons per unit volume that have not yet collided with a core at time t.

Now let us impose an external electric field $\mathscr{E}$ on the crystal. The field will accelerate the conduction electrons. Since the force on an electron is $-e\mathscr{E}$ (constant), the change in velocity of an electron in time t is, from Newton's second law:

$$\Delta\mathbf{v}(t) = -\frac{e\mathscr{E}t}{m} \tag{23.5-3}$$

where e is the magnitude of the charge on the electron and m is its mass. This change in velocity is imposed on whatever velocity the electron originally had. Before the field is imposed, no current is flowing, so that the original velocities of the conduction electrons vanish on the average. After the change in velocity is imposed on every electron, the average velocity is nonzero, and is similar to the drift velocity in the discussions of diffusion and ionic conductivity in earlier chapters. We treat the initial velocity as zero and take the right-hand side of Eq. (23.5-3) as the final velocity. The distance traveled (in excess of the distance due to the original velocity) from time 0 to time t' is obtained by integrating Eq. (23.5-3) from time 0 to time t':

$$\mathbf{r}(t') = -\frac{e\mathscr{E}t'^2}{2m} \tag{23.5-4}$$

We assume that with each collision the electron velocity is again randomized, so that on the average the velocity returns to zero value after the collision.

The rate at which electrons are undergoing collisions at time t is

$$\frac{dn}{dt} = -\frac{n(t)}{\tau} = -\frac{n(0)}{\tau}\,e^{-t/\tau} \tag{23.5-5}$$

The contribution of all electrons to the "electron transport" (equivalent to the electron flux times the time of transport) is

$$\int_0^\infty \mathbf{r}(t)\,\frac{dn}{dt}\,dt = \frac{-e\mathscr{E}n(0)}{2m\tau}\int_0^\infty t^2 e^{-t/\tau}dt = -\frac{e\mathscr{E}n(0)\tau^2}{m} \tag{23.5-6}$$

This formula for the electron transport is the same as if $n(0)$ electrons all had the "drift velocity" given by Eq. (23.5-3) for an acceleration time equal to τ,

$$\mathbf{v}_{\text{drift}} = -\frac{e\mathscr{E}\tau}{m} \tag{23.5-7}$$

and traveled for a time equal to τ. The electric current per unit area, **j**, is equal to the charge on one electron, $-e$, times the electron flux

$$\mathbf{j} = (-e)\left(\frac{-e\mathscr{E}n(0)\tau}{m}\right) = \frac{ne^2\tau}{m}\mathscr{E} \tag{23.5-8}$$

This equation is the same as Ohm's law, Eq. (17.5-5), if the conductivity is given by

$$\boxed{\sigma = \frac{ne^2\tau}{m}} \tag{23.5-9}$$

EXAMPLE 23.4

From the density of gold and the assumption 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

$$\sigma = \frac{1}{2.24\ \text{microohm cm}}\left(\frac{10^6\ \text{microohm}}{1\ \text{ohm}}\right)\left(\frac{100\ \text{cm}}{1\ \text{m}}\right)$$

$$= 4.46 \times 10^7\ \text{ohm}^{-1}\ \text{m}^{-1}$$

$$\tau = \frac{m\sigma}{ne^2} = \frac{(9.1 \times 10^{-31}\ \text{kg})(4.46 \times 10^7\ \text{ohm}^{-1}\ \text{m}^{-1})}{(5.90 \times 10^{28}\ \text{m}^{-3})(1.60 \times 10^{-19}\ \text{C})^2} = 2.7 \times 10^{-14}\ \text{s}$$

Exercise 23.14

a. Verify the units of the answer of Example 23.4, obtaining the SI units of ohms from Ohm's law.

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 20°C, find the mean drift speed. Find the ratio of the mean drift speed to the root-mean-square speed of electrons (using the classical formula) at this temperature.

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

$$\lambda = \langle v \rangle \tau \tag{23.5-10}$$

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, due to the smallness of the drift velocity. If we use the root-mean-square speed of Eq. (10.3-9), the conductivity is

$$\sigma = \frac{ne^2\lambda}{(3mk_{\mathrm{B}}T)^{1/2}} \tag{23.5-11}$$

EXAMPLE 23.5

Find the mean free path for electrons in gold at 20°C.

Solution

$$\lambda = \frac{(3mk_BT)^{1/2}\sigma}{ne^2}$$

$$= \frac{[3(9.11\times 10^{-31}\text{ kg})(1.38\times 10^{-23}\text{ J K}^{-1})(293\text{ K})]^{1/2}(4.46\times 10^{7}\text{ ohm}^{-1}\text{ m}^{-1})}{(5.90\times 10^{28}\text{ m}^{-3})(1.60\times 10^{-19}\text{ C})}$$

$$= 3.1\times 10^{-9}\text{ m}$$

This value seems reasonable, as it is roughly 10 lattice distances, and an electron would be expected to 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. One problem is that the conductivities of most common metals are found experimentally to be nearly inversely proportional to the temperature, instead of being inversely proportional to the square root of the temperature as in Eq. (23.5-11). One can rationalize this by arguing that the mean free path should decrease as the temperature rises, due to the increased vibrational amplitude of the cores, making them larger effective targets. 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. (23.5-9). The major differences are in the interpretation of the quantities n, τ, and m.[24]

Superconductivity

This phenomenon was discovered in 1911 by Onnes,[25] who found that the conductivity of mercury suddenly rose to a value at least as large as 10^{15} ohm^{-1} m^{-1} (and possibly infinite) when the mercury was cooled below a **transition temperature**, T_c, of 4.2 K. Onnes coined the name "superconductivity" for the phenomenon. Since that time, numerous substances have been found to exhibit superconductivity, generally with a transition temperature below 23 K. The transition to the superconducting state is a second-order phase transition (see Section 6.4). It is also found that a superconducting material rejects a magnetic field. That is, within the surface of the sample of material, a compensating magnetic field is generated that exactly cancels the magnetic field within the material, except for a surface layer of thickness 10–100 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.[26] This theory is based on the notion that under certain conditions the electrons interact with the lattice of the solid and modify the lattice vibrations 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 there is an input of energy to break up the pair, it is not possible for one of the electrons to be scattered by a nucleus.

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[24] J. S. Blakemore, *op. cit.*, pp. 162ff (Note 23).

[25] H. Kamerlingh Onnes, *Akad. van Wetenschappen (Amsterdam)*, **14**, 113 (1911).

[26] J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.*, **108**, 1175 (1957). This theory is known as the BCS theory.

At low temperature, there is not enough thermal energy to break up the pair, so that scattering does not occur. The electrons remain as a pair, even though they do not necessarily remain close to each other. A small voltage can now induce a current of Cooper pairs, conducting electrical current without observable resistance.

Beginning in 1986, a number of ceramic compounds were discovered that exhibit superconductivity with transition temperatures as high as 125 K.[27] However, the theory of Cooper pairs does not seem adequate to explain the superconductivity of these materials. The "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 compound to exhibit a transition above that of boiling liquid nitrogen was $YBa_2Cu_3O_x$, where x appears to range in value from about 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. The crystal structure of the superconducting material was determined by X-ray diffraction, and corresponds to four oxygen atoms around each copper atom, all in the plane of the copper atoms.[28]

In 1988, $Tl_2Ca_2Ba_2Cu_3O_{10+y}$, where y is smaller than unity, 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.[29] The relationship of this structure to the superconductivity of the compounds is apparently not yet clear.

Summary of the Chapter

In this chapter, we have examined several theories of nonequilibrium processes. The principal theory discussed for chemical reactions is the activated complex theory, in which it is assumed that the reactants in an elementary process form an activated complex that can be assumed to be at chemical equilibrium with the reactants.

A case history of the gas-phase chemical reaction was presented:

$$F + H_2 \rightarrow H + HF$$

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.

The activated complex theory was also applied to diffusion in liquids, in which the motion of a molecule from one "cage" into an adjacent cage is treated similarly to motion along a reaction coordinate of a chemical reaction, and during which an activated complex is assumed to form.

Nonequilibrium electrochemistry was discussed. The important physical fact is that, with a finite current flowing, the cell voltage can be different from its equilibrium value. The difference is partly due to the overpotential, which was discussed.

Electrical conduction in metals was briefly discussed in terms of the Drude model, in which electrical resistance is assumed to be due to collisions of conducting electrons with atomic cores (ions produced when conduction electrons are removed from atoms). Superconductivity was discussed briefly.

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[27] A. M. Thayer, *Chem. Eng. News*, **67**(48), 9 (Nov. 27, 1989).

[28] R. Dagani, *Chem. Eng. News*, **65**(19), 7 (May 11, 1987).

[29] R. Dagani, *Chem. Eng. News*, **66**(20), 24 (May 16, 1988); S. S. P. Parkin, *Phys. Rev. Letters*, **61**, 750 (1988).

PROBLEMS

Problem for Section 23.1

***23.15.** **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 K to the rate at 300 K. State any assumptions.

Problems for Section 23.3

23.16. The self-diffusion coefficient of liquid CCl_4 is given by Rathbun and Babb:[30]

$t_C/°C$	25	40	50	60
$D/10^{-9}\ m^2\ s^{-1}$	1.30	1.78	2.00	2.44

Find the value of A_d and the value of E_{ad} in Eq. (23.3-8). Assuming that $a = 4 \times 10^{-10}$ m, find $\Delta S^{\ddagger\circ}$ and $\Delta G^{\ddagger\circ}$.

***23.17.** The viscosity of water at 20°C is equal to $0.001005\ kg\ m^{-1}\ s^{-1}$, and at 50°C it is equal to $0.0005494\ kg\ m^{-1}\ s^{-1}$. Calculate the Arrhenius activation energy for viscosity in water.

23.18. Using the data in Problem 23.16, calculate the value of the correlation time τ in Eq. (23.3-14) for carbon tetrachloride at 50°C. Explain the temperature dependence of this parameter.

23.19. The representation of Example 23.2 for a velocity–time correlation function is not the only crude approximation that can be used.

***a.** Find the value of the parameter a in the representation

$$\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle = \frac{3k_BT}{m} e^{-t^2/2a^2}$$

for carbon tetrachloride at 25°C.

b. Construct graphs of the two representations of $\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle$.

c. How do you think the parameter a will depend on temperature?

Problems for Section 23.4

23.20. 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.

***23.21.** 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 the electrolysis cell of Example 23.3.

23.22. 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 $1.00\ cm^2$.

***23.23.** 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 $4.8 \times 10^{-6}\ A\ cm^{-2}$ at an overpotential of 0.60 V, and was equal to $3.7 \times 10^{-7}\ A\ cm^{-2}$ at an overpotential of 0.50 V. Find the values of the parameters in the Tafel equation, Eq. (23.4-26).

Problems for Section 23.5

23.24. The restivity 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 23.5).

d. Without looking up the value, estimate the resistivity of copper. Look up the correct value and compare your estimate to it.

23.25. 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.

23.26. **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. State any assumptions.

General Problem

23.27. Label each of the following statements as either true or false. If a statement is true only under special circumstances, label it as false.

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[30] R. E. Rathbun and A. L. Babb, *J. Phys. Chem.*, **65**, 1072 (1961).

a. The usual source of energy to populate the transition state in a unimolecular reaction is an inelastic collision.

b. The RRKM theory of unimolecular reactions is outmoded and no longer useful.

c. The mechanisms of most chemical reactions are not well characterized and understood.

d. Nonequilibrium electrochemical reactions can be understood with the same theories as other chemical reactions in the liquid phase.

e. By changing the amount of current flowing in an electrolytic cell, it is possible to change the products of the reaction.

f. The electrical conductivity of a typical metal increases with increasing temperature.

g. Zinc should be a better electrical conductor than copper because it has two 4*s* electrons while copper has only one.

h. It is reasonable that the activated complex should resemble the reactants more than the products if the reaction is highly exoergic.

i. It is reasonable that the activated complex should resemble the reactants more than the products if the activation energy of a given reaction is small.

A

Appendices
Tables of Numerical Data

Table A.1 Isothermal Compressibilities of Liquids

		$\kappa_T \times 10^{10}/\mathrm{Pa}^{-1}$			
		Temperature/°C			
Substance	Pressure/atm	25	45	65	85
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, FL, 1985, pp. F12–15ff.

Table A.2 Coefficients of Thermal Expansion at 20°C

Substance	$\alpha \times 10^3/\mathrm{K}^{-1}$
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*, 33d ed., Chemical Rubber Publishing Co., Cleveland, OH, 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/Pa m^6 mol^{-2}	$b \times 10^5$/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/Pa m^6 mol^{-2} K	$b \times 10^5$/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/Pa m^6 mol^{-2}	$b \times 10^5$/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	$V_{mc} \times 10^6\ \mathrm{m^3\ mol^{-1}}$	$P_c V_{mc}/RT$
Ammonia	405.6	114.0	70.4	0.238
Argon	151	49	75.2	0.291
Carbon dioxide	304	73.9	98.2	0.287
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., CRC Press, Boca Raton, FL, 1983, pp. F66–F67.

Table A.6 Molar Heat Capacities

Gases

$C_{P,\mathrm{m}} = a + bT + cT^{-2}$

(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	$C_{P,\mathrm{m}}$/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	$C_{P,\mathrm{m}}$/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	MP/°C	$\Delta_{\mathrm{fus}}H$/J g^{-1}	BP/°C	$\Delta_{\mathrm{vap}}H$/J g^{-1}
Ammonia	66.7		−33.35	1372
Benzene	5.5	127.4	80.1	549.24
Carbon dioxide	−56.6[a]	180.7	−78.5[b]	526.6
Carbon monoxide	−199	29.8	−191.5	240.98
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[a]

			Quantities			
$\frac{T}{\mathrm{K}}$	$\frac{C^\circ_{P,\mathrm{m}}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{S^\circ_\mathrm{m}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$-\frac{(G^\circ_\mathrm{m}-H^\circ_{\mathrm{m}298})}{T}$ / $\mathrm{J\,K^{-1}\,mol^{-1}}$	$\frac{H^\circ_\mathrm{m}-H^\circ_{\mathrm{m}298}}{\mathrm{kJ\,mol^{-1}}}$	$\frac{\Delta H^\circ_\mathrm{f}}{\mathrm{kJ\,mol^{-1}}}$	$\frac{\Delta G^\circ_\mathrm{f}}{\mathrm{kJ\,mol^{-1}}}$
			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
			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
			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
			C(cr, graphite)			
0	0	0		−1.051	0	0
298	0.517	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

(continued)

Table A.8 (*continued*)

			Quantities			
$\frac{T}{\text{K}}$	$\frac{C^\circ_{P,\text{m}}}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{S^\circ_\text{m}}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{-\frac{(G^\circ_\text{m}-H^\circ_{\text{m}298})}{T}}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{H^\circ_\text{m}-H^\circ_{\text{m}298}}{\text{kJ mol}^{-1}}$	$\frac{\Delta H^\circ_\text{f}}{\text{kJ mol}^{-1}}$	$\frac{\Delta G^\circ_\text{f}}{\text{kJ mol}^{-1}}$
			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	39.794	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
			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				0	−69.132	
298	52.63	229.60		(11.950)	−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

Table A.8 *(continued)*

			Quantities			
$\frac{T}{\mathrm{K}}$	$\frac{C^{\circ}_{P,\mathrm{m}}}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	$\frac{S^{\circ}_{\mathrm{m}}}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	$\frac{-\frac{(G^{\circ}_{\mathrm{m}}-H^{\circ}_{\mathrm{m}298})}{T}}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	$\frac{H^{\circ}_{\mathrm{m}}-H^{\circ}_{\mathrm{m}298}}{\mathrm{kJ\ mol^{-1}}}$	$\frac{\Delta H^{\circ}_{\mathrm{f}}}{\mathrm{kJ\ mol^{-1}}}$	$\frac{\Delta G^{\circ}_{\mathrm{f}}}{\mathrm{kJ\ mol^{-1}}}$
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	81.67	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
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-trimethylpentane), C_8H_{18}(g)						
298		423.2			−224.1	13.7
Iso-octane (2,2,4-trimethylpentane), 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
Cl(g)						
0	0	0		−6.272	119.621	119.621
298	21.838	165.189	165.189	0	121.302	105.306

(continued)

Table A.8 *(continued)*

			Quantities			
$\frac{T}{\mathrm{K}}$	$\frac{C^\circ_{P,\mathrm{m}}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{S^\circ_\mathrm{m}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$-\frac{(G^\circ_\mathrm{m}-H^\circ_\mathrm{m298})}{T}$ / $\mathrm{J\,K^{-1}\,mol^{-1}}$	$\frac{H^\circ_\mathrm{m}-H^\circ_\mathrm{m298}}{\mathrm{kJ\,mol^{-1}}}$	$\frac{\Delta H^\circ_\mathrm{f}}{\mathrm{kJ\,mol^{-1}}}$	$\frac{\Delta G^\circ_\mathrm{f}}{\mathrm{kJ\,mol^{-1}}}$
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	233.079	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
			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	73.390	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

Table A.8 (*continued*)

			Quantities			
$\frac{T}{\text{K}}$	$\frac{C^\circ_{P,\text{m}}}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{S^\circ_\text{m}}{\text{J K}^{-1}\text{ mol}^{-1}}$	$-\frac{(G^\circ_\text{m} - H^\circ_{\text{m}298})}{T}$ / $\text{J K}^{-1}\text{ mol}^{-1}$	$\frac{H^\circ_\text{m} - H^\circ_{\text{m}298}}{\text{kJ mol}^{-1}}$	$\frac{\Delta H^\circ_\text{f}}{\text{kJ mol}^{-1}}$	$\frac{\Delta G^\circ_\text{f}}{\text{kJ mol}^{-1}}$
500	29.260	145.737	133.973	5.882	0	0
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	216.035	216.035
298	20.784	114.713		0	217.999	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
			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	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
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
			HO_2(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

(continued)

Table A.8 *(continued)*

			Quantities			
$\frac{T}{\mathrm{K}}$	$\frac{C^\circ_{P,\mathrm{m}}}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	$\frac{S^\circ_\mathrm{m}}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	$\frac{-\frac{(G^\circ_\mathrm{m}-H^\circ_{\mathrm{m}298})}{T}}{\mathrm{J\ K^{-1}\ mol^{-1}}}$	$\frac{H^\circ_\mathrm{m}-H^\circ_{\mathrm{m}298}}{\mathrm{kJ\ mol^{-1}}}$	$\frac{\Delta H^\circ_\mathrm{f}}{\mathrm{kJ\ mol^{-1}}}$	$\frac{\Delta G^\circ_\mathrm{f}}{\mathrm{kJ\ mol^{-1}}}$
			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	153.2
			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
			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

Table A.8 (*continued*)

Quantities						
$\frac{T}{\mathrm{K}}$	$\frac{C^\circ_{P,\mathrm{m}}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{S^\circ_\mathrm{m}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$-\frac{(G^\circ_\mathrm{m}-H^\circ_{\mathrm{m}298})/T}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\frac{H^\circ_\mathrm{m}-H^\circ_{\mathrm{m}298}}{\mathrm{kJ\,mol^{-1}}}$	$\frac{\Delta H^\circ_\mathrm{f}}{\mathrm{kJ\,mol^{-1}}}$	$\frac{\Delta G^\circ_\mathrm{f}}{\mathrm{kJ\,mol^{-1}}}$
MgO(cr, macrocrystal)						
0				−5.167	−597.530	
298	37.15	26.74		0	−60.170	−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
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)						
298	77.256	305.376	304.376	0	9.179	97.787
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

(*continued*)

Table A.8 (*continued*)

			Quantities			
$\frac{T}{\text{K}}$	$\frac{C^\circ_{P,\text{m}}}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{S^\circ_\text{m}}{\text{J K}^{-1}\text{ mol}^{-1}}$	$-\frac{(G^\circ_\text{m}-H^\circ_{\text{m}298})}{T}$ / $\text{J K}^{-1}\text{ mol}^{-1}$	$\frac{H^\circ_\text{m}-H^\circ_{\text{m}298}}{\text{kJ mol}^{-1}}$	$\frac{\Delta H^\circ_\text{f}}{\text{kJ mol}^{-1}}$	$\frac{\Delta G^\circ_\text{f}}{\text{kJ mol}^{-1}}$
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	131.736
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
			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
			PCl_3(g)			
0				−15.932		
298	71.581	311.682	311.682	0	−288.696	−269.610
			PCl_5(g)			
0				−22.852		
298	111.890	364.288	364.288	0	−360.184	−290.271
			Pb(cr)			
0				−6.878		
298	26.44	64.81		0	0	0
			PbO_2(cr)			
298	64.64	68.6			−277.4	−217.33
			$PbSO_4$(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	

Table A.8 *(continued)*

			Quantities			
$\dfrac{T}{\mathrm{K}}$	$\dfrac{C^{\circ}_{P,\mathrm{m}}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\dfrac{S^{\circ}_{\mathrm{m}}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\dfrac{-\dfrac{(G^{\circ}_{\mathrm{m}}-H^{\circ}_{\mathrm{m298}})}{T}}{\mathrm{J\,K^{-1}\,mol^{-1}}}$	$\dfrac{H^{\circ}_{\mathrm{m}}-H^{\circ}_{\mathrm{m298}}}{\mathrm{kJ\,mol^{-1}}}$	$\dfrac{\Delta H^{\circ}_{\mathrm{f}}}{\mathrm{kJ\,mol^{-1}}}$	$\dfrac{\Delta G^{\circ}_{\mathrm{f}}}{\mathrm{kJ\,mol^{-1}}}$
			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
			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*, 3d 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.

[a] *Abbreviations*: cr = crystal; l = liquid; g = gas; ao = aqueous, molality standard state without (further) ionization; ai = aqueous, molality standard state with ionization.

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*, 3d 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/mol kg^{-1}					
Substance	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*, 2d 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 $P^\circ = 1$ bar

Half-cell symbol	Half-reaction	E°/V
$F^-\|F_2\|Pt$	$F_2(g) + 2e^- \rightarrow 2F^-$	+2.87
$H_2SO_4\|PbSO_4\|PbO_2$	$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$	+1.685
Ce^{3+}, $Ce^{4+}\|Pt$ (in 1 mol L^{-1} HNO_3)	$Ce^{4+} + e^- \rightarrow Ce^{3+}$	+1.61
Mn^{2+}, $MnO_4^-\|Pt$	$MnO_4^- + 8H^+ 5e^- \rightarrow Mn^{2+} + 4H_2O$	+1.491
$Au^{3+}\|Au$	$Au^{3+} + 3e^- \rightarrow Au$	+1.42
$Cl^-\|Cl_2\|Pt$	$Cl_2 + 2e^- \rightarrow 2Cl^-$	+1.3583
$Br^-\|Br_2\|Pt$	$Br_2 + 2e^- \rightarrow 2Br^-$	+1.065
$Au\|AuCl_4^-\|Cl^-$	$AuCl_4^- + 3e^- \rightarrow Au(s) + 4Cl^-$	+1.002
$Ag\|Ag^+$	$Ag^+ + e^- \rightarrow Ag$	+0.7986
$Hg_2^{2+}\|Hg(l)\|Pt$	$Hg_2^{2+} + 2e^- \rightarrow 2Hg(l)$	+0.7961
$Fe^{2+}\|Fe^{3+}\|Pt$	$Fe^{3+} + e^- \rightarrow Fe^{2+}$	+0.770
$MnO_2\|MnO_4^-\|Pt$	$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$	+0.588
$I^-\|I_2(s)\|Pt$	$I_2(s) + 2e^- \rightarrow 2I^-$	+0.535
$I^-\|I_2(aq)\|Pt$	$I_2(aq) + 2e^- \rightarrow 2I^-$	+0.6197
I^-, $I_3^-\|Pt$	$I_3^- + 2e^- \rightarrow 3I^-$	+0.5338
$OH^-\|O_2(g)\|Pt$	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	+0.401
$Cu(s)\|Cu^{2+}$	$Cu^{2+} + 2e^- \rightarrow Cu(s)$	+0.3402
$Cl^-\|Hg_2Cl_2(s)\|Hg(l)$	$Hg_2Cl_{2(s)} + 2e^- \rightarrow 2Hg(l) + 2Cl^-$	+0.268
$Cl^- AgCl(s)\|Ag(s)$	$AgCl(s) + e^- \rightarrow Ag(s) + Cl^-$	+0.2223
Sn^{4+}, $Sn^{2+}\|Pt$	$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	+0.15
$Br^-\|AgBr(s)\|Ag(s)$	$AgBr(s) + e^- \rightarrow Ag(s) + Br^-$	+0.0713
$H^+\|H_2\|Pt$	$2H^+ + 2e^- \rightarrow H_2$	0.000
$Fe^{3+}\|Fe(s)$	$Fe^{3+} + 3e^- \rightarrow Fe(s)$	−0.036
$Pb^{2+}\|Pb(s)$	$Pb^{2+} + 2e^- \rightarrow Pb(s)$	−0.1263
$I^-\|AgI(s)\|Ag(s)$	$AgI(s) + e^- \rightarrow Ag(s) + I^-$	−0.1519
$Cd^{2+}\|Cd(Hg)$	$Cd^{2+} + 2e^- \rightarrow Cd(Hg)$	−0.3521
$SO_4^{2-}\|PbSO_4(s)\|Pb(s)$	$PbSO_4(s) + 2e^- \rightarrow Pb(s) + SO_4^{2-}$	−0.356
$Cd^{2+}\|Cd(s)$	$Cd^{2+} + 2e^- \rightarrow Cd(s)$	−0.4026
$Fe^{2+}\|Fe(s)$	$Fe^{2+} + 2e^- \rightarrow Fe(s)$	−0.44
$S^{2-}\|Ag_2S(s)\|Ag(s)$	$Ag_2S(s) + 2e^- \rightarrow 2Ag(s) + S^{2-}$	−0.7051
$Zn^{2+}\|Zn(s)$	$Zn^{2+} + 2e^- \rightarrow Zn(s)$	−0.7628
$OH^-\|H_2(g)\|Pt$	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.8277
$Mg^{2+}\|Mg(s)$	$Mg^{2+} + 2e^- \rightarrow Mg(s)$	−2.375
$Na^+\|Na(s)$	$Na + e^- \rightarrow Na(s)$	−2.7109
$Ca^{2+}\|Ca(s)$	$Ca^{2+} + 2e^- \rightarrow Ca(s)$	−2.868
$K^+\|K(s)$	$K^+ + e^- \rightarrow K(s)$	−2.925
$Li^+\|Li(s)$	$Li^+ + e^- \rightarrow Li(s)$	−3.045

Table A.14 Parameters for the Lennard-Jones Potential

Substance	$\sigma \times 10^{10}$/m	(ε/k_B)/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, pp. 1110ff.

Table A.15 Effective Hard-Sphere Diameters

Substance	Temperature/K	$d \times 10^{10}/\mathrm{m}$
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, pp. F43ff.

Table A.16 Thermal Conductivities

Substance	Temperature/°C	$\kappa/\mathrm{J\ s^{-1}\ m^{-1}\ K^{-1}}$
	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	
Aluminium	25	237
Iron	25	80.4

From R. C. Weast, ed., *Handbook of Chemistry and Physics*, 64th ed., CRC Press, Boca Raton, FL, 1983, p. E2–E15.

Table A.17 Diffusion Coefficients for Dilute Solutes in Liquid Solutions

Solute	Solvent	Temperature/°C	$D \times 10^9/\mathrm{m^2\ s^{-1}}$
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, p. 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	12110
		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
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	0.2018
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, pp. F38ff.

Table A.19 Self-Diffusion Coefficients at $P = 1.000$ atm

Substance	Temperature/K	$D \times 10^4/\mathrm{m}^2\ \mathrm{s}^{-1}$
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	$\lambda_0 \times 10^3/\mathrm{m}^2\ \mathrm{ohm}^{-1}\ \mathrm{mol}^{-1}$	$u \times 10^8/\mathrm{m}^2\ \mathrm{s}^{-1}\ \mathrm{V}^{-1}$
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	Electronegativity	Element	Electronegativity
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

Molecule/term	$\frac{D_e/hc}{\mathrm{cm}^{-1}}$	$\frac{\tilde{\nu}_e}{\mathrm{cm}^{-1}}$	$\frac{\tilde{\nu}_e x_e}{\mathrm{cm}^{-1}}$	$\frac{\tilde{B}_e}{\mathrm{cm}^{-1}}$	$\frac{R_e}{\mathrm{Å}}$	$\frac{\tilde{\alpha}_e}{\mathrm{cm}^{-1}}$	$\frac{\tilde{\mathfrak{D}}_e}{10^{-4}\ \mathrm{cm}^{-1}}$
${}^{79}\mathrm{Br}_2/{}^1\Sigma_g^+$		325.32	1.077	0.0821	2.2821	0.000319	0.00021
${}^{12}\mathrm{C}^{16}\mathrm{O}/{}^1\Sigma^+$	90544	216.8	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
${}^{16}\mathrm{O}_2/{}^3\Sigma_g^-$		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	~2250

Table A.25 Characteristic Proton Chemical Shifts Relative to Tetramethyl Silane (TMS)

Group	δ/ppm
$-\mathrm{CO_2H}$	11–13
−CHO	9–10
Ar−H[a]	7–8
−C=CH	5–7
ROH[a]	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

[a] R stands for an aliphatic radical, Ar stands for an aromatic radical.

Table A.26 Character Tables for a Few Common Point Groups

C_{2v}	E	C_2	σ_{yz}	σ_{xz}	Function
A_1	1	1	1	1	z, z^2
A_2	1	1	−1	−1	xy, R_z
B_1	1	−1	−1	1	xz, R_y
B_2	1	−1	1	−1	yz, R_x

C_{3v}	E	$2C_3$	$3\sigma_v$	Function
A_1	1	1	1	z^2
A_2	1	1	−1	R_z
E	2	−1	0	x, y, R_x, R_y

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$	Function
A_g	1	1	1	1	1	1	1	1	z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	yz
Au	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	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$	Function
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	

Table A.26 *(continued)*

O_h	E	$8C_3$	$6C_4$	$6C_2$	$3C_2$	i	$6S_4$	$8S_6$	$3\sigma_h$	$6\sigma_d$	Function
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*, 3d ed., Academic Press, 1986, pp. 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 with independent variables x, y, and z is

$$df = \left(\frac{\partial f}{\partial x}\right)_{y,z} dx + \left(\frac{\partial f}{\partial y}\right)_{x,z} dy + \left(\frac{\partial f}{\partial z}\right)_{x,y} dz \tag{B-1}$$

where $(\partial f/\partial x)_{y,z}$, $(\partial f/\partial y)_{x,z}$, and $(\partial f/\partial z)_{x,y}$ are **partial derivatives.** A partial derivative with respect to one independent variable is obtained by the ordinary procedures of differentiation, treating all other independent variables as though they were constants. An example of Eq. (B-1) is

$$dP = \left(\frac{\partial P}{\partial T}\right)_{V,n} dT + \left(\frac{\partial P}{\partial V}\right)_{T,n} dV + \left(\frac{\partial P}{\partial n}\right)_{T,V} dn \tag{B-2}$$

This equation represents the value of an infinitesimal change in pressure that is produced when we impose arbitrary infinitesimal changes dT, dV, and dn on the system.

An approximate version of Eq. (B-2) can be written for finite increments in P, T, V, and n, equal respectively to ΔP, ΔT, ΔV, and Δn:

$$\Delta P \approx \left(\frac{\partial P}{\partial T}\right)_{V,n} \Delta T + \left(\frac{\partial P}{\partial V}\right)_{T,n} \Delta V + \left(\frac{\partial P}{\partial n}\right)_{T,V} \Delta n \tag{B-3}$$

where $\approx$ means "is approximately equal to." Equation (B-3) will usually be more nearly correct if the finite increments ΔT, ΔV, and Δn are small, and less nearly correct if the increments are large.

An Identity for a Change of Variables The expression for the differential of a function U 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, V, and n are used as the independent variables. If T, P, and n are used as the independent variables, then dU is given by

$$dU = \left(\frac{\partial U}{\partial T}\right)_{P,n} dT + \left(\frac{\partial U}{\partial P}\right)_{T,n} dP + \left(\frac{\partial U}{\partial n}\right)_{T,P} dn \tag{B-5}$$

In a nonrigorous fashion, 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 T 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 role 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 a second variable, this 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

$$df=\frac{df}{du}\left[\left(\frac{\partial u}{\partial x}\right)_{y,z}dx+\left(\frac{\partial u}{\partial y}\right)_{x,z}dy+\left(\frac{\partial u}{\partial z}\right)_{x,y}dz\right] \tag{B-11}$$

Second Derivatives and 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 Eqs. (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:

$$\left(\frac{\partial L}{\partial y}\right)_{x,z} = \left(\frac{\partial M}{\partial x}\right)_{y,z} \quad \text{(exact differential)} \tag{B-20a}$$

$$\left(\frac{\partial L}{\partial z}\right)_{x,y} = \left(\frac{\partial N}{\partial x}\right)_{y,z} \quad \text{(exact differential)} \tag{B-20b}$$

$$\left(\frac{\partial M}{\partial z}\right)_{x,y} = \left(\frac{\partial N}{\partial y}\right)_{x,z} \quad \text{(exact differential)} \tag{B-20c}$$

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

$$\int_c du = \int_c [M(x, y)\, dx + N(x, y)\, dy] \tag{B-21}$$

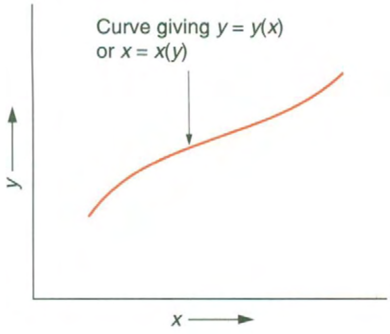

Figure B.1. A Curve Giving y as a Function of x or Giving x as a Function of y.

where the letter c denotes a curve in the x–y 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 $x(y)$:

$$\int_c du = \int_{x_1}^{x_2} M(x, y(x))\, dx + \int_{y_1}^{y_2} N(x(y), y,)\, dy \tag{B-22}$$

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 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. If T, V, and n are the independent variables, then this function is $z = z(T, V, n)$ and a line integral of dz is equal to the value of z at the endpoint of the integration minus the value of z at the starting point:

$$\begin{aligned}\int_c dz &= \int_c \left[\left(\frac{\partial z}{\partial T}\right)_{V,n} dT + \left(\frac{\partial z}{\partial V}\right)_{T,n} dV + \left(\frac{\partial z}{\partial n}\right)_{T,V} dn \right] \\ &= z(T_2, V_2, n_2) - z(T_1, V_1, n_1) \end{aligned} \tag{B-23}$$

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**. However, 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

$$I(a_1, a_2, b_1, b_2, c_1, c_2) = \int_{a_1}^{a_2} \int_{b_1}^{b_2} \int_{c_1}^{c_2} f(x, y, z)\, dz\, dy\, dx \tag{B-24}$$

The integrations are carried out sequentially. The left-most differential and the right-most 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.

If the variables are cartesian coordinates and the limits are constants, the region of integration is a rectangular parallepiped (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.

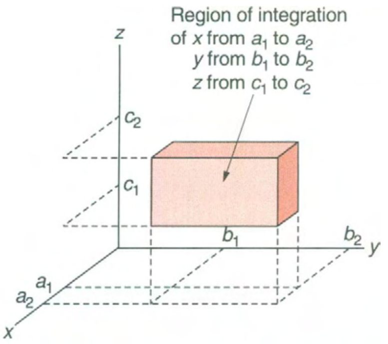

Figure B.2. An Integration Region in Cartesian Coordinates with Constant Limits.

The integration process can be depicted geometrically as follows: The product $dx\, dy\, dz$ is considered to be a **volume element**, which is depicted in Figure B.3 as a little box of finite size (the box of dimensions dx by dy by dz 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:

$$\text{(Contribution of the volume element } dx\, dy\, dz) = f(x, y, z)\, dx\, dy\, dz$$

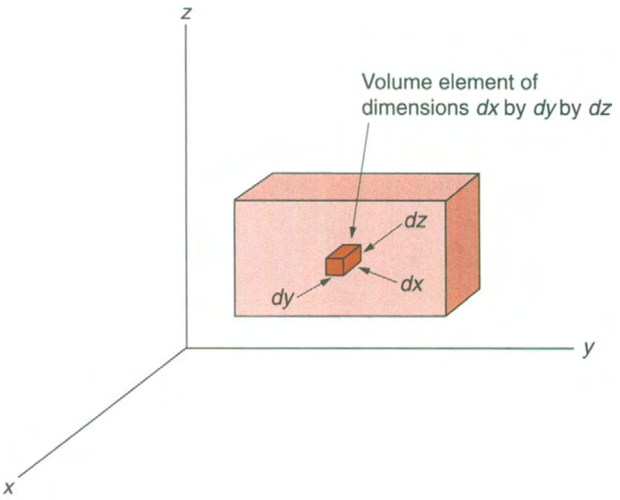

Figure B.3. An Infinitesimal Volume Element in Cartesian Coordinates.

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 a three-dimensional space is needed and spherical polar coordinates are used, the volume element is as depicted in Figure B.4. The length 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 $r\,d\theta$ 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 x–y plane has length $r\sin(\theta)$, as shown in the figure. The volume of the element of volume is thus

$$d^3\mathbf{r} = r^2\sin(\theta)\,d\phi\,d\theta\,dr \tag{B-25}$$

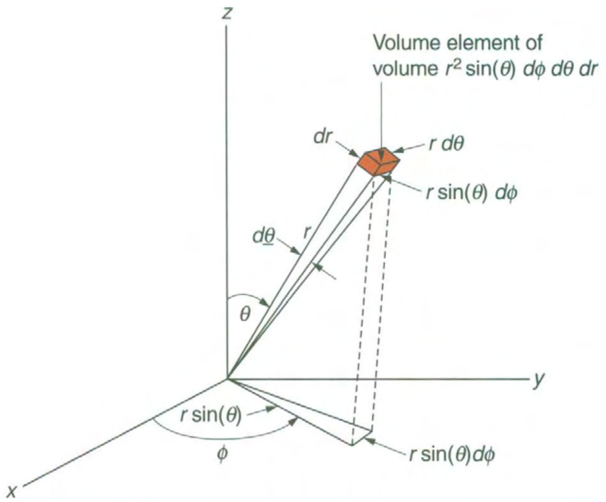

Figure B.4. An Infinitesimal Volume Element in Spherical Polar Coodinates.

where $d^3\mathbf{r}$ is a general abbreviation for a volume element in any coordinate system. An integral over all of space using spherical polar coordinates is

$$I = \int_0^\infty \int_0^\pi \int_0^{2\pi} f(r, \theta, \phi) r^2 \sin(\theta)\, d\phi\, d\theta\, dr \tag{B-26}$$

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 x–y plane), the Jacobian is the factor ρ, so that the element of volume is $\rho\, d\rho\, dz\, d\phi$.

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:

$$\mathbf{A} = \mathbf{i}A_x + \mathbf{j}A_y + \mathbf{k}A_z \tag{B-27}$$

where **i**, **j**, and **k** are unit vectors in the x, y, and z directions, respectively.

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:

$$\mathbf{A} \cdot \mathbf{B} = |\mathbf{A}||\mathbf{B}| \cos(\alpha) = AB \cos(\alpha) \tag{B-28}$$

where α is the angle between the vectors. The scalar product is commutative:

$$\mathbf{A} \cdot \mathbf{B} = \mathbf{B} \cdot \mathbf{A} \tag{B-29}$$

The scalar product of a vector with itself is the square of the magnitude of the vector:

$$\mathbf{A} \cdot \mathbf{A} = |\mathbf{A}|^2 = A^2 \tag{B-30}$$

The scalar products of the unit vectors are

$$\mathbf{i} \cdot \mathbf{j} = \mathbf{i} \cdot \mathbf{k} = \mathbf{j} \cdot \mathbf{k} = 0 \tag{B-31a}$$

$$\mathbf{i} \cdot \mathbf{i} = \mathbf{j} \cdot \mathbf{j} = \mathbf{k} \cdot \mathbf{k} = 1 \tag{B-31b}$$

If the vectors **A** and **B** are represented by cartesian components as in Eq. (B-27), Eq. (B-31) implies that six of the nine terms in the product **A** · **B** vanish, leaving

$$\mathbf{A} \cdot \mathbf{B} = A_x B_x + A_y B_y + A_z B_z \tag{B-32}$$

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:

$$|\mathbf{A} \times \mathbf{B}| = |\mathbf{A}||\mathbf{B}| \sin(\alpha) \tag{B-33}$$

The direction of the product vector is the direction in which an ordinary (right-handed) screw moves it if 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:

$$\mathbf{A} \times \mathbf{B} = -\mathbf{B} \times \mathbf{A} \tag{B-34}$$

The cross products of the unit vectors are

$$\mathbf{i} \times \mathbf{i} = 0, \qquad \mathbf{j} \times \mathbf{j} = 0, \qquad \mathbf{k} \times \mathbf{k} = 0 \tag{B-35a}$$

$$\mathbf{i} \times \mathbf{j} = \mathbf{k}, \qquad \mathbf{i} \times \mathbf{k} = -\mathbf{j}, \qquad \mathbf{j} \times \mathbf{k} = \mathbf{i} \tag{B-35b}$$

In terms of cartesian components, we can deduce from Eq. (B-35) that

$$\mathbf{A} \times \mathbf{B} = \mathbf{i}[A_y B_z - A_z B_y] + \mathbf{j}[A_z B_x - A_x B_z] + \mathbf{k}[A_x B_y - A_y B_x] \tag{B-36}$$

The product of a vector and a scalar is a vector whose magnitude is equal to the magnitude of the vector times the magnitude of the scalar. Its direction is the same as the direction of the first vector if the scalar is positive, and its direction is the opposite of the direction of the first vector if the scalar is negative.

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

$$\nabla f = \mathbf{i}\left(\frac{\partial f}{\partial x}\right) + \mathbf{j}\left(\frac{\partial f}{\partial y}\right) + \mathbf{k}\left(\frac{\partial f}{\partial z}\right) \tag{B-37}$$

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-37). The gradient of a vector quantity 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

$$\nabla \cdot \mathbf{F} = \left(\frac{\partial F_x}{\partial x}\right) + \left(\frac{\partial F_y}{\partial y}\right) + \left(\frac{\partial F_z}{\partial z}\right) \tag{B-38}$$

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 **curl** is a vector derivative of a vector function. The curl of **F** is somewhat similar to the vector product (cross product) of two vectors, and is denoted by $\nabla \times \mathbf{F}$ and defined by

$$\nabla \times \mathbf{F} = \mathbf{i}\left[\left(\frac{\partial F_z}{\partial y}\right) - \left(\frac{\partial F_y}{\partial z}\right)\right] + \mathbf{j}\left[\left(\frac{\partial F_x}{\partial z}\right) - \left(\frac{\partial F_z}{\partial x}\right) + \mathbf{k}\left[\left(\frac{\partial F_y}{\partial x}\right) - \left(\frac{\partial F_x}{\partial y}\right)\right] \tag{B-39}$$

The curl of a vector function is a measure of the turning of the vector as a function of position, and has also been called the "rotation." The curl of **F** has also been denoted as curl **F** and rot **F**.

The divergence of the gradient is called the **laplacian**. The laplacian of a scalar function f is given in cartesian coordinates by

$$\nabla^2 f = \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} + \frac{\partial^2 f}{\partial z^2} \tag{B-40}$$

The vector derivative operators can be expressed in other coordinate systems. In spherical polar coordinates, the gradient of the scalar function f is

$$\nabla f = \mathbf{e}_r \frac{\partial f}{\partial r} + \mathbf{e}_\theta \frac{1}{r} \frac{\partial f}{\partial \theta} + \mathbf{e}_\phi \frac{1}{r\sin(\theta)} \frac{\partial f}{\partial \phi} \tag{B-41}$$

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

$$\nabla^2 f = \frac{1}{r^2}\left[\frac{d}{dr}\left[r^2 \frac{df}{dr}\right] + \frac{1}{\sin(\theta)} \frac{\partial}{\partial \theta}\left[\sin(\theta) \frac{\partial f}{\partial \theta}\right] + \frac{1}{\sin^2(\theta)} \frac{\partial^2 f}{\partial \phi^2}\right] \tag{B-42}$$

B.4 Solution of a Differential Equation in Chapter 12

Equation (12.5-5) can be put into the form

$$dz = M\, d[\mathrm{B}] + N\, dt = 0 \tag{B-43}$$

where M and N are functions of t and [B], the concentration of substance B. The equation shown in Eq. (B-43) is called a **Pfaffian differential equation**. An equation of this type is called an **exact differential equation** if dz is an exact differential. We can determine whether dz is exact by finding out whether M and N conform to the Euler reciprocity relation. 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):

$$\frac{\partial M}{\partial t} = \frac{\partial^2 z}{\partial t\, \partial[\mathrm{B}]} = \frac{\partial^2 z}{\partial[\mathrm{B}]\, \partial t} = \frac{\partial N}{\partial[\mathrm{B}]} \tag{B-44}$$

We multiply Eq. (12.5-5) by dt and recognize that $(d[\mathrm{B}]/dt)dt = d[\mathrm{B}]$ to obtain an equation in Pfaffian form:

$$d[\mathrm{B}] + (k_2[\mathrm{B}] - k_1[\mathrm{A}]_0 e^{-k_1 t})\, dt = 0 \tag{B-45}$$

This equation is not an exact differential equation, since it corresponds to M equal to 1 and N equal to the expression in parentheses. 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

$$e^{k_2 t}\, d[\mathrm{B}] + (k_2[\mathrm{B}]e^{k_2 t} - k_1[\mathrm{A}]_0 e^{(k_2 - k_1)t})\, dt = 0 \tag{B-46}$$

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**. Since multiplication of any equation on both sides by the same factor yields a valid equation containing the same variables, this equation has the same solution as did the original equation. Finding an integrating factor for a particular equation is not always easy. However, mathematicians have shown that if one integrating factor exists, there is an infinite number of other integrating factors, so that trial and error might lead to a usable integrating factor.

Consider the special case that no B or F is present at time $t = 0$. We denote the differential in Eq. (B-46) by dz and perform a line integral of dz on the path shown in Figure B.5. The result of the integration must equal zero, since the differential equals zero if it satisfies the differential equation and the function z must therefore have the same value at the two ends of the path. The path of an exact differential depends only on the endpoints of the path, so any other path could have been chosen.

The d[B] term in dz gives no contribution on the first leg of the path. On the second leg we replace t by t' and obtain

$$\int_0^{[\mathrm{B}]_{t'}} e^{k_2 t'}\, d[\mathrm{B}] = e^{k_2 t'}[\mathrm{B}]_{t'} \qquad \text{(B-47)}$$

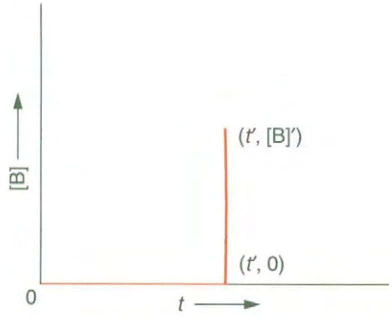

Figure B.5. The Path of Integration to Solve Eq. (12.5-9).

On the first leg of the path we replace [B] by zero, and the result is

$$-\int_0^{t'} k_1[\mathrm{A}]_0 e^{(k_2-k_1)t}\, dt = -\frac{k_1[\mathrm{A}]_0}{k_2-k_1}\left(e^{(k_2-k_1)t'} - 1\right) \qquad \text{(B-48)}$$

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-47) and (B-48) are combined and set equal to zero:

$$z(t', [\mathrm{B}]_{t'}) - z(0,0) = e^{-k_2 t'}[\mathrm{B}]_{t'} - \frac{k_1[\mathrm{A}]_0}{k_2-k_1}\left(e^{(k_2-k_1)t'} - 1\right) = 0 \qquad \text{(B-49)}$$

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:

$$[\mathrm{B}]_t = \frac{k[\mathrm{A}]_0}{k_2-k_1}\left(e^{-k_1 t} - e^{-k_2 t}\right) \qquad \text{(B-50)}$$

where we omit the prime symbol on t'.

B.5

Complex and Imaginary Quantities

Any complex quantity z can be written in the form

$$z = x + iy \qquad \text{(B-51)}$$

where x and y are real quantities and where i is the **imaginary unit**, defined to equal $\sqrt{-1}$. The quantity x is called the **real part** of z and y is called the **imaginary part** of z. Note that y is a real number, although it is called the imaginary part of z. The **complex conjugate** of z is denoted by z^* and is defined to have the same real part as z and an imaginary part that is the negative of that of z:

$$z^* = x - iy \quad \text{(definition of } z^*\text{)} \qquad \text{(B-52)}$$

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,

$$(e^{i\alpha})^* = e^{-i\alpha} \qquad \text{(B-53)}$$

as can be shown by using the identity

$$e^{i\alpha} = \cos(\alpha) + i\sin(\alpha) \qquad \text{(B-54)}$$

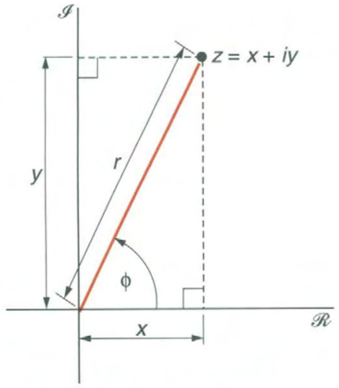

Figure B.6. The Argand Plane. A point in this diagram represents a complex number either in the form $x + iy$ or $re^{i\phi}$.

The product of any complex number and its complex conjugate is defined to be 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 $|z|^2$.

$$|z| = r = \sqrt{|z|^2} = \sqrt{z^*z} \tag{B-55}$$

where we use the common symbol r for the magnitude of z. If a complex number is written in the form of Eq. (B-51),

$$|z|^2 = z^*z = (x - iy)(x + iy) = x^2 + iyx - ixy + y^2 = x^2 + y^2 \tag{B-56}$$

Complex numbers are sometimes represented by the position of a point in the **Argand plane**, in which the real part $\mathscr{R}$ is plotted on the horizontal axis, and the imaginary part $\mathscr{I}$ is plotted on the vertical axis, as shown in Figure B.6. By the theorem of Pythagoras, the magnitude of a complex number r 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:

$$\phi = \arctan\left(\frac{y}{x}\right) \tag{B-57}$$

By using the identity in Eq. (B-54), we can show that a complex number can be represented in terms of r and ϕ:

$$z = re^{i\phi} \tag{B-58}$$

From this equation, we obtain

$$|z|^2 = z^*z = (re^{-i\phi}re^{i\phi}) = r^2 \tag{B-59}$$

B.6 Some Properties of Hermitian Operators

In Chapter 15 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

$$\hat{A}f_j(q) = a_j f_j(q) \tag{B-60}$$

We multiply both sides by the complex conjugate of the eigenfunction f_j, and integrate over all values of the coordinates:

$$\int f_j^* \hat{A} f_j \, dq = a_j \int f_j^* f_j \, dq \tag{B-61}$$

We now apply the definition of a hermitian operator, Eq. (15.2-10) to the left-hand side of this equation:

$$\int f_j^* \hat{A} f_j \, dq = \int (\hat{A}^* f_j^*) f_j \, dq \tag{B-62}$$

From the complex conjugate of the eigenvalue equation, Eq. (B-60), we can replace $\hat{A}^*f_j^*$ by $a_j^*f_j^*$, and by using Eq. (B-61) we obtain

$$\int f_j^*\hat{A}f_j\,dq = a_j\int f_j^*f_j\,dq = \int(\hat{A}^*f_j^*)f_j\,dq = a_j^*\int f_j^*f_j\,dq \tag{B-63}$$

Therefore,

$$a_j^* = a_j \tag{B-64}$$

A quantity equals its complex conjugate if and only if it is 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

$$\int f^*g\,dq = \int g^*f\,dq = 0 \quad \begin{pmatrix}\text{definition of}\\ \text{orthogonality}\end{pmatrix} \tag{B-65}$$

where f^* is the complex conjugate of f and g^* is the complex conjugate of g. The two integrals in Eq. (B-65) 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-60), by f_k^*, the complex conjugate of a different eigenfunction, and integrate:

$$\int f_k^*\hat{A}f_j\,dq = a_j\int f_k^*f_j\,dq \tag{B-66}$$

Now apply the hermitian property to the left-hand side of this equation:

$$\int f_k^*\hat{A}f_j\,dq = \int(\hat{A}^*f_k^*)f_j\,dq = a_k^*\int f_k^*f_j\,dq = a_k\int f_k^*f_j\,dq \tag{B-67}$$

where we have replaced a_k^* by a_k because we know a_k to be real. The left-hand sides of Eqs. (B-66) and (B-67) are equal, so the difference of the right-hand sides vanishes:

$$(a_j - a_k)\int f_k^*f_j\,dq = 0 \tag{B-68}$$

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:

$$\int f_k^*f_j\,dq = 0 \tag{B-69}$$

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 numbers 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

$$\mathbf{A} = \begin{bmatrix} A_{11} & A_{12} & A_{13} & \dots & A_{1n} \\ A_{21} & A_{22} & A_{23} & \dots & A_{2n} \\ A_{31} & A_{32} & A_{33} & \dots & A_{3n} \\ \dots & \dots & \dots & \dots & \dots \\ A_{m1} & A_{m2} & A_{m3} & \dots & A_{mn} \end{bmatrix} \tag{B-70}$$

The quantities that are 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 denoted by $\mathbf{C} = \mathbf{A} + \mathbf{B}$ and defined by

$$C_{ij} = A_{ij} + B_{ij} \qquad \text{for every } i \text{ and } j \tag{B-71}$$

The matrices **A**, **B**, and **C** must all have the same number of rows and the same number of columns.

The product of a matrix **A** and a scalar c is denoted by $\mathbf{B} = c\mathbf{A}$ and defined by

$$B_{ij} = cA_{ij} \qquad \text{for every } i \text{ and } j \tag{B-72}$$

The product of two matrices is similar to the scalar product of two vectors as written in Eq. (B-32). 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. Equation (B-32) is the same as

$$\mathbf{F} \cdot \mathbf{G} = F_1G_1 + F_2G_2 + F_3G_3 = \sum_{k=1}^{3} F_kG_k \tag{B-73}$$

We define matrix multiplication in a similar way. If **A**, **B**, and **C** are matrices such that **C** is the product **AB**, then

$$C_{ij} = \sum_{k=1}^{n} A_{ik}B_{kj} \tag{B-74}$$

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-73) 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-73) is then a special case of Eq. (B-74):

$$\mathbf{F} \cdot \mathbf{G} = [F_1 \quad F_2 \quad F_3] \begin{bmatrix} G_1 \\ G_2 \\ G_3 \end{bmatrix} \tag{B-75}$$

If two matrices are square, they can be multiplied together in either order. However, the multiplication is not always commutative. It is possible that

$$\mathbf{AB} \neq \mathbf{BA} \quad \text{(in some cases)} \tag{B-76}$$

However, matrix multiplication is associative:

$$\mathbf{A}(\mathbf{BC}) = (\mathbf{AB})\mathbf{C} \tag{B-77}$$

and matrix multiplication and addition are distributive:

$$\mathbf{A}(\mathbf{B}+\mathbf{C}) = \mathbf{AB}+\mathbf{AC} \tag{B-78}$$

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

$$\mathbf{EA} = \mathbf{AE} = \mathbf{A} \tag{B-79}$$

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. An identity matrix can have any number of rows and columns. It has the form

$$\mathbf{E} = \begin{bmatrix} 1 & 0 & 0 & \ldots & 0 \\ 0 & 1 & 0 & \ldots & 0 \\ 0 & 0 & 1 & \ldots & 0 \\ \ldots & \ldots & \ldots & \ldots & \ldots \\ 0 & 0 & 0 & \ldots & 1 \end{bmatrix} \tag{B-80}$$

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:

$$E_{ij} = \delta_{ij} = \begin{cases} 1 & \text{if } i = j \\ 0 & \text{if } i \neq j \end{cases} \tag{B-81}$$

The quantity δ_{ij} is called the **Kronecker delta**.

Just as in operator algebra, we do not define division by a matrix, but define the **inverse** of a square matrix. We denote the inverse of **A** by $\mathbf{A}^{-1}$ and require that

(B-82)

This multiplication of a matrix by its inverse is commutative, so that **A** is also the inverse of $\mathbf{A}^{-1}$. Finding the inverse of a matrix can involve a lot of computation, but BASIC processors such as TrueBASIC contain programs to carry out the calculation automatically.

There are several terms that apply to square matrices. Associated with each square matrix is a determinant (see later). 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 matrix is the sum of the diagonal elements of the matrix:

$$\mathrm{Tr}(\mathbf{A}) = \sum_{i=1}^{n} A_{ii} \tag{B-83}$$

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, 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").

$$(\tilde{A})_{ij} = A_{ji} \tag{B-84}$$

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 $\mathbf{A}^{\dagger}$.

$$(A^{\dagger})_{ij} = A_{ji}^{*} \tag{B-85}$$

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

$$\mathbf{A}^{-1} = \tilde{\mathbf{A}} \qquad \text{(orthogonal matrix)} \tag{B-86}$$

A **unitary matrix** is one whose inverse is equal to its hermitian conjugate. If **A** is unitary, then

$$\mathbf{A}^{-1} = \mathbf{A}^{\dagger} = \tilde{\mathbf{A}}{*} \qquad \text{(unitary matrix)} \tag{B-87}$$

Determinants A square matrix has a quantity associated with it 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 the matrix are constants, its determinant is a single constant. A 2 by 2 determinant is defined to equal

$$\begin{vmatrix} A_{11} & A_{12} \\ a_{21} & A_{22} \end{vmatrix} = A_{11}A_{22} - A_{12}A_{21} \tag{B-88}$$

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 matrix is an $n - 1$ by $n - 1$ matrix. 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 Equation (B-88).

Expanding a 3 by 3 determinant gives six terms, as follows:

$$\begin{vmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{vmatrix} = A_{11}\begin{vmatrix} A_{22} & A_{23} \\ A_{32} & A_{33} \end{vmatrix} - A_{12}\begin{vmatrix} A_{21} & A_{23} \\ A_{31} & A_{33} \end{vmatrix} + A_{13}\begin{vmatrix} A_{21} & A_{22} \\ A_{31} & A_{32} \end{vmatrix}$$

$$= A_{11}(A_{22}A_{33} - A_{23}A_{32}) - A_{12}(A_{21}A_{33} - A_{23}A_{31}) + A_{13}(A_{21}A_{32} - A_{22}A_{31}) \tag{B-89}$$

Expanding larger determinants can be tedious.

Determinants have a number of important properties:

Property 1. If two rows of a determinant are interchanged, the result will be 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 equal, the determinant has value zero.

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 zero, the value of the determinant is 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,

$$\begin{vmatrix} A_{11} + CA_{12} & A_{12} & A_{13} \\ A_{21} + CA_{22} & A_{22} & A_{23} \\ A_{31} + CA_{32} & A_{32} & A_{33} \end{vmatrix} = \begin{vmatrix} A_{11} & A_{12} & A_{13} \\ A_{21} & A_{22} & A_{23} \\ A_{31} & A_{32} & A_{33} \end{vmatrix} \tag{B-90}$$

Property 6. The determinant of a triangular matrix (a **triangular determinant**) is equal to the product of the diagonal elements. For example,

$$\begin{vmatrix} A_{11} & 0 & 0 \\ A_{21} & A_{22} & 0 \\ A_{31} & A_{32} & A_{33} \end{vmatrix} = A_{11}A_{22}A_{33} \tag{B-91}$$

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.

$$\det(\tilde{\mathbf{A}}) = \det(\mathbf{A}) \tag{B-92}$$

These properties can be verified using the expansion of a determinant by minors.

B.8 Fourier Series

Fourier series are important examples of series that are linear combinations of basis functions. Each term of the series is a constant coefficient times one of the basis functions. The basis functions in Fourier series are sine and cosine functions, which are periodic functions. Fourier series are therefore used to represent periodic function. A Fourier series that represents a periodic function of period $2L$ is

$$f(x) = a_0 + \sum_{n=1}^{\infty} a_n \cos\left(\frac{n\pi x}{L}\right) + \sum_{n=1}^{\infty} b_n \sin\left(\frac{n\pi x}{L}\right) \tag{B-93}$$

A periodic function of arbitrary shape is thus represented by having different amplitudes assigned to the different sine and cosine functions. This is analogous to the constructive and destructive interference of waves resulting from the addition of their displacements.

Fourier provided 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- 93) 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, related to equations in Appendix C. If m and n are integers,

$$\int_{-L}^{L} \cos\left(\frac{m\pi x}{L}\right) \cos\left(\frac{n\pi x}{L}\right) dx = L\delta_{mn} = \begin{cases} L & \text{if } m = n \neq 0 \\ 0 & \text{if } m \neq n \end{cases} \tag{B-94}$$

$$\int_{-L}^{L} \sin\left(\frac{m\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) dx = L\delta_{mn} = \begin{cases} L & \text{if } m = n \\ 0 & \text{if } m \neq n \end{cases} \tag{B-95}$$

$$\int_{-L}^{L} \cos\left(\frac{m\pi x}{L}\right) \sin\left(\frac{n\pi x}{L}\right) dx = 0 \tag{B-96}$$

The quantity δ_{mn} is called the **Kronecker delta**. It is equal to unity if its two indices are equal, and is equal to zero otherwise.

To find a_m for $m \neq 0$ we multiply both sides of Eq. (B-93) by $\cos(m\pi x/L)$ and integrate from $-L$ to L:

$$\begin{aligned}\int_{-L}^{L} f(x) \cos\left(\frac{m\pi x}{L}\right) dx &= \sum_{n=0}^{\infty} a_n \int_{-L}^{L} \cos\left(\frac{n\pi x}{L}\right) \cos\left(\frac{m\pi x}{L}\right) dx \\ &\quad + \sum_{n=1}^{\infty} b_n \int_{-L}^{L} \sin\left(\frac{n\pi x}{L}\right) \cos\left(\frac{m\pi x}{L}\right) dx \end{aligned} \tag{B-97}$$

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-97) vanish except for the term with two cosines in which $n = m$. The result is (unless $m = 0$):

$$\int_{-L}^{L} f(x) \cos\left(\frac{m\pi x}{L}\right) dx = a_m L \tag{B-98}$$

or

$$a_m = \frac{1}{L} \int_{-L}^{L} f(x) \cos\left(\frac{m\pi x}{L}\right) dx \qquad (m \neq 0) \tag{B-99}$$

This is a formula for finding all of the a coefficients except for a_0.

To find a_0, we use the fact that

$$\int_{-L}^{L} \cos(0)\cos(0)\,dx = \int_{-L}^{L} dx = 2L \tag{B-100}$$

which leads to

$$a_0 = \frac{1}{2L}\int_{-L}^{L} f(x)\,dx \tag{B-101}$$

A similar procedure consisting of multiplication by $\sin(m\pi x/L)$ and integration from $-L$ to L yields

$$b_m = \frac{1}{L}\int_{-L}^{L} f(x)\sin\left(\frac{m\pi x}{L}\right) dx \qquad (m = 1, 2, 3, \ldots) \tag{B-102}$$

A function does not have to be continuous in order to be represented by a Fourier series, but it must be integrable. 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.

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 the function $f(x)$ is an even function, 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, only the sine terms will appear, and the series is called a **Fourier sine series**. 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 as 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-54). One can write

$$b_n \sin\left(\frac{n\pi x}{L}\right) + a_n \cos\left(\frac{n\pi x}{L}\right) = \frac{1}{2}(a_n - ib_n)e^{in\pi x/L} + \frac{1}{2}(a_n + ib_n)e^{-in\pi x/L} \tag{B-103}$$

It is therefore possible to rewrite Eq. (B-93) as an **exponential Fourier series**:

$$f(x) = \sum_{n=-\infty}^{\infty} c_n e^{in\pi x/L} \tag{B-104}$$

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 being 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

$$k = \frac{n\pi}{L} \tag{B-105}$$

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-104) becomes an integral, which is called a **Fourier integral** or a **Fourier transform**.

$$f(x) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} F(k) e^{-ikx}\, dk \tag{B-106}$$

where the coefficient c_n in Eq. (B-104) is replaced by a function of k that is denoted by $F(k)/\sqrt{2\pi}$. The factor $1/\sqrt{2\pi}$ is included to make the formula for determining $F(k)$ look like this formula.

The equation for determining $F(k)$ is analogous to Eqs. (B-98), (B-101), and (B-102):

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) e^{-ikx}\, dx \tag{B-107}$$

We have introduced a factor of $1/\sqrt{2\pi}$ in front of the integral in Eq. (B-106) in order to have the same factor in front of this integral and the integral in Eq. (B-107).

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 $f(k)$ 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-107) to converge, the following integral must converge:

$$\int_{-\infty}^{\infty} |f(x)|^2\, dk < \infty \tag{B-108}$$

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**:

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) \cos(kx)\, dx = \sqrt{\frac{2}{\pi}} \int_{0}^{\infty} f(x) \cos(kx)\, dx \tag{B-109}$$

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**:

$$F(k) = \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} f(x) \sin(kx)\, dx = \sqrt{\frac{2}{\pi}} \int_{0}^{\infty} f(x) \sin(kx)\, dx \tag{B-110}$$

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

$$\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} f(y)g(x-y)\,dx \tag{B-111}$$

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 $f(k)$ 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

$$\frac{1}{\sqrt{2\pi}}\int_{-\infty}^{\infty} F(l)G(k-l)\,dl \tag{B-112}$$

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, pp. 464ff.

C

A Short Table of Integrals

C.1 Indefinite Integrals

$$\int \sin^2(x)\,dx = \frac{x}{2} - \frac{\sin(2x)}{4}$$

$$\int \cos^2(x)\,dx = \frac{x}{2} + \frac{\sin(2x)}{4}$$

$$\int \cos^n(x)\sin(x)\,dx = \frac{-1}{n+1}\cos^{n+1}(x) \qquad n = 1, 2, \ldots$$

$$\int \sin^n(x)\cos(x)\,dx = \frac{1}{n+1}\sin^{n+1}(x) \qquad n = 1, 2, \ldots$$

$$\int x\sin^2(x)\,dx = \frac{x^2}{4} - \frac{x\sin(2x)}{4} - \frac{\cos(2x)}{8}$$

$$\int x\cos^2(x)\,dx = \frac{x^2}{4} + \frac{x\sin(2x)}{4} + \frac{\cos(2x)}{8}$$

$$\int x^2\sin^2(x)\,dx = \frac{x^3}{6} - \left(\frac{x^2}{4} - \frac{1}{8}\right)\sin(2x) - \frac{x\cos(2x)}{4}$$

$$\int e^{ax}\,dx = \frac{1}{a}e^{ax}$$

C.2 Definite Integrals

$$\int_0^{\pi} \sin(mx)\sin(nx)\,dx = \begin{cases} \dfrac{\pi}{2} & \text{if } m = n \\ 0 & \text{if } m \neq n \end{cases} \qquad (m \text{ and } n \text{ integers})$$

$$\int_0^{\pi} \cos(mx)\cos(nx)\,dx = \begin{cases} \dfrac{\pi}{2} & \text{if } m = n \\ 0 & \text{if } m \neq n \end{cases} \qquad (m \text{ and } n \text{ integers})$$

$$\int_0^\pi \sin(mx)\cos(nx)\,dx = \begin{cases} 0 & \text{if } m = n \\ 0 & \text{if } m \neq n \ (m+n \text{ even}) \\ \dfrac{2m}{m^2 - n^2} & \text{if } m \neq n \ (m+n \text{ odd}) \end{cases}$$

$$\int_0^\infty e^{-ax}\,dx = \frac{1}{a}, \qquad a > 0$$

$$\int_0^\infty x^n e^{-ax}\,dx = \frac{1}{a^{n+1}}n! \qquad a > 0, n = 0, 1, 2, \dots$$

$$\int_0^\infty e^{-ax^2}\,dx = \frac{1}{2}\sqrt{\frac{\pi}{a}}, \qquad a > 0$$

$$\int_0^\infty xe^{-ax^2}\,dx = \frac{1}{2a}, \qquad a > 0$$

$$\int_0^\infty x^2 e^{-ax^2}\,dx = \frac{1}{4}\sqrt{\frac{\pi}{a^3}}, \qquad a > 0$$

$$\int_0^\infty x^3 e^{-ax^2}\,dx = \frac{1}{2a^2}, \qquad a > 0$$

$$\int_0^\infty x^{2n} e^{-ax^2}\,dx = \frac{(1)(3)(5)\cdots(2n-1)}{2^{n+1}a^{n+1/2}}\sqrt{\pi}, \qquad a > 0$$

$$\int_0^\infty x^{2n+1} e^{-ax^2}\,dx = \frac{n!}{2a^{n+1}}, \qquad a > 0$$

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

$$\operatorname{erf}(0) = 0, \qquad \operatorname{erf}(\infty) = 1$$

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 is a short table of values:

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 first 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

Classical Mechanics

Classical mechanics was the accepted version of mechanics prior to the development of relativity and quantum mechanics. It is accepted as correct in the limit of 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 formulated by Isaac Newton, and is summarized by Newton's three laws of motion.

D.1

Newton's Laws of Motion

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, the most important of the three laws, is the **law of acceleration**:

$$\mathbf{F} = m\mathbf{a} = m\,\frac{d\mathbf{v}}{dt} = \frac{d^2\mathbf{r}}{dt^2}$$

or

$$\mathbf{i}F_x + \mathbf{j}F_y + \mathbf{k}F_z = m\left(\mathbf{i}\,\frac{d^2x}{dt^2} + \mathbf{j}\,\frac{d^2y}{dt^2} + \mathbf{k}\,\frac{d^2z}{dt^2}\right) \tag{D-1}$$

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 vector $\mathbf{a}$, the time derivative of the velocity $\mathbf{v}$ and the second time derivative of the position vector $\mathbf{r}$, is called the **acceleration**. Newton's second law provides an equation of motion for an object obeying classical mechanics. See the example of the harmonic oscillator in Section 10.1.

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 which is equal in magnitude to the first force and opposite in direction.*

If the force is a known function of position, Eq. (D-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**.

All mechanical quantities have values that are determined by the values of coordinates and velocities. The energy is such a state function and is the sum of the kinetic and potential energies. The kinetic energy of a point mass particle is

$$\mathcal{K} = \tfrac{1}{2}mv^2 = \tfrac{1}{2}m(v_x^2 + v_y^2 + v_z^2) \tag{D-2}$$

If the forces on the particles of a system depend only on the particles' positions, these forces can be derived from the potential energy. Consider motion in the z direction. If z'

and z'' are two values of z, the difference in the potential energy $\mathcal{V}$ 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''.

$$\mathcal{V}(z'') - \mathcal{V}(z') = \int_{z_1}^{z_2} F_{\mathrm{ext(rev)}}(z)\, dz \tag{D-3}$$

Since only the difference in potential energy is defined in Eq. (D-3), we have the option of deciding at what location we want to have the potential energy equal zero. We accomplish this by adding an appropriate constant to a formula for the potential energy.

The external force $F_{\mathrm{ext(rev)}}$ must exactly balance the force due to the other particles in order for the process to be reversible:

$$F_{\mathrm{ext(rev)}}(z) = -F_z \tag{D-4}$$

By the principles of calculus, the integrand in Eq. (D-3) is equal to the derivative of the function $\mathcal{V}$, so that

$$F_z = -\frac{d\mathcal{V}}{dz} \tag{D-5}$$

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

$$F = \mathbf{i}F_x + \mathbf{j}F_y + \mathbf{k}F_z = -\mathbf{i}\left(\frac{\partial \mathcal{V}}{\partial x}\right) - \mathbf{j}\left(\frac{\partial \mathcal{V}}{\partial y}\right) - \mathbf{k}\left(\frac{\partial \mathcal{V}}{\partial z}\right) = -\nabla \mathcal{V} \tag{D-6}$$

where the symbol ∇ ("del") stands for the three-term **gradient operator** in the right-hand side of the first line of Eq. (D-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**. An example of this conservation is seen in the case of the harmonic oscillator. See Eq. (14.1-15).

D.2 The Wave Equation for a Flexible String

Consider a small portion of the string lying between x and $x + \Delta x$, as shown in Figure D-1. The 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 any part of 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. If the string is curved, the forces at the two ends of a portion of the string will not cancel, but the forces at the two ends of a straight portion do cancel.

We denote the angles between the x axis and the two tangent lines by α_1 and α_2. For small displacements, the net force on the string segment will lie in the z direction:

$$\begin{aligned} F_z &= F_{2z} + F_{1z} = T\sin(\alpha_2) - T\sin(\alpha_1) \approx T[\tan(\alpha_2) - \tan(\alpha_1)] \\ &\approx T\left[\left(\frac{\partial z}{\partial x}\right)\bigg|_{x+\Delta x} - \left(\frac{\partial z}{\partial x}\right)\bigg|_{x}\right] \end{aligned} \tag{D-7}$$

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. The measure of the angle in radians is also nearly equal to the sine and the tangent for this small angle. We have also

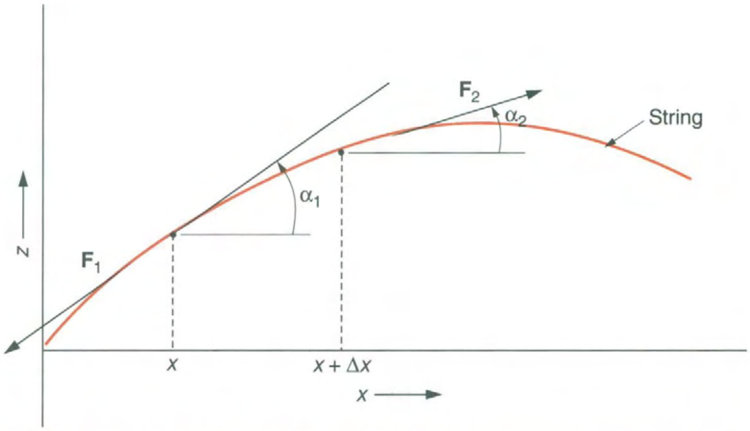

Figure D.1. The Position of a Flexible String and the Forces on a Segment of the String. This arbitary conformation of the string as a function of length along the string is used to describe the forces on a small segment of the string.

used the fact that the first derivative is equal to the tangent of the angle between the horizontal and the tangent line.

Denote the mass per unit length of the string by ρ. The mass of the string segment is $\rho\ \Delta x$ and its acceleration is $(\partial^2 z/\partial t^2)$, so that from Newton's second law,

$$T\left[\left(\frac{\partial z}{\partial x}\right)\bigg|_{x+\Delta x} - \left(\frac{\partial z}{\partial x}\right)\bigg|_{x}\right] = \rho\ \Delta x\ \frac{\partial^2 z}{\partial t^2} \tag{D-8}$$

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:

$$\lim_{\Delta x \to 0}\left[\frac{\left(\frac{\partial z}{\partial x}\right)\Big|_{x+\Delta x} - \left(\frac{\partial z}{\partial x}\right)\Big|_{x}}{\Delta x}\right] = \frac{\partial^2 x}{\partial x^2}$$

This equation is substituted into Eq. (D-8) to obtain the classical wave equation:

$$\frac{\partial^2 z}{\partial x^2} = \frac{1}{c^2}\frac{\partial^2 z}{\partial t^2} \tag{D-9}$$

where $c^2 = T/\rho$.

D.3 Lagrangian Mechanics

The method of Lagrange and the method of Hamilton are designed for problems in which cartesian coordinates cannot conveniently be used. We denote 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, etc. To specify the state of the system, some measures of the particles's velocities are needed in addition to coordinates. The Lagrangian method uses the time derivatives of the coordinates:

$$\dot{q}_i = \frac{dq_i}{dt} \qquad (i = 1, 2, \ldots, n) \tag{D-10}$$

We use a symbol with a dot over it to represent a time derivative.

The Lagrangian function is defined by

$$\mathscr{L} = \mathscr{K} - \mathscr{V} \quad \text{(definition of the Lagrangian)} \tag{D-11}$$

where $\mathscr{K}$ and $\mathscr{V}$ are the kinetic and potential energy expressed in terms of the q's and the $\dot{q}$'s. The *Lagrangian equations of motion* are

$$\frac{d}{dt}\frac{\partial \mathscr{L}}{\partial \dot{q}_i} - \frac{\partial \mathscr{L}}{\partial q_i} = 0 \qquad (i = 1, 2, \ldots, n) \tag{D-12}$$

These equations are equivalent to Newton's second law. The convenient thing about them is that they 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.[1]

One application of Lagrange's equations of motion is to a particle orbiting about a fixed point in a plane. Using plane polar coordinates ρ and ϕ (measured in radians), with the origin 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

$$\mathscr{L} = \tfrac{1}{2}m\dot{\rho}^2 + \tfrac{1}{2}m\rho^2\dot{\phi}^2 - \mathscr{V}(\rho, \phi) \tag{D-13}$$

and the Lagrangian equations of motion are

$$\frac{d(2m\dot{\rho})}{dt} - m\rho\dot{\phi}^2 + \frac{\partial \mathscr{V}}{\partial \rho} = 0 \tag{D-14}$$

$$\frac{d(m\rho^2\dot{\phi})}{dt} + \frac{\partial \mathscr{V}}{\partial \phi} = 0 \tag{D-15}$$

The second term in Eq. (D-14) produces a rate of change in $\dot{\rho}$ if $\mathscr{V}$ does not depend on ρ. This is due to 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:

$$F(\text{centripetal}) = -\frac{\partial \mathscr{V}}{\partial \rho} = -m\rho\dot{\phi}^2 = -\frac{mv^2}{\rho} \tag{D-16}$$

where the speed v in a circular orbit equals $\rho\dot{\phi}$.

An important quantity for an orbiting object is the **angular momentum** around a fixed center. This is the vector

$$\mathbf{L} = m\mathbf{r} \times \mathbf{v} \tag{D-17}$$

where $\mathbf{r}$ is the position vector from the fixed center to the particle, $\mathbf{v}$ is the velocity vector, and × stands for the cross product of two vectors. Figure D.2 illustrates the angular momentum of a single orbiting particle. For a circular orbit, the angular momentum vector has the magnitude

$$L = m\rho v = m\rho^2\dot{\phi} \tag{D-18}$$

In any system not subject to friction or external forces, the angular momentum is conserved (remains constant). The orbit of the moving mass remains in the same plane, and the angular momentum remains in a fixed direction with a fixed magnitude. If a

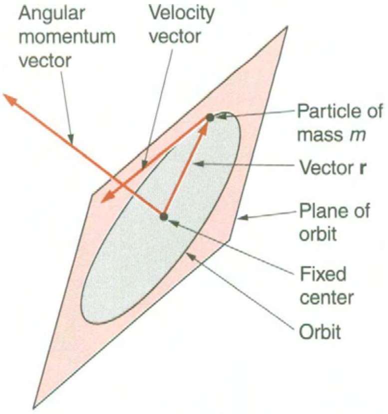

Figure D.2. Diagram to Illustrate the Definition of the Angular Momentum Vector. The angular momentum vector, **L**, is perpendicular to the vector **r** and the vector **v**, and has magnitude equal to $m|\mathbf{r}||\mathbf{v}|$.

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[1] This fact is proved in J. C. Slater and N. Frank, *Mechanics*, McGraw-Hill, New York, 1947, pp. 69ff, or in any other book on the same subject.

system consists of several interacting particles, the vector sum of their angular momenta is conserved. If the set of particles constitutes a rotating rigid symmetrical body such as a gyroscope spinning on its axis, the angular momentum vector of every particle points along that axis, and has magnitude proportional to its rate of rotation. The total angular momentum of a set of particles is the vector sum of the individual angular momenta.

Figure D-3 shows a simple gyroscope. If a gyroscope stands on one end of its axis at an angle in a gravitational field, the gravitational torque, instead of making the gyroscope fall on its side, makes the axis move (precess) around a vertical cone, as shown in the figure. In a central-force system, the quantized angular momentum points along similar cones.

D.4 Hamiltonian Mechanics

The aim of the method of Hamilton is similar to that of Lagrange in that it provides equations of motion that have the same form in any coordinate system. However, it uses variables called **conjugate momenta** instead of coordinate time derivatives as state variables. The conjugate momentum to the ith coordinate q_i is defined by

$$p_i = \frac{\partial \mathscr{L}}{\partial \dot{q}_i} \qquad (i = 1, 2, \ldots, n) \quad \text{(definition)} \tag{D-19}$$

The momentum conjugate to a cartesian coordinate is a component of the ordinary (linear) momentum:

$$p_x = mv_x, \quad p_y = mv_y, \quad p_z = mv_z \tag{D-20}$$

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. That is, the total vector momentum is conserved.

The **Hamiltonian function**, also called **Hamilton's principal function**, is defined by

$$\mathscr{H} = \sum_{i=1}^{n} p_i \dot{q}_i - \mathscr{L} \tag{D-21}$$

The Hamiltonian must be expressed as a function of coordinates and conjugate momenta. It is equal to the total energy of the system (kinetic plus potential).[2]

$$\mathscr{H} = \mathscr{K} + \mathscr{V} \tag{D-22}$$

The Hamiltonian equations of motion are

$$\dot{q}_i = \frac{\partial \mathscr{H}}{\partial p_i}, \qquad \dot{p}_i = -\frac{\partial \mathscr{H}}{\partial q_i} \qquad (i = 1, 2, \ldots, n) \tag{D-23}$$

There is one pair of equations for each value of i, as indicated.

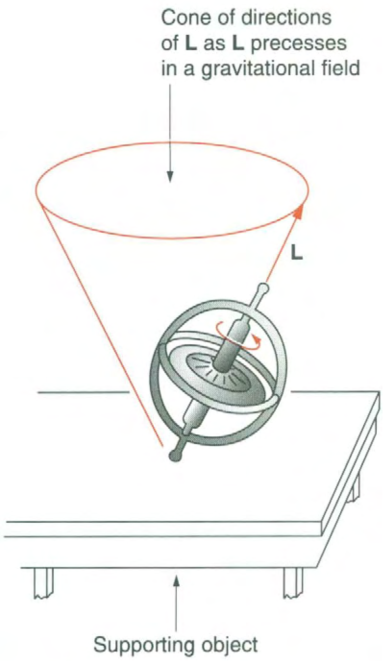

Figure D.3. A Simple Gyroscope. If a torque is placed on a gyroscope, as by supporting one end of the gyroscope in a graviational field, the gyroscope will precess, which means that its axis of rotation will move around a cone with a vertical axis.

D.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

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[2] Slater and Frank, *op. cit.*, p. 74ff (Note 1).

of a rotating diatomic molecule. We first examine the case in which there is motion only in the x direction. The Lagrangian of the system is

$$\mathcal{L} = \mathcal{K} - \mathcal{V} = \tfrac{1}{2}m_1\dot{x}_1^2 + \tfrac{1}{2}m_2\dot{x}_2^2 - \mathcal{V}(x_2 - x_1) \tag{D-24}$$

where x_1 and m_1 are the coordinate and the mass of the first particle and x_2 and m_2 are the coordinate and the mass of the second particle.

We now change to a different set of coordinates:

$$X = \frac{m_1x_1 + m_2x_2}{m_1 + m_2} \tag{D-25}$$

$$x = x_2 - x_1 \tag{D-26}$$

The coordinate X is the **center of mass coordinate**, and the coordinate x is called the **relative coordinate**. These two coordinates have separate equations of motion. We solve Eqs. (D-25) and (D-26) for x_1 and x_2:

$$x_1 = X - \frac{m_2x}{M} \tag{D-27}$$

$$x_2 = X + \frac{m_1x}{M} \tag{D-28}$$

where $M = m_1 + m_2$.

Taking the time derivatives of Eqs. (D-27) and (D-28), we can write the Lagrangian as

$$\begin{aligned}\mathcal{L} &= \frac{1}{2}m_1\left(\dot{X} - \frac{m_2\dot{x}}{M}\right)^2 + \frac{1}{2}m_2\left(\dot{X} + \frac{m_1\dot{x}}{M}\right)^2 - \mathcal{V}(x)\\ &= \frac{1}{2}m_1\left[\dot{X}^2 - 2m_2\frac{\dot{X}\dot{x}}{M} + \left(\frac{m_2\dot{x}}{M}\right)^2\right] + \frac{1}{2}m_2\left[\dot{X}^2 + 2m_1\frac{\dot{X}\dot{x}}{M} + \left(\frac{m_1\dot{x}}{M}\right)^2\right] - \mathcal{V}(x)\\ &= \frac{1}{2}M\dot{X}^2 + \frac{1}{2}\mu\dot{x}^2 - \mathcal{V}(x)\end{aligned} \tag{D-29}$$

where we have introduced the **reduced mass** of the pair of particles, defined by

$$\mu = \frac{m_1m_2}{m_1 + m_2} = \frac{m_1m_2}{M} \tag{D-30}$$

Since the variables are separated, we obtain separate equations of motion for X and x:

$$M\frac{d\dot{X}}{dt} = \frac{\partial\mathcal{L}}{\partial X} = 0 \tag{D-31}$$

$$\mu\frac{d\dot{x}}{dt} = \frac{\partial\mathcal{L}}{\partial x} = -\frac{d\mathcal{V}}{dx} \tag{D-32}$$

These equations imply that the center of mass of the two particles moves like a particle of mass M which 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 $\mathcal{V}(x)$. The motion of the two-particle system has been separated into two one-body problems. For motion in three dimensions, the separation is completely analogous. *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.*

E Some Derivations of Thermodynamic Formulas and Methods

We now present some material that explains or derives some of the things presented without derivation in the chapters on thermodynamics.

E.1 Caratheodory's Theorem

We want to show that the mathematical statement of the second law of thermodynamics follows from the physical statements. The first part of the argument is presented in Chapter 4, where it is shown that two reversible adiabats (curves representing reversible adiabatic processes) cannot cross. The next part is the proof that there exists a function y (an **integrating factor**) such that $y\,dq_{\text{rev}}$ is an exact differential even though dq_{rev} is an inexact differential. This theorem was proved by Caratheodory.[1] The final part is to show that $1/T$ is an acceptable integrating factor.

We will give only a nonrigorous outline of Caratheodory's proof.[2] The main idea is that if there is a single curve along which dq_{rev} vanishes there is also a differential of a function, dS, which vanishes on the same curve. If dS and dq_{rev} vanish on the same curve, we will establish that

$$dS = y\,dq_{\text{rev}} \tag{E-1}$$

where y is a function that does not vanish in this vicinity. Consider reversible adiabatic processes of a closed simple system starting from a particular initial state. Since we have established that no two adiabats can cross, let the reversible adiabat in the V–T state space be represented mathematically by the function

$$T = f(V) \tag{E-2}$$

Equation (3.4-22) 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 (E-2) is the same as

$$0 = f(V) - T \quad \text{(valid only on the curve)} \tag{E-3}$$

Let S be defined by

$$S = S(T, V) = f(V) - T + C \tag{E-4}$$

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[1] C. Caratheodory, *Math. Ann.*, **67**, 335 (1909).

[2] J. G. Kirkwood and I. Oppenheim, *Chemical Thermodynamics*, McGraw-Hill, New York, 1961, pp. 31ff; J. deHeer, *Phenomenological Thermodynamics*, Prentice-Hall, Englewood Cliffs, NJ, 1986, pp. 123ff.

where C is a constant. Equation (E-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. For reversible adiabatic processes T is equal to $f(V)$, and S is equal to the constant C. Therefore, for reversible adiabatic processes,

$$dS = 0 \quad \text{(reversible adiabatic processes)} \tag{E-5}$$

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

$$dS = y\, dq_{\text{rev}} \tag{E-6}$$

where y is a function that is nonzero in the vicinity of the curve. Since S is a function, y is an integrating factor, and we have proved the theorem of Caratheodory.

The line integral of an exact differential is independent of the path between a given initial point and a given final point. The converse is also true. If a line integral of a differential between two given points is path-independent for all possible paths, then the differential is exact. If the initial and final points are the same point (a cyclic path) then the line integral of an exact differential must vanish. Conversely, if a line integral vanishes for all cyclic paths (not just for a particular cyclic path) then the differential must be exact.

We now show that $1/T$ is a possible choice for the integrating factor y by showing that

$$\oint \frac{dq_{\text{rev}}}{T} = 0 \tag{E-7}$$

for all reversible cyclic processes. The symbol $\oint$ represents the line integral around a closed curve in the state space. We begin with a Carnot cycle. From Eqs. (4.1-13) and (4.1-23),

$$\frac{q_1}{T_{\text{h}}} = -\frac{q_3}{T_{\text{c}}} \tag{E-8}$$

Since T is constant on the isothermal segments and since $dq_{\text{rev}} = 0$ on the adiabatic segments, the line integral for a Carnot cycle is

$$\oint \frac{dq_{\text{rev}}}{T} = \frac{q_1}{T_{\text{h}}} + \frac{q_3}{T_{\text{c}}} = 0 \tag{E-9}$$

So that Eq. (E-7) is established for any Carnot cycle.

Now consider the reversible cyclic process of Figure E.1a. Steps 1, 3, and 5 are isothermal steps, and steps 2, 4, and 6 are adiabatic steps. We show that the line integral of Eq. (E-7) vanishes for this cycle, as follows: 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 E.1b. We now carry out the reversible cyclic process 7 → 1 → 2 → 3 → 7, which is a Carnot cycle (although we started in a different corner than previously). For this cycle, 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, on the way from state 7 to state 4, 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, these two paths exactly cancel each other and, if we leave them both out, the sum of the two line integrals is unchanged. We now have a vanishing line integral for the cyclic

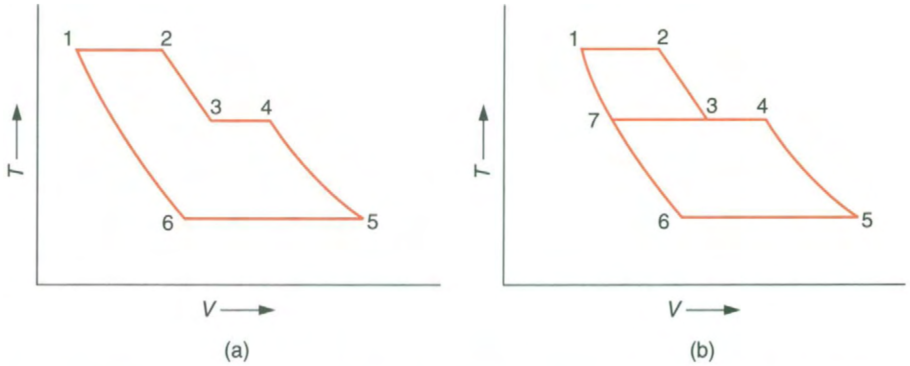

Figure E.1. A Reversible Cycle of Isotherms and Adiabats. (a) **The original cycle.** (b) **The cycle with an added process.** The additional process from state 3 to state 7 allows us to show that this cycle is equivalent to two Carnot cycles.

process 7 → 1 → 2 → 3 → 4 → 5 → 6 → 7, which is the cycle of Figure E.1a, except for starting in a different place. We have proved that Eq. (E-7) holds for the cycle of Figure E.1a.

We can similarly prove that Eq. (E-7) holds for more complicated cyclic processes made up of isothermal and adiabatic reversible steps. Consider the process of Figure E.2a, which can be divided into three Carnot cycles, just as that of Figure E.1a 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, 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. (E-7) is shown to vanish around the cycle. For example, Figure E.2b shows a more complicated cycle divided into Carnnot cycles.

In order to represent an arbitrary cycle we construct isothermal and adiabatic steps that are smaller and smaller in size, until the curve of the arbitrary cycle is more and more closely approximated, as crudely indicated in Figure E.2c. In the limit that the sizes of the steps approach zero, any curve is exactly represented. The line integral of Eq. (E-7) still vanishes, since even in the limit, the cycle can be divided into Carnot cycles.

E.2 Euler's Theorem[3]

Statement: A function f which depends on $n_1, n_2, n_3, \ldots, n_c$, is said to be **homogeneous of degree *m*** in the n's if

$$f(\lambda n_1, \lambda n_2, \ldots, \lambda n_c) = \lambda^m f(n_1, n_2, \ldots, n_c) \tag{E-10}$$

for every positive real value of λ.

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[3] E. A. Desloge, *Statistical Physics*, Holt Rinehart and Winston, New York, 1966, Appendix 10.

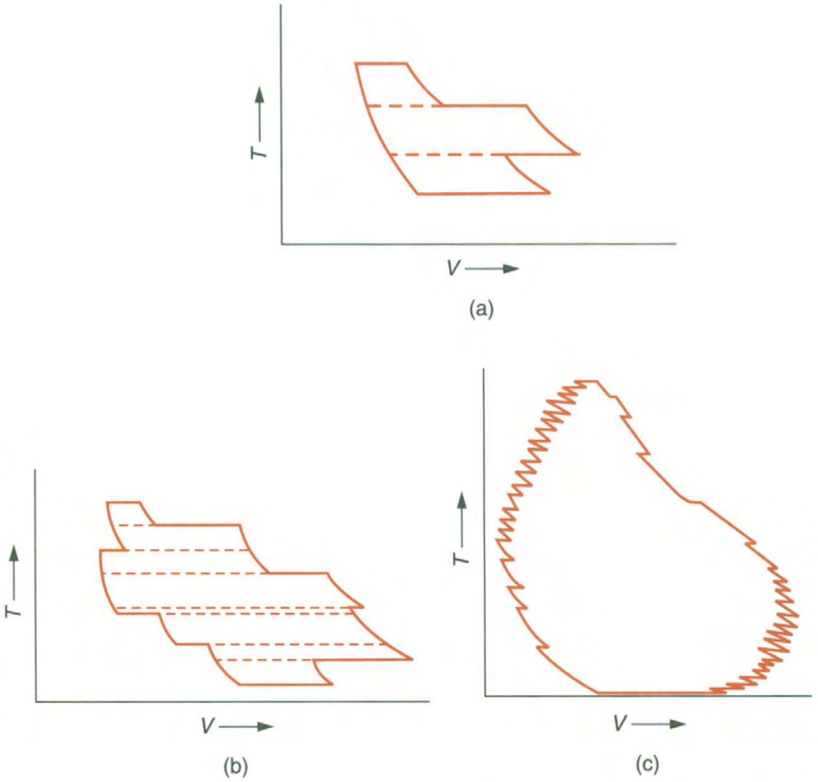

Figure E.2. A Reversible Cycle of Isotherms and Adiabats. (a) **A cycle equivalent to three Carnot cycles.** (b) **A cycle equivalent to eight Carnot cycles.** (c) **A cycle equivalent to a large number of Carnot cycles.**

Euler's theorem states that for such a function

$$mf = \sum_{i=1}^{c} n_1 \left(\frac{\partial f}{\partial n_i}\right)_{n'} \tag{E-11}$$

where the subscript n' means that all of the n's are held fixed except for n_i.

Proof: Differentiate Eq. (E-10) with respect to λ, using the chain rule:

$$\sum_{i=1}^{c} \left(\frac{\partial f}{\partial(\lambda n_i)}\right)_{n'} \left(\frac{\partial(\lambda n_i)}{\partial(\lambda)}\right)_{n'} = m\lambda^{m-1} f(n_1, n_2, \ldots, n_c) \tag{E-12}$$

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

$$\left(\frac{\partial(\lambda n_i)}{\partial(\lambda)}\right)_{n'} = n_i \tag{E-13}$$

and set λ equal to unity in Eq. (E-12) to obtain Eq. (E-11), and the theorem is proved.

E.3 Thermodynamic Applications of Euler's Theorem

If T and P are held fixed, then U, H, A, G, V, etc., are homogeneous of degree 1 in the n's. That is, they are extensive quantities. If T and P are held fixed, then the molar quantities U_{m}, H_{m}, A_{m}, G_{m}, V_{m}, etc. are homogeneous of degree 0. That is, they are intensive quantities. For example,

$$G = \sum_{i=1}^{c} n_i \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n'} = \sum_{i=1}^{c} n_i \mu_i \tag{E-14}$$

E.4 The Method of Intercepts

The value of the derivative $(\partial Y_{\mathrm{m}}/\partial x_1)_{TP}$ gives the slope of the desired tangent line when evaluated at $x_1 = x_1'$. The derivative of Eq. (5.6-15) with respect to x_1 is

$$\left(\frac{\partial Y_{\mathrm{m}}}{\partial x_1}\right)_{T,P} = \bar{Y}_1 + x_1\left(\frac{\partial \bar{Y}_1}{\partial x_1}\right)_{T,P} - \bar{Y}_2 + x_2\left(\frac{\partial \bar{Y}_2}{\partial x_1}\right)_{T,P} \tag{E-15}$$

where we have used the fact that $(\partial x_2/\partial x_1) = -1$. The second and fourth terms on the right-hand side of Eq. (E-15) sum to zero by the analogue of Eq. (5.6-13), giving

$$\left(\frac{\partial Y_{\mathrm{m}}}{\partial x_1}\right) = \bar{Y}_1 - \bar{Y}_2 \tag{E-16}$$

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

$$y = [\bar{Y}_1(x_1') - \bar{Y}_2(x_1')]x_1 + b \tag{E-17}$$

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. (5.6-16) and (E-17),

$$\bar{Y}_2(x_1') + x_1'[\bar{Y}_1(x_1') - \bar{Y}_2(x_1')] = [\bar{Y}_1(x_1') - \bar{Y}_2(x_1')]x_1' + b$$

Canceling equal terms on both sides of the equation, we get

$$\bar{Y}_2(x_1') = b \tag{E-18}$$

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 $x_1 = 1$.

$$y(1) = [\bar{Y}_1(x_1') - \bar{Y}_2(x_1')] + \bar{Y}_2(x_1') = \bar{Y}_1(x_1') \tag{E-19}$$

Thus, the intercept at $x_1 = 1$ is equal to $\bar{Y}_1(x_1')$.

F

Some Mathematics in Quantum Mechanics

We now give more details about things presented without derivation in Chapters 14 and 16.

F.1

The Particle in a Three-Dimensional Box

We have a model system consisting of a single point mass particle absolutely confined in a three-dimensional rectangular box. We place a cartesian coordinate system with its origin at the lower left rear corner of the box and with the coordinate axes perpendicular to the box walls. 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. We choose the potential energy function:

$$\mathcal{V} = \begin{cases} 0 & \text{if } 0 < x < a \text{ and } 0 < y < b \text{ and } 0 < z < c \\ \mathcal{V}_0 & \text{otherwise (outside the box)} \end{cases} \tag{F-1}$$

and then take the limit that $\mathcal{V}_0$ approaches $+\infty$.

We divide our space into two regions: region I outside the box, and region II inside the box. For reasons exactly the same as in the one-dimensional case, the coordinate wave function vanishes in region I. The time-independent Schrödinger equation for the interior of the box is

$$\left(\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}\right) = -\frac{2mE}{\hbar^2}\psi \tag{F-2}$$

We assume the trial solution:

$$\psi(x, y, z) = X(x)Y(y)Z(z) \tag{F-3}$$

Substitution of the trial function into the Schrödinger equation (F-2) and division by XYZ completes the separation of variables:

$$\frac{1}{X}\frac{d^2X}{dx^2} + \frac{1}{Y}\frac{d^2Y}{dy^2} + \frac{1}{Z}\frac{d^2Z}{dz^2} = \frac{2mE}{\hbar^2} \tag{F-4}$$

Since x, y, and z are independent variables, we can, if we wish, keep and two of these variables fixed while allowing the other to vary. Every term must be a constant function:

$$\frac{1}{X}\frac{d^2X}{dx^2} = K_x = -\frac{2mE_x}{\hbar^2} \tag{F-5}$$

$$\frac{1}{Y}\frac{d^2Y}{dy^2} = K_y = -\frac{2mE_y}{\hbar^2} \tag{F-6}$$

$$\frac{1}{Z}\frac{d^2Z}{dz^2} = K_z = -\frac{2mE_z}{\hbar^2} \tag{F-7}$$

where E_x, E_y, and E_z are newly defined constants. To satisfy Eq. (F-2),

$$E = E_x + E_y + E_z \tag{F-8}$$

We multiply Eq. (F-5) by the function X:

$$\frac{d^2X}{dx^2} = -\frac{2mE_x}{\hbar^2}X \tag{F-9}$$

This equation is identical with Eq. (14.5-4) except for the symbols used, and has the same boundary conditions, so that we can transcribe the solution of the one-dimensional problem:

$$X_{n_x}(x) = C_x \sin\left(\frac{n_x\pi x}{a}\right) \tag{F-10}$$

$$E_x = \frac{h^2}{8ma^2}n_x^2 \tag{F-11}$$

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:

$$Y_{n_y}(y) = C_y \sin\left(\frac{n_y\pi y}{b}\right) \tag{F-12}$$

$$Z_{n_z}(z) = C_z \sin\left(\frac{n_z\pi z}{c}\right) \tag{F-13}$$

$$E_y = \frac{h^2}{8mb^2}n_y^2 \tag{F-14}$$

$$E_z = \frac{h^2}{8mc^2}n_z^2 \tag{F-15}$$

Here n_y and n_z are positive integers that are not necessarily equal to n_x.

The energy eigenfunction is

$$\psi_{n_xn_yn_z}(x,y,z) = C\sin\left(\frac{n_x\pi x}{a}\right)\sin\left(\frac{n_y\pi y}{b}\right)\sin\left(\frac{n_z\pi z}{c}\right) \tag{F-16}$$

where we let $C = C_xC_yC_z$. The energy eigenvalue is

$$\boxed{E_{n_xn_yn_z} = \frac{h^2}{8m}\left(\frac{n_x^2}{a^2} + \frac{n_y^2}{b^2} + \frac{n_z^2}{c^2}\right)} \tag{F-17}$$

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 do by writing the three quantum numbers in parentheses: (n_x, n_y, n_z).

If $a = b = c$, we call the box a cubical box. In this case, we can have several states that have equal energy eigenvalues (are degenerate). For example, the two sets of quantum numbers $(1, 2, 3)$ and $(3, 2, 1)$ both correspond to the same energy. The energy eigenvalue for a particle in a cubical box is

$$E_{n_x n_y n_z} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2) \tag{F-18}$$

Consider the energy level that includes the state with quantum numbers $n_x = 1$, $n_y = 2$, and $n_z = 3$. There are six permutations of the three distinct numbers: $(1, 2, 3)$, $(2, 3, 1)$, $(3, 1, 2)$, $(3, 2, 1)$, $(1, 3, 2)$ and $(2, 1, 3)$. There are no other sets of three integers whose squares add up to 14, so the degeneracy of this energy level is 6.

F.2 The Solution of the Time-Independent Schrödinger Equation for the Harmonic Oscillator (the Hermite Equation)

After we define the constants as in Eq. (14.6-2),

$$b = \frac{2mE}{\hbar^2}, \qquad a = \frac{\sqrt{km}}{\hbar} \tag{F-19}$$

the Schrödinger equation for the harmonic oscillator becomes

$$\frac{d^2\psi}{dz^2} + (b - a^2z^2)\psi = 0 \tag{F-20}$$

The first step is to find an **asymptotic solution**, which is a solution that applies for very large magnitudes of z. If z has a very large magnitude, b will be negligible compared with a^2z^2, so that

$$\frac{d^2\psi}{dz^2} - a^2z^2\psi = 0 \quad \text{(for large magnitudes of } z\text{)} \tag{F-21}$$

The solution to this equation (the asymptotic solution) is

$$\psi_\infty \approx e^{\pm az^2/2} \tag{F-22}$$

There are two possible signs in the exponent in Eq. (F-22). If the positive sign is taken, the function would grow without bound as $|z|$ becomes large, violating our boundary condition that the wave function is finite. We therefore reject the positive sign.

In order to find a general solution to Eq. (F-20), we choose a trial solution of the form

$$\psi(z) = \psi_\infty(z)S(z) = e^{-az^2/2}S(z) \tag{F-23}$$

where $S(z)$ is a power series

$$S(z) = c_0 + c_1 z + c_2 z^2 + c_3 z^3 + \cdots = \sum_{n=0}^{\infty} c_n z^n \tag{F-24}$$

with constant coefficients $c_0, c_1, c_2, c_3, \ldots$. 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 turns out to be intractable.[1]

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[1] Ira N. Levine, *Quantum Chemistry*, 4th ed., Prentice-Hall, Englewood Cliffs, NJ, 1991, pp. 64ff.

The second derivative of our trial solution is

$$\frac{d^2\psi}{dz^2} = e^{-az^2/2}\left(\frac{d^2S}{dz^2} - 2az\,\frac{dS}{dz} + (a^2z^2 - a)S\right) \tag{F-25}$$

Substitution of this expression into Eq. (F-20) gives (after cancellation of two terms)

$$e^{-az^2/2}\left[\frac{d^2S}{dz^2} - 2az\,\frac{dS}{dz} + (b-a)S\right] = 0 \tag{F-26}$$

The exponential factor does not vanish for any finite real value of z, so the quantity in square brackets must vanish. From Eq. (F-24), the first two derivatives of S are

$$\frac{dS}{dz} = \sum_{n=1}^{\infty} nc_n z^{n-1} \tag{F-27}$$

$$\frac{d^2S}{dz^2} = \sum_{n=2}^{\infty} n(n-1)c_n z^{n-2} = \sum_{j=0}^{\infty}(j+2)(j+1)c_{j+2}z^j = \sum_{n=0}^{\infty}(n+2)(n+1)c_{n+2}z^n \tag{F-28}$$

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/dz without any change, since the $n = 0$ term has a factor of zero. We substitute Eq. (F-27) and (F-28) into Eq. (F-26) and cancel a common factor of $e^{-az^2/2}$. The result is

$$\sum_{n=0}^{\infty}[(n+2)(n+1)c_{n+2} - 2anc_n + (b-a)c_n]z^n = 0 \tag{F-29}$$

The quantity in the square brackets must vanish for each value of n, since every power of z on the right-hand side of the equation has a zero coefficient, and every power of z must have the same coefficient on both sides of the equation. Therefore,

$$c_{n+2} = \frac{2an + a - b}{(n+2)(n+1)}c_n \qquad (n = 0, 1, 2, \ldots) \tag{F-30}$$

Equation (F-30) is called a **recursion relation**. Given a value of c_n, it provides a value for c_{n+2}. For example, if c_1 is given, then c_3 is determined, and thus c_5, etc. If c_0 is known, then c_2 is determined, and thus c_4, etc. 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. (F-23) gives a solution to the Schrödinger equation.

Our solution must be finite for all values of z, including the limit as $|z|$ approaches infinity. However, if the series is permitted to have infinitely many terms, it is found that the series becomes large very rapidly for large values of $|z|$. It overcomes the rapidly decreasing gaussian factor, and the wave function fails to remain finite for large values of $|z|$.[2] Therefore, the series cannot have infinitely many terms. It obeys the Schrödinger equation if it does, but it does not obey the boundary condition that the wave function remain finite for all values of z.

If the series does not have an infinite number of terms, then it might have one term, it might have two terms, it might have three terms, and so on. Each of these cases can occur. However, 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

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[2] This assertion is not obvious. See Levine, *op. cit.*, pp. 67–78 (Note 1).

satisfy the Schrödinger equation. We must have a termination of the series that satisfies the recursion relation. Let us say that c_{v+2} is a vanishing coefficient, where c_v does not vanish. The numerator in the right-hand side of Eq. (F-30) must then vanish for $n = v$:

$$2av + a - b = 2av + a - \frac{2mE}{\hbar^2} = 0 \tag{F-31}$$

If v is an even integer, all of the odd-numbered coefficients must vanish, because there is no second recursion relation to terminate the part of the series containing odd-numbered coefficients. Therefore, a single solution will contain even powers of z or odd powers of z, but not both. The series factor in the solution will be a polynomial containing one term, two terms, etc. The polynomials are called Hermite polynomials. The first three normalized energy eigenfunctions are

$$\psi_0 = \left(\frac{a}{\pi}\right)^{1/4} e^{-az^2/2} \tag{F-32}$$

$$\psi_1 = \left(\frac{4a^3}{\pi}\right)^{1/4} z e^{-az^2/2} \tag{F-33}$$

$$\psi_2 = \left(\frac{a}{4\pi}\right)^{1/4} (2az^2 - 1) e^{-az^2/2} \tag{F-34}$$

corresponding to the first three Hermite polynomials:

$$H_0(x) = 1 \tag{F-35}$$

$$H_1(x) = 2x \tag{F-36}$$

$$H_2(x) = 4x^2 - 2 \tag{F-37}$$

where, in order to correspond with our wave functions, $x = \sqrt{a}z$. The normalization must be accomplished by an additional factor in the formula for the wave function.

All of the Hermite polynomials can be generated by the formula:

$$H_n(x) = (-1)^n e^{x^2} \frac{d^n}{dx^n}(e^{-x^2}) \tag{F-38}$$

or the formula[3]

$$H_n(x) = n! \sum_{m=0}^{[n/2]} \frac{(-1)^m (2x)^{n-2m}}{m!(n-2m)!} \tag{F-39}$$

where $[n/2]$ 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.[4] One useful identity is

$$xH_n(x) = nH_{n-1}(x) + \tfrac{1}{2}H_{n+1}(x) \tag{F-40}$$

An important fact is that if n is even, then $H_n(x)$ is an even function of x, and if n is odd, then $H_n(x)$ is an odd function of x:

$$H_n(-x) = H_n(x) \qquad (n \text{ even}) \tag{F-41}$$

$$H_n(-x) = -H_n(x) \qquad (n \text{ odd}) \tag{F-42}$$

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[3] A. Erdelyi, *et al.*, eds., *Higher Transcendental Functions*, Vol. II, McGraw-Hill, New York, 1953, pp. 192ff.

[4] A. Erdelyi, *op. cit.* (Note 3).

F.3 The Hydrogenlike Energy Eigenfunctions

The eigenfunctions are written as

$$\psi_{nlm} = R_{nl}(r)Y_{lm}(\theta, \phi) = R_{nl}(r)\Theta_{lm}(\theta)\Phi_m(\phi) \qquad \text{(F-43)}$$

where the Y_{lm} functions are spherical harmonic functions. The Y functions are the same for any central-force system, including the rigid rotor and the rotating diatomic molecule in the Born–Oppenheimer approximation, as well as the hydrogenlike atom.

The Φ functions are

$$\Phi_m = \frac{1}{\sqrt{2\pi}} e^{im\phi} \qquad \text{(F-44)}$$

where m is an integer.

The Θ_{lm} functions obey the equation

$$\sin(\theta) \frac{d}{d\theta} \sin(\theta) \frac{d\Theta}{d\theta} - m^2\Theta + K\sin^2(\theta)\,\Theta = 0 \qquad \text{(F-45)}$$

where K is a constant. With a change of variables, $y = \cos(\theta)$, $P(y) = \Theta(\theta)$, the equation becomes, after quite a bit of manipulation,

$$(1 - y^2)\frac{d^2P}{dy^2} - 2y\frac{dP}{dy} - \frac{m^2}{1 - y^2}P + KP = 0 \qquad \text{(F-46)}$$

Equation (F-46) is the same as the **associated Legendre equation** if $K = l(l+1)$, where l is an integer which must be at least as large as $|m|$. The set of solutions is known as the **associated Legendre functions**, given for nonnegative values of m by[5]

$$P_l^m(y) = (1 - y^2)^{m/2} \frac{d^m P_l(y)}{dy^m} \qquad \text{(F-47)}$$

where $P_l(y)$ is the Legendre polynomial

$$P_l(y) = \frac{1}{2^l l!} \frac{d^l}{dy^l}(y^2 - 1)^l \qquad \text{(F-48)}$$

With suitable normalization,

$$\Theta = \Theta_{lm} = \left(\frac{(2l+1)(l-m)!}{2(l+m)!}\right)^{1/2} P_l^m(\cos(\theta)) \qquad \text{(F-49)}$$

This equation is valid only for nonnegative values of the integer m, but Eq. (F-45) contains only the square of m, so that the solution of the Schrödinger equation is the same for any integral value of m and for the negative of that value. Therefore,

$$\Theta_{lm} = \Theta_{l,-m} \qquad \text{(F-50)}$$

We insert a comma to avoid confusing two subscripts having values l and $-m$ with a single subscript having a value equal to $l - m$. Equations (F-47)–(F-49) can be used to construct all of the Θ functions in normalized form.

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[5] J. C. Davis, Jr., *Advanced Physical Chemistry*, Ronald Press, New York, 1965, pp. 596ff.

The R functions obey the equation

$$r^2\frac{d^2R}{dr^2}+2r\frac{dR}{dr}-\frac{2\mu r^2}{\hbar^2}\left(E+\frac{Ze^2}{4\pi\varepsilon_0 r}\right)R+l(l+1)R=0 \tag{F-51}$$

We make the following substitutions:

$$\alpha^2=-\frac{2\mu E}{\hbar^2},\qquad \beta=\frac{Ze^2}{4\pi\varepsilon_0\alpha\hbar^2},\qquad \rho=2\alpha r \tag{F-52}$$

The resulting equation is divided by ρ^2, giving the associated Laguerre equation:

$$\frac{d^2R}{d\rho^2}+\frac{2}{\rho}\frac{dR}{dr}-\frac{R}{4}+\frac{\beta R}{\rho}+\frac{l(l+1)R}{\rho^2}=0 \tag{F-53}$$

This has the solution

$$R(\rho)=G(\rho)e^{-\rho/2} \tag{F-54}$$

where $G(\rho)$ is a power series

$$G(\rho)=\sum_{j=1}^{\infty}a_j\rho^j \tag{F-55}$$

with constant coefficients $a_1, a_2, a_3, \ldots$. This series must terminate after a finite number of terms in order to keep the wave function from becoming infinite for large values of ρ.[6] In order for the series to terminate, making it into a polynomial, the parameter β must equal an integer, n. The variable ρ is given by

$$\rho=2\alpha r=\frac{2Zr}{na} \tag{F-56}$$

where a is the Bohr radius, given by

$$a=\frac{\hbar^2 4\pi\varepsilon_0}{\mu e^2} \tag{F-57}$$

The polynomial G is given in terms of associated Laguerre functions:

$$G(\rho)=N_{nl}\rho^l L_{n+l}^{2l+1}(\rho) \tag{F-58}$$

where N_{nl} is a normalizing factor,

$$N_{nl}=\left[\left(\frac{2Z}{na}\right)^3\frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{1/2} \tag{F-59}$$

The associated Laguerre functions are

$$L_u^s(\rho)=\frac{d^s}{d\rho^s}L_u(\rho) \tag{F-60}$$

where L_u is the Laguerre polynomial

$$L_u(\rho)=e^{\rho}\frac{d^u}{d\rho^u}(\rho^u e^{-\rho}) \tag{F-61}$$

The first few R functions for the hydrogenlike atom are given in Table 16.2.

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[6] J. C. Davis, *op. cit.* (Note 5).

G

The Perturbation Method

The perturbation method is applied to a problem in which the Hamiltonian operator can be separated into two terms:

$$\hat{H} = \hat{H}^{(0)} + \lambda \hat{H}' \tag{G-1}$$

where λ is a fictitious parameter that delivers the actual Hamiltonian when $\lambda = 1$.

We assume that the energy eigenvalues and energy eigenfunctions of state number n can be represented by a power series in λ:

$$E_n = E_n^{(0)} + E_n^{(1)}\lambda + E_n^{(2)}\lambda^2 + \cdots \tag{G-2}$$

$$\Psi_n = \Psi_n^{(0)} + \Psi_n^{(1)}\lambda + \Psi_n^{(2)}\lambda^2 + \cdots \tag{G-3}$$

When the power series of Eqs. (G-2) and (G-3) are substituted into the time-independent Schrödinger equation, we obtain

$$\begin{aligned}(\hat{H}^{(0)} + \lambda\hat{H}')(\Psi_n^{(0)} + \Psi_n^{(1)}\lambda + \Psi_n^{(2)}\lambda^2 + \cdots)& \\ = (E_n^{(0)} + E_n^{(1)}\lambda + E_n^{(2)}\lambda^2 + \cdots)(\Psi_n^{(0)} + \Psi_n^{(1)}\lambda + \Psi_n^{(2)}\lambda^2 + \cdots)&\end{aligned} \tag{G-4}$$

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 equal to each other. We equate the constant terms on the two sides of the equation, after which we equate the coefficients of the linear terms, etc. The constant (zero-order) terms obey the relation:

$$\hat{H}^{(0)}\Psi_n^{(0)} = E_n^{(0)}\Psi_n^{(0)} \tag{G-5}$$

The coefficients of the linear (first-degree) terms obey the relation:

$$\hat{H}'\Psi_n^{(0)} + \hat{H}^{(0)}\Psi_n^{(1)} = E_n^{(1)}\Psi_n^{(0)} + E_n^{(0)}\Psi_n^{(1)} \tag{G-6}$$

To obtain an equation for $E_n^{(1)}$ we express the first-order correction to the wave function as a linear combination of the unperturbed (zero-order) wave functions:

$$\Psi_n^{(1)} = \sum_{j=1}^{\infty} a_{nj}\Psi_j^{(0)} \tag{G-7}$$

where we assume that there are infinitely many zero-order wave functions. Since $\hat{H}^{(0)}$ is a hermitian operator, its eigenfunctions presumably form a complete set, allowing this to be an exact representation if all of the infinitely many eigenfunctions are included. This representation is substituted into Eq. (G-6), giving

$$\hat{H}'\Psi_n^{(0)} + \hat{H}^{(0)}\sum_{j=1}^{\infty} a_{nj}\Psi_j^{(0)} = E_n^{(1)}\Psi_n^{(0)} + E_n^{(0)}\sum_{j=1}^{\infty} a_{nj}\Psi_j^{(0)} \tag{G-8}$$

Since $\Psi_j^{(0)}$ is an eigenfunction of $\hat{H}^{(0)}$ with eigenvalue $E_j^{(0)}$,

$$\hat{H}'\Psi_n^{(0)} + \sum_{j=1}^{\infty} a_{nj}E_j^{(0)}\Psi_j^{(0)} = E_n^{(1)}\Psi_n^{(0)} + E_n^{(0)} \sum_{j=1}^{\infty} a_{nj}\Psi_j^{(0)} \tag{G-9}$$

We now multiply each term of Eq. (G-9) by $\Psi_n^{(0)*}$ and integrate over all coordinates on which the wave function depends. The two sums contain constants multiplied by zero-order wave functions. 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. We now have only one term surviving in each sum, and with the terms not included in the sums, we now have

$$\int \Psi_n^{(0)*}\hat{H}'\Psi_n^{(0)}\,dq + a_{nn}E_n^{(0)} = E_n^{(1)} + a_{nn}E_n^{(0)} \tag{G-10}$$

where we abbreviate the coordinates of the system by q. The second term on each side cancels.

The result for the first-order correction to the energy eigenvalue is

$$E_n^{(1)} = \int \Psi_n^{(0)*}\hat{H}'\Psi_n^{(0)}\,dq \tag{G-11}$$

We do not discuss the first-order and higher-order corrections to the wave function, or the higher-order corrections to the energy eigenvalue, which are considerably more complicated, and cannot be evaluated exactly.

H

The Hückel Method

The Hückel method is introduced in Section 18.8. It is a semiempirical method of determining approximate LCAO molecular orbitals. It treats electrons in delocalized π bonds, and assumes that the framework of σ bonds has been treated separately, using sp^2 hybrid orbitals.

As an example, we treat the allyl radical, $CH_2{=}CH{-}CH_2{\cdot}$. If the plane of the molecule is the x–y plane, the molecule has three unhybridized $2p_z$ orbitals, one on each of the carbon atoms, that are not involved in the σ bonds. We construct linear combinations from these atomic orbitals, as in Eq. (18.7-12):

$$\varphi_i = c_1^{(i)}\psi_1 + c_2^{(i)}\psi_2 + c_3^{(i)}\psi_3 \tag{H-1}$$

where i is an index specifying which LCAO-MO is meant, and where ψ_1 is the $2p_z$ orbital on carbon number 1, etc. From three independent atomic orbitals, three LCAO molecular orbitals can be made, so i ranges from 1 to 3.

We assume that there is some effective Hamiltonian operator for an electron, called $\hat{H}_1^{\text{eff}}$, in which all attractions and repulsions are expressed in an approximate way that allows each electron to move independently of the others. We apply the variational method, seeking the lowest value of the variational orbital energy,

$$W_i = \frac{\int \varphi_i^* \hat{H}_1^{\text{eff}} \varphi_i \, d^3\mathbf{r}}{\int \varphi_i^* \varphi_i \, d^3\mathbf{r}} \tag{H-2}$$

When the expression of Eq. (H-1) is substituted into Eq. (H-2), we obtain an expression for W that contains two types of integrals:

$$H_{ab} = \int \psi_a^* \hat{H}_1^{\text{eff}} \psi_b \, d^3\mathbf{r} \tag{H-3}$$

$$S_{ab} = \int \psi_a^* \psi_b \, d^3\mathbf{r} \tag{H-4}$$

where ψ_a and ψ_b are two of the $2p_z$ atomic orbitals. The integral H_{ab} is called a **matrix element of the Hamiltonian**. The integral S_{ab} is an **overlap integral** if $a \neq b$, and is a **normalization integral** if $a = b$.

When the orbital variational energy is expressed in terms of these integrals, we have

$$W_i = \frac{\sum_{a=1}^{3}\sum_{b=1}^{3} c_a^{(i)} c_b^{(i)} H_{ab}}{\sum_{a=1}^{3}\sum_{b=1}^{3} c_a^{(i)} c_b^{(i)} S_{ab}} = \frac{N}{D} \tag{H-5}$$

where we assume that the c coefficients are real, as are the ψ functions, so that $H_{ab} = H_{ba}$. We temporarily denote the numerator of this expression by N and the denominator by D. 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 these derivatives equal to zero. This gives us three equations for the three c coefficients, which would seem to be the right number of equations to solve for the three c coefficients.

The derivative of W with respect to c_j is (where we temporarily omit the superscript (i) and the upper limits on the sums)

$$\begin{aligned}\frac{\partial W}{\partial c_j} &= \frac{1}{D}\left(\sum_b c_b H_{jb} + \sum_a c_a H_{aj}\right) - \frac{N}{D^2}\left(\sum_b c_b S_{jb} + \sum_a c_a S_{aj}\right)\\ &= \frac{2}{D}\left(\sum_b c_b H_{jb}\right) - \frac{2N}{D^2}\left(\sum_b c_b S_{jb}\right)\\ &= \frac{2}{D}\left(\sum_b c_b H_{jb}\right) - \frac{2W}{D}\left(\sum_b c_b S_{jb}\right)\end{aligned} \tag{H-6}$$

where we use the fact that for real functions $H_{ab} = H_{ba}$ and $S_{ab} = S_{ba}$. We set the expression in Eq. (H-6) equal to zero to find the minimum, and the result is a set of three equations, one for each value of j. We multiply by $D/2$ and obtain

$$0 = \sum_{a=1}^{3}(H_{aj} - WS_{aj})c_a \qquad (j = 1, 2, 3) \tag{H-7}$$

This is a set of three simultaneous linear homogeneous equations with a different set of c coefficients that satisfies each set of equations.

By inspection, we can see that the equations are satisfied by the so-called "trivial solution" in which all the c's vanish. Furthermore, we can see that there are not really three independent c coefficients, since the set of three c coefficients can all be multiplied or divided by any constant and the equations are still satisfied. If we divide each equation by c_1, we have only two remaining unknown variables. If W is arbitrary, the system of equations is therefore overdetermined. That is, there is one equation too many to have a solution. In order for a nontrivial solution to exist, a condition must be satisfied, that the determinant of the matrix of the coefficients must vanish.[1]

$$\det(H_{ab} - WS_{ab}) = 0 \tag{H-8}$$

Equation (H-8) is called a **secular equation**.

We now introduce some assumptions and approximations that further define the Hückel method. We assume the $2p_z$ orbitals are normalized, so that the normalization integrals (S_{aa}) equal unity. We assume that all of the overlap integrals (S_{ab} with $a \neq b$) vanish. We assume that H_{aa} has one value, called α, and H_{ab} another value, called β, when a and b represent orbitals on atoms bonded to each other. We assume that H_{ab}

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[1] Ira N. Levine, *Quantum Chemistry*, 4th ed., Prentice-Hall, Englewood Cliffs, NJ, 1991, pp. 202ff.

vanishes when orbitals a and b are on atoms that are not bonded to each other. The secular equation for the allyl radical now becomes

$$\begin{vmatrix} \alpha - W & \beta & 0 \\ \beta & \alpha - W & \beta \\ 0 & \beta & \alpha - W \end{vmatrix} = 0 \tag{H-9}$$

The secular equation is simplified by dividing each element of the determinant by β and letting

$$x = \frac{\alpha - W}{\beta} \tag{H-10}$$

so that

$$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \tag{H-11}$$

This determinant is expanded by minors using the top row:

$$x\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} - 1\begin{vmatrix} 1 & 1 \\ 0 & x \end{vmatrix} = 0 \tag{H-12a}$$

$$x(x^2 - 1) - 1(x - 0) = x^3 - 2x = x(x^2 - 2) = 0 \tag{H-12b}$$

There are three roots, which we call x_1, x_2, and x_3:

$$x_1 = -\sqrt{2}, \qquad x_2 = 0, \qquad x_3 = \sqrt{2} \tag{H-13}$$

corresponding to

$$W_1 = \alpha + \sqrt{2}\beta \tag{H-14a}$$

$$W_2 = \alpha \tag{H-14b}$$

$$W_3 = \alpha - \sqrt{2}\beta \tag{H-14c}$$

For each of these roots, there is a set of three equations for the three c coefficients. Applying the same approximations as used in the secular equation and dividing these simultaneous equations by β, 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 three orbitals:

$$\varphi_1 = c_1^{(1)}(\psi_1 + \sqrt{2}\psi_2 + \psi_3) \tag{H-16a}$$

$$\varphi_2 = c_1^{(2)}(\psi_1 - \psi_3) \tag{H-16b}$$

$$\varphi_3 = c_1^{(3)}(\psi_1 - \sqrt{2}\psi_2 + \psi_3) \tag{H-16c}$$

Since β turns out to be negative, W_1 is the lowest energy. W_2 turns out to correspond to a relative maximum in the energy, and W_3 corresponds to a relative minimum. However, these are the best approximations to the excited orbitals that can be obtained in this method.

The orbitals and orbital energies of benzene and 1,3-butadiene described in Chapter 18 are obtained in an analogous manner. The delocalized π orbitals in benzene are linear combinations of six unhybridized p orbitals:

$$\varphi_i = c_1^{(i)}\psi_1 + c_2^{(i)}\psi_2 + c_3^{(i)}\psi_3 + c_4^{(i)}\psi_4 + c_5^{(i)}\psi_5 + c_6^{(i)}\psi_6 \qquad \text{(H-17)}$$

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:

$$\begin{vmatrix} \alpha - W & \beta & 0 & 0 & 0 & \beta \\ \beta & \alpha - W & \beta & 0 & 0 & 0 \\ 0 & \beta & \alpha - W & \beta & 0 & 0 \\ 0 & 0 & \beta & \alpha - W & \beta & 0 \\ 0 & 0 & 0 & \beta & \alpha - W & \beta \\ \beta & 0 & 0 & 0 & \beta & \alpha - W \end{vmatrix} = 0 \qquad \text{(H-18)}$$

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

$$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 1 \\ 1 & x & 1 & 0 & 0 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 0 & 0 & 1 & x & 1 \\ 1 & 0 & 0 & 0 & 1 & x \end{vmatrix} = 0 \qquad \text{(H-19)}$$

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 18.26.

I

Matrix Representations of Groups

Groups of symmetry operations are introduced in Chapter 18, and matrices are introduced in Appendix B. Matrix multiplication has exactly the same characteristics as 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 given symmetry group. This set of matrices is a **representation** of that group. Since the members of a group must be capable of being multiplied together in either order, a representation must consist of square matrices and all of the matrices in the representation must have the same dimension (number of rows and columns). A given group can have a number of different representations with various numbers of rows and columns in the matrices. 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 matrix inverses.

I.1 Representations of the C_{2v} Group

The C_{2v} group is the group to which the water molecule belongs. We can consider the group to consist either of symmetry operators or of symmetry operations. For our present purposes, we use the operator notation. The operators in the group are $\hat{E}$, $\hat{C}_2$, $\hat{\sigma}_{yz}$ and $\hat{\sigma}_{xz}$, as labeled in Example 18.8. The effect of the $\hat{C}_2$ operation is to move a point from (x, y, z) to a point (x', y', z') such that

$$\hat{C}_2(x, y, z) = (x', y', z') = (-x, -y, z) \tag{I-1}$$

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 $\hat{C}_2$, denoted by $R(\hat{C}_2)$. The representative matrices of the other three operations in the group are

$$R(\hat{E}) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{I-4}$$

$$R(\hat{\sigma}_{yz}) = \begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{I-5}$$

$$R(\hat{\sigma}_{xz}) = \begin{bmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{bmatrix} \tag{I-6}$$

These matrices, when applied to the cartesian coordinates of an arbitrary point as in Eq. (I-3) give the same results as the symmetry operators. They also have the same multiplication table as the symmetry operators and form a representation of the group C_{2v}.

I.2 Reducible and Irreducible Representations

The representation of the C_{2v} group that we just obtained is a **reducible representation**. This means that it can be divided somehow into representations with fewer rows and columns (smaller dimension). It 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, etc. 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

$$R(\hat{E}) = [1] \tag{I-7}$$

$$R(\hat{C}_2) = [-1] \tag{I-8}$$

$$R(\hat{\sigma}_{yz}) = [-1] \tag{I-9}$$

$$R(\hat{\sigma}_{xz}) = [1] \tag{I-10}$$

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 $\hat{C}_2$ operator turns x into $-x$, and $R(\hat{C}_2)$ 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,

$$R(\hat{\sigma}_{yz})R(\hat{C}_2) = [-1][-1] = [1] = R(\hat{\sigma}_{xz}) \tag{I-11}$$

The other two one-dimensional representations also have the same multiplication table.

The representation in Eq. (I-3)–(I-6) consists of diagonal matrices and could therefore be identified as a reducible representation. Another type of matrix can immediately be identified as belonging to a reducible representation. 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** and can be subdivided in a similar way. 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. All elements outside of the blocks on the principal diagonal must equal zero for the matrix to be block-diagonal.

If a representation consists of a set of matrices that are all block-diagonal with blocks of the same sizes in the same orders, it is a reducible representation. A new set of matrices obtained by taking the block out of the same position in each matrix is a representation. 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 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 matrix of the same size as **B**, but its inverse must be used on the left of the expression. 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.3 Classes in a Group

A group can often be divided into classes. If **A** and **B** are both members of the same group, the similarity transformation as in Eq. (I-13) will yield **C**, which is another 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, it is found in many cases that only certain members of the group will occur in the place of **C** on the left- hand side of this equation for a given matrix **B**. These members constitute a **class** within the group. Every operator of the C_{2v} group is in a class by itself, as is the case with any abelian group. All of the operators commute with each other so that if **A** and **B** are members of an abelian group

$$\mathbf{A}^{-1}\mathbf{B}\mathbf{A} = \mathbf{A}^{-1}\mathbf{A}\mathbf{B} = \mathbf{B} \qquad (\text{if } \mathbf{A},\ \mathbf{A}^{-1},\ \text{and } \mathbf{B} \text{ commute}) \tag{I-14}$$

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.4 Character Tables

For many 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**. For example, the character table for the representation of Eqs. (I-3)–(I-6) is

C_{2v}	E	C_2	σ_{yz}	σ_{xz}
Γ	3	1	1	1

In this character table, the letter Γ is a generic symbol for a representation, and each character is listed below the symbol for the symmetry operation. The character table for each of the three one-dimensional representations is just the list of the elements of the one-by-one matrices, since there is only one term to add up to get each trace. We include all three in the same character table:

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 nomenclature attached to these representations is as follows:[1] 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 180° rotation in this case) and are designated by B if they are antisymmetric to this rotation. The subscripts 1 or 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**.

I.5 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

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[1] A. W. Adamson, *A Textbook of Physical Chemistry*, 3d ed., Academic Press, Orlando, 1986, pp. 747ff.

coordinates x, y, and z. The C_2 operation changes x to $-x$, and multiplication by -1 accomplishes the same thing, so that 1 by 1 matrix representing C_2 has -1 as its only element.

We say that we used x, y, and z as the **basis of the 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 results by using the functions xz, yz, and z^2 as the basis of a representation.

A theorem that we quote later implies that there must be four irreducible representations of the C_{2v} group. The fourth representation is obtained by using xy as an additional 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 typical character table for the C_{2v} group.[2]

The hydrogenlike atomic orbitals have definite symmetry properties, and are eigenfunctions of specific symmetry operators. When we use 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 basis:

	E	C_2	σ_{yz}	σ_{xz}	Function
A_1	1	1	1	1	ψ_{2p_z}
B_1	1	-1	-1	1	ψ_{2p_x}
B_2	1	-1	1	-1	ψ_{2p_y}

Character tables can be obtained for any group. Table A.26 of Appendix A lists character tables for 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.

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.[3] We state a few of them without proof.

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[2] Adamson, *op. cit.*, pp. 748ff (Note 1).

[3] G. L. Meissler and D. A. Tarr, *Inorganic Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1991, p. 104.

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 in Table A.26 of Appendix A.
3. The number of irreducible representations equals the number of classes. Therefore, in a complete character table, 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. If the dimension of irreducible representation number i is called l_i and if the order of the group (the number of operators in 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.

$$\sum_O [\chi(O)]^2 = h \tag{I-17}$$

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 groups 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.
7. 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.

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 $R(\hat{E})$ not displayed, since it is just the identity matrix):

$$R(\hat{C}_2) = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{I-20}$$

$$R(\hat{\sigma}_{xz}) = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{I-21}$$

$$R(\hat{\sigma}_{yz}) = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 \\ 0 & 1 & 0 & 0 & 0 \\ 0 & 0 & -1 & 0 & 0 \\ 0 & 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{I-22}$$

I.6 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 18 we first described the bonding in the water molecule in terms of hybrid orbitals on the oxygen atom in order to have only LCAO-MOs containing two basis functions. In Hartree–Fock–Roothaan calculations, the LCAO-MOs are linear combinations of the entire set of basis functions. We described a basis set for the water molecules such that the basis orbitals 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 a_1, etc., and this label is called its **symmetry species**, which identifies the irreducible representation to which it corresponds. The two linear combinations of Eqs. (18.6-19) and (18.6-20) were

$$\psi_{a_1} = \psi_{1s\mathrm{Ha}} + \psi_{1s\mathrm{Hb}} \tag{I-23}$$

$$\psi_{b_2} = \psi_{1s\mathrm{Ha}} - \psi_{1s\mathrm{Hb}} \tag{I-24}$$

where we have labeled these linear combinations with their symmetry species. 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 18.6. 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 $2p_z$ 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. 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 $2p_x$ and $2p_y$ orbitals from the σ molecular orbitals that we formed for the lithium hydride molecule in Section 18.4.

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 some symmetry of the integrand function. Group theory provides a systematic means of doing this.[4] Consider an overlap integral

$$\int f_1 f_2 \, dq$$

where f_1 and f_2 are two orbitals of a given molecule. 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 f_1 and that for orbital f_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 $\psi_{b_2} = \psi_{1sHa} - \psi_{1sHb}$ 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:

$$n_{A_1} = \frac{1}{4}(1 - 1 + 1 - 1) = 0$$

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

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[4] Adamson, *op. cit.*, pp. 762ff (Note 1).

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 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.

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 some cases, the section in which the quantity first appears is listed with the symbol. In addition to the quantities in this list, various letters are used for constants that appear in only one section.

Symbol	Quantity
a	Constant parameter in various equations of state
a	Distance of closest ionic approach in Debye–Hückel theory (Section 6.4)
a	Bohr radius
a_0	Bohr radius with nucleus assumed infinitely massive
a_i	Activity of substance i
a	Absorptivity
a_j	Coupling constant
$\mathbf{a}$	Acceleration
$\mathscr{A}$	Area
A	Helmholtz energy
A_n	nth pressure virial coefficient
$A(\lambda)$	Absorbance of an absorbing solution at wavelength λ
A	Preexponential factor in Arrhenius expression for a rate constant
$\hat{A}$	General symbol for an operator
$[\hat{A}, \hat{B}]$	Commutator of the operators $\hat{A}$ and $\hat{B}$
b	Constant parameter in various equations of state
b	Parameter in extended Debye–Hückel theory
b	Impact parameter for a molecular collision
B_n	nth virial coefficient
B	Magnetic induction (also called magnetic field)
B	Rotational constant
$\tilde{B}$	Rotational constant $= B/c$
c	Speed of light
c	Speed of propagation of any wave
c	Number of components
c_i	Concentration of substance i, also denoted by $[\mathscr{F}_i]$
c°	1 mol L^{-1} (exactly)
C_V	Heat capacity at constant volume
C_P	Heat capacity at constant pressure
$\hat{C}_n$	A rotation operator
d	Collision diameter
d	Reaction diameter
d	Distance between crystal planes
$\mathbf{D}$	Electric displacement vector
D_e	Dissociation energy
$\tilde{\mathfrak{D}}$	Parameter in molecular energy level

(*continued*)

Symbol	Quantity
D_i	Diffusion constant of substance i
D	Debye function
e	The base of natural logarithms, 2.71828182846...
$\mathscr{e}$	Charge on a proton
E	General symbol for a mechanical energy
E_c	Center-of-mass energy
E_r	Relative energy
$E^{(n)}$	nth-Order perturbation correction to an 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
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	fugacity
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_i	Degeneracy of level i
$g(\lambda)\,d\lambda$	Number of possible standing waves in wavelength range $d\lambda$
g	Electron g-factor
g_{N}	Nuclear g-factor
g_c	Coordinate probability distribution
$g(r)$	Radial distribution function
G	Probability density for coordinates and velocities
G	Newtonian constant of gravitation
G	Gibbs energy
$G^{(\sigma)}$	Surface Gibbs energy
ΔG_{mix}	Gibbs energy change of mixing
G^{E}	Excess Gibbs energy
h	Planck's constant
$\hbar = h/2\pi$	Planck's constant divided by 2π
h, k, and l	Miller indices
H	Enthalpy
$\mathbf{H}$	Magnetic field strength
$\Delta H_{\mathrm{int},i}$	Integral heat of solution of substance i
$\Delta H_{\mathrm{diff},i}$	Differential heat of solution of substance i
$\mathscr{H}(p, q)$	Classical Hamiltonian, equal to the energy E, expressed in terms of coordinates and conjugate momenta
$\hat{H}$	Hamiltonian operator
$\hat{i}$	Inversion operator
i	Degree of inhibition
$\mathbf{i}$	Unit vector in x direction
I	Ionic strength
I	Moment of inertia
$\mathbf{I}$	Nuclear spin angular momentum
I	Quantum number for a nuclear spin angular momentum

Symbol	Quantity
I	Electric current
$\mathbf{j}$	Unit vector in y direction
$\mathbf{j}$	Electric current density
$\mathbf{J}$	Total angular momentum
J	Quantum number for a total angular momentum
J	Quantum number for the rotation of a molecule
J_{ij}	Spin–spin coupling constant for nuclei i and j
J	Rate of absorption of photons
J_i	Diffusion flux of substance i
J	Analogue to Gibbs energy
k_i	Henry's law constant
k	Force constant
k	Usual symbol for a rate constant
$\mathbf{k}$	Unit vector in 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	Analogue to enthalpy
K	Proportionality constant in relation between intrinsic viscosity and average molecular mass
K_{a}	Acid ionization constant
K_{m}	Michaelis–Menten constant
l	Quantum number for the magnitude of the orbital angular momentum in a hydrogenlike atom
L	Usual symbol for a length
$\mathbf{L}$	Angular momentum, usually the orbital angular momentum
L	Quantum number for the magnitude of an orbital angular momentum
m	General symbol for a mass
m_e	Electron rest-mass
m_i	Molality of substance i
$m_{\pm}$	Mean ionic molality
m°	$1\,\mathrm{mol\,kg^{-1}}$ (exactly)
m_{N}	Neutron rest-mass
m	Quantum number for the z projection of the orbital angular momentum in a hydrogenlike atom
m_s	Quantum number for the z projection of the spin angular momentum of a single particle
M	Molecular mass of a polymer
$\bar{M}_n$	Number-average molecular mass of a polymer
$\bar{M}_w$	Number-average molecular mass of a polymer
$\bar{M}_v$	Viscosity-average molecular mass of a polymer
M_i	Molar mass of substance i
M_i	Effective mass of normal mode i
M	Symbol sometimes used for a sum of masses
M_I	Quantum number for the z component of a nuclear spin angular momentum
M_J	Quantum number for the z component of a total angular momentum of an atom or molecule
M_L	Quantum number for the z component of an orbital angular momentum of an atom or molecule
M_S	Quantum number for the z component of a spin angular momentum of an atom or molecule
n_i	The amount of substance i (measured in moles)

(continued)

Symbol	Quantity
$n_j(r)$	Charge density around a given ion
$n_i^{(\sigma)}$	Surface amount of substance *i*
n	Principal quantum number of a hydrogenlike atom
n	Refractive index
$n^{(2)}$	Two-body reduced distribution function
N_{Av}	Avogadro's constant
N_i	Number of molecules of substance *i*
$\{N\}$	Notation for a distribution $N_1, N_2, N_3, \ldots$
$\mathscr{N}_i$	Number density of substance *i*
$\mathbf{p}$	Momentum vector
p	A general abbreviation for conjugate momenta
p	A general symbol for a probability
p_i	Probability of state *i*
p	Number of phases
p	Fraction of functional groups reacted
pH	$-\log_{10}[a(\mathrm{H}^+)]$
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_1^*	Vapor pressure of pure substance *i*
P°	Standard pressure, equal to 1 bar
q	An amount of heat
q	A general abbreviation for coordinates
$\mathbf{q}$	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	Molar gas constant
$\mathfrak{R}$	Rydberg constant
R_{nl}	Radial factor in the wave function of a hydrogenlike atom
R	Electrical resistance
R	Internuclear distance (also denoted by *r*)
$\mathscr{R}$	Reynolds number
S	Entropy
$\mathbf{S}$	Spin angular momentum vector
S	Quantum number for the magnitude of a spin angular momentum
S	Overlap integral
S	Sedimentation coefficient
t	Time
$t_{1/2}$	Half-life of a chemical reaction
t_{C}	Celsius temperature
T	Absolute temperature
T_{c}	Critical temperature
T	Tension force on a vibrating string
$T(\lambda)$	Transmittance of an absorbing solution at wavelength λ
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
$u(x)$	Bloch function

Symbol	Quantity
U	Thermodynamic energy (also called internal energy)
$\mathbf{v}$	Velocity vector
v	Speed (magnitude of a velocity)
$\langle v \rangle$	Mean speed
v_p	Most probable speed
v_rms	Root-mean-square speed
v	Vibrational quantum number
V	Volume
V_m	Molar volume
V_mc	Critical molar volume
V_r	Reduced volume
v_rel	Relative speed
V	Voltage
$\mathcal{V}$	Potential energy
w	An amount of work
w_net	Work other than compression work
w_rev	Reversible work
w_i	Mass of substance i
$w(\lambda)\,d\lambda$	Energy per unit volume in wavelength range $d\lambda$
$W(\{N\})$	Number of system states corresponding to the distribution $\{N\}$
W_x	Mass fraction of polymer molecules with degree of polymerization x
x_i	Mole fraction of substance i
X_i	Electronegativity of element i
x_e	Parameter in molecule energy level
x	Degree of polymerization
$\mathbf{X}$	External force
X_x	Number of 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, etc.
$\Delta_\mathrm{f} Y(i)$	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 used to stand for a general partial molar quantity, such as $\bar{G}_i$, $\bar{V}_i$, etc.
$\bar{Y}_i^\circ$	Symbol used to stand for a general partial molar quantity, such as $\bar{G}_i$, $\bar{V}_i$, etc., 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.
$Y(\theta, \phi)$	Spherical harmonic function
$z_{i(j)}$	Rate of collisions of one molecule of substance i with molecules of substance j
z_i	Valence of ion i
z^*	Complex conjugage of z
$\mathscr{z}$	Molecular partition function
Z	Compression factor of a gas
Z_{ij}	Total rate of collisions per unit volume of molecules of substance i with molecules of substance j
Z	Atomic number; number of protons in a nucleus
$\mathscr{Z}$	Canonical partition function
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	Parameter in hydrogen-atom wave function

(continued)

Symbol	Quantity
α	Spin function (spin up)
$\tilde{\alpha}$	Parameter in molecule energy level
α	Polarizability
α	Angle of rotation of polarized light
$[\alpha]$	Specific rotation
α	Lagrange multiplier
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
β	Spin function (spin down)
β_e	Bohr magneton
β_N	Nuclear magneton
β	Lagrange multiplier
γ, γ'	Critical exponent for the compressibility
γ	Surface or interfacial tension
γ_i	Activity coefficient of substance *i*
$\gamma_\pm$	Mean ionic activity coefficient
δ	Critical exponent for the pressure
δ	Chemical shift in NMR spectroscopy
Δ	Symbol for a difference or an increment
ε	Permittivity of a medium
ε_0	Permittivity of the vacuum
ε_i	Energy eigenvalue of molecule state *i*
ε_F	Fermi level
$\zeta(t)$	Time factor in a wave function
ζ	Configuration integral
η	Efficiency or coefficient of performance
η	Spectral radiant emittance
η	Viscosity coefficient
η_sp	Specific viscosity
$[\eta]$	Intrinsic viscosity
η	Overpotential
θ	Thermodynamic temperature
θ	Angle coordinate in spherical polar coordinates. Also often used for an arbitrary angle
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	Einstein 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 one molecule of substance *i* with molecules of substance *j*
λ	Wavelength
λ	Perturbation parameter
Λ_i	Molar conductivity of substance *i*
Λ	Quantum number for the magnitude of the *z* component of the orbital angular momentum
μ	Reduced mass
μ	Usual symbol for the mean value of a distribution
μ_i	Chemical potential of component *i*
μ_i°	Chemical potential of component *i* in the standard state

Symbol	Quantity
μ_i^*	Chemical potential of component *i* in the pure liquid or solid state
$\mu_{i(\mathrm{chem})}$	Chemical part of the chemical potential
μ	Permeability of a medium
μ_0	Permeability of the vacuum
$\boldsymbol{\mu}$	Electric dipole vector
ν_i	Stoichiometric coefficient of substance *i*
$\nu_\pm$	Mean ionic stoichiometric coefficient
ν	Frequency of oscillation of a photon or an oscillating object
$\tilde{\nu}$	Reciprocal wavelength; photon frequency divided by the speed of light
$\tilde{\nu}_\mathrm{e}$	Vibrational parameter in molecule energy level
ν	Rate of wall collisions
ν_D	Debye frequency
ξ	Reaction coordinate
ξ	Reaction progress variable
π	3.14159265359...
$\prod$	Symbol for a product of factors
Π	Osmotic pressure
ρ	Density
ρ	Mass per unit length of a vibrating string
ρ	Radial variable in hydrogen atom wave function
ρ_c	Charge density
σ	Stefan–Boltzmann constant
σ	Standard deviation
σ	Electrical conductivity
$\hat{\sigma}$	A reflection operator
σ	Shielding constant
σ	Symmetry number
$\sum$	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 one molecule of substance *i* with molecules of substance *j*
τ	Tension force
φ	Electrical potential
φ	Steric factor
ϕ	Angular coordinate in spherical polar and cylindrical polar coordinates
ϕ	Osmotic coefficient
$\varphi(L)$	Function of length in theory of rubber elasticity
ϕ	Volume fraction of a suspension of spheres or polymer molecules
Φ	Quantum yield of a photochemical reaction
$\Phi(\phi)$	An angular factor in a central-force wave function
χ	Center of mass wave function
ψ	Usual symbol for a coordinate wave function; usual symbol for an orbital
Ψ	Usual symbol for a time-dependent wave function or for a coordinate wave function of a multiparticle system
ω	Angular speed
Ω	Number of possibly occupied mechanical states (thermodynamic probability)
∇	Gradient operator
$\nabla\cdot$	Divergence operator
∇^2	Laplacian operator

K

Answers to Selected Exercises and Problems

Chapter 1

Answer to selected exercises

1.1

$m = 4.5 \times 10^{-12}$ kg

1.2

Time $\approx 3.8 \times 10^{7}$ years

1.3

$R = 0.082058$ L atm K^{-1} mol^{-1}

$R = 1.9872$ cal K^{-1} mol^{-1}

$R = 82.058$ cm^3 atm K^{-1} mol^{-1}

$R = 83145$ cm bar K^{-1} mol^{-1}

1.4

a. $V = 97.86$ L
b. $P = 2.052$ atm

1.5

$F_z = -9.8$ N

1.6

$\langle w \rangle = 79.4$

1.7

$\langle w^2 \rangle = 6326$

$w_{\mathrm{rms}} = 79.5$

1.8

$P = 0.55$ atm

1.9

$v_z(t) = -gt$

$x(t) = -\frac{1}{2}gt^2$

Answers to selected problems

1.11

a. 0.5662 g O_2
b. 1.4453 g $KClO_3$

1.13

$c = 1.802617 \times 10^{12}$ furlongs $fortnight^{-1}$

1.15

a. $g = 32.3$ ft s^{-2}
b. $R = 22.591$ ft-poundals $(°R)^{-1}$ mol^{-1}

1.17

Value	*Probability*
2	$\frac{1}{36}$
3	$\frac{2}{36}$
4	$\frac{3}{36}$
5	$\frac{4}{36}$
6	$\frac{5}{36}$
7	$\frac{6}{36}$
8	$\frac{5}{36}$
9	$\frac{4}{36}$
10	$\frac{3}{36}$
11	$\frac{2}{36}$
12	$\frac{1}{36}$

1.19

$\Delta\rho = -0.0000679\ \text{kg m}^{-3}$

Chapter 2

Answers to selected exercises

2.1

$V = nV_{\text{m0}}[1 - \kappa'(P - P_0) + \alpha'(T - T_0)]$

2.2

a. $\kappa_T = \dfrac{1}{P}$

$\alpha = \dfrac{1}{T}$

b. $\kappa_T = 1.000\ \text{atm}^{-1}$

$\dfrac{\kappa_T(\text{ideal gas})}{\kappa_T(\text{water})} = 21595$

c. $\alpha = 16.5$

2.3

$V(100.0°\text{C}) = 2.00154\ \text{L}$

2.4

$V_{\text{m}}(1.000\,\text{bar}) = 73.53\ \text{cm}^3\ \text{mol}^{-1}$

$V_{\text{m}}(1.000\,\text{bar}) \approx 72.63\ \text{cm}^3\ \text{mol}^{-1}$

2.5

a. $\lim\limits_{V_{\text{m}}\to\infty}(PV_{\text{m}}) = \lim\limits_{V_{\text{m}}\to\infty}\left(\dfrac{RT}{V_{\text{m}} - b}\,V_{\text{m}} - \dfrac{a}{V_{\text{m}}^2}\,V_{\text{m}}\right) = RT$

b. $P = 101{,}250\ \text{Pa} = 1.0125\ \text{bar} = 0.9993\ \text{atm}$

Ideal value $= 101{,}323\ \text{Pa} = 0.99998\ \text{atm}$, for a difference of -0.06%

c. $PV_{\text{m}} = 4.8157 \times 10^6\ \text{Pa} = 48.157\ \text{bar} = 47.527\ \text{atm}$

Ideal value $= 4.9579 \times 10^6\ \text{Pa} = 48.931\ \text{atm}$, for a difference of -2.87%

2.7

a. $T_{\text{Boyle}} = \dfrac{a}{bR}$

b. $T_{\text{Boyle}} = 505\ \text{K}$

c. $V_{\text{m}} = \dfrac{ab}{a - RTb} = \left(\dfrac{1}{b} - \dfrac{RT}{a}\right)^{-1}$

d. $P = 2.14 \times 10^7\ \text{Pa} = 211\ \text{atm}$

2.11

$a = 1.56\ \text{Pa K}^{1/2}\ \text{m}^6\ \text{mol}^{-2}$

$b = 2.68 \times 10^{-5}\ \text{m}^3\ \text{mol}^{-1}$

Answers to selected problems

2.15

$\left(\dfrac{\partial P}{\partial V}\right)_{T,n} = -4.03394 \times 10^{-6}\ \text{Pa m}^{-3}$

$\left(\dfrac{\partial V}{\partial T}\right)_{P,n} = 8.3145 \times 10^{-5}\ \text{m}^3\ \text{K}^{-1}$

$\left(\dfrac{\partial T}{\partial P}\right)_{V,n} = 2.9815 \times 10^{-3}\ \text{K Pa}^{-1}$

2.19

a. $\left(\dfrac{\partial z}{\partial x}\right)_y = a\cos(y/b)$

$\left(\dfrac{\partial x}{\partial y}\right)_z = \dfrac{z\tan(y/b)}{ab\cos(y/b)}$

$\left(\dfrac{\partial y}{\partial z}\right)_x = -\dfrac{b}{ax\sin(y/b)}$

2.21

a. $\dfrac{\Delta V}{V} \approx -9.730 \times 10^{-4} = -0.0973\%$

b. $\dfrac{\Delta V}{V} \approx 2.4 \times 10^{-2} = 2.42\%$

2.25

a. $P = 1.547\ \text{atm}$

$P(\text{const. } V) = 1.549\ \text{atm}$

b. $P = 1.5469\ \text{atm}$

2.27

a. $\alpha = \dfrac{\alpha' + 2\beta' t_{\text{C}} + 3\gamma' t_{\text{C}}^2}{1 + \alpha' t_{\text{C}} + \beta' t_{\text{C}}^2 + \gamma' t_{\text{C}}^3}$

b. $\alpha = 1.208 \times 10^{-3}\ \text{K}^{-1}$

This compares with $1.237 \times 10^{-3}\ \text{K}^{-1}$ from Table A.2.

2.31

a. $\kappa_T = \left(\dfrac{RTV_{\text{m}}}{(V_{\text{m}} - b)^2} - \dfrac{2a}{V_{\text{m}}^2}\right)^{-1}$

b. $\kappa_T = 9.857 \times 10^{-6}\ \text{Pa}^{-1}$

2.33

$$\alpha = \frac{V_{\text{m}} - b + \dfrac{a}{V_{\text{m}}RT}(V_{\text{m}} - b)}{T\left(V_{\text{m}} - \dfrac{a(V_{\text{m}} - b)}{RTV_{\text{m}}}\right)}$$

2.37

Van der Waals;	$Z = 1.1434$	(0.86% error)
Dieterici:	$Z = 1.1255$	(0.71% error)
Redlich–Kwong:	$Z = 1.1153$	(1.6% error)

2.41

a. $a = \dfrac{R^2 T_c^2}{9(2^{1/3} - 1)P_c}$

$b = \dfrac{(2^{1/3} - 1)RT_c}{3P_c}$

b. $a = 0.139 \text{ Pa m}^6 \text{ mol}^{-2}$

$b = 2.68 \times 10^{-5} \text{ m}^3 \text{ mol}^{-1}$

2.45

a. $\alpha = \dfrac{(\alpha' + 2\beta' t_C + 3\gamma' t_C^2 + 4\delta' t_C^3)}{(1 + \alpha' t_C + \beta' t_C^2 + \gamma' t_C^3 + \delta' t_C^4)}$

b. From the first set of parameters, $V(25°\text{C}) = 1.00294 \text{ cm}^3$
From the second set of parameters, $V(25°\text{C}) = 1.00294 \text{ cm}^3$

d. $\dfrac{dV}{dT} = \dfrac{dV}{dt_C} = V_0(\alpha' + 2\beta' t_C + 3\gamma' t_C^2 + 4\delta' t_C^3) = 0$ at the minimum
The minimum is at 3.9601°C from the first set of parameters, and at 3.6066°C from the second set of parameters

e. $\alpha = 2.069 \times 10^{-4} \text{ K}^{-1}$, in agreement with the tabulated value of $2.07 \times 10^{-4} \text{ K}^{-1}$

Chapter 3

Answers to selected exercises

3.1
$w = 405 \text{ J}$

3.3
a. $w_{\text{surr}} = 507 \text{ N m} = 507 \text{ J}$
b. $\Delta P = -3.06 \text{ atm}$

3.4
a. $w_{\text{rev}} = -9197 \text{ J}$
b. $w_{\text{rev}} = -9197 \text{ J}$
c. $w = -4053 \text{ J}$

3.5
a. $q = 1690 \text{ J} = 1.69 \text{ kJ}$
b. $T = 296.8 \text{ K}$, $t_C = 23.6°\text{C}$

3.6
$m_{\text{max}} = 719 \text{ g}$

3.7
$\Delta T = 0.0937 \text{ K}$

3.8
a. $E_{\text{rest-mass}} = 3.5903 \times 10^{15} \text{ J}$
b. $U = 3718 \text{ J}$

Ratio $= 1.036 \times 10^{-12}$

$\Delta m = 4.14 \times 10^{-14} \text{ kg}$

3.9
$q = 8106 \text{ J}$

3.12
a. $\Delta U = 83 \text{ J}$, $w = -1824 \text{ J}$, $q = 1907 \text{ J}$
For an ideal gas, $\Delta U = 0$, $w = -1824 \text{ J}$, $q = 1824 \text{ J}$
From Example 3.7, $\Delta U = 83 \text{ J}$, $w = -5690 \text{ J}$, $q = 5773 \text{ J}$
b. $\Delta T = -6.66 \text{ K}$

3.13
a. $w = -5690 \text{ J}$

$q = 6708 \text{ J}$
b. $w = -7138 \text{ J}$

$q = 8151 \text{ J}$
c. $\Delta U = 1013 \text{ J}$

3.14
a. $T_2 = 235 \text{ K}$
b. $V = 7.98 \text{ L}$

3.18
$T_2 = 316 \text{ K}$, $t_{C,2} = 33°\text{C}$

3.19
a. At 298.15 K, $C_{P,\text{m}} = 29.37 \text{ J K}^{-1} \text{ mol}^{-1}$

$\frac{7}{2}R = 29.10 \text{ J K}^{-1} \text{ mol}^{-1}$ (0.93% difference)

At 1000 K, $C_{P,\text{m}} = 34.0 \text{ J K}^{-1} \text{ mol}^{-1}$

$\frac{7}{2}R = 29.10 \text{ J K}^{-1} \text{ mol}^{-1}$ (16.9% difference)
b. For iron, $C_{P,\text{m}} = 25.12 \text{ J K}^{-1} \text{ mol}^{-1}$
For copper, $C_{P,\text{m}} = 24.56 \text{ J K}^{-1} \text{ mol}^{-1}$
$3R = 24.94 \text{ J K}^{-1} \text{ mol}^{-1}$
There is a 0.7% difference for iron and a −1.5% difference for copper.

3.22
a. $\Delta U = 935 \text{ J}$
b. $\Delta H = 1559 \text{ J}$
$q = 3086 \text{ J}$
$w = -2151 \text{ J}$

3.23
$\Delta H° = 57.011 \text{ kJ mol}^{-1}$

3.24
$\Delta C_P^\circ = -3.508 \text{ J K}^{-1} \text{ mol}^{-1}$
$\Delta H^\circ_{473 \text{ K}} = 56.40 \text{ kJ mol}^{-1}$

3.25
$T_f = 5229 \text{ K}$

3.26
$T_f = 7263\ \text{K}$

3.27
$\Delta(PV) = -7340\ \text{J mol}^{-1}$

3.28
$\Delta U^\circ = 54.532\ \text{kJ mol}^{-1}$

3.29
$\Delta T_{\text{cal}} = 3.771\ \text{K}$

3.30
From average bond energies, $\Delta H \approx \Delta U \approx -323\ \text{kJ mol}^{-1}$
From enthalpy changes of formation, $\Delta H^\circ = -311.41\ \text{kJ mol}^{-1}$

Answers to selected problems

3.33
a. $w = n\left(-RT\ \ln\left(\frac{V_2 - nb}{V_1 - nb}\right) + \frac{na}{V_2} - \frac{na}{V_1}\right)$
b. $w = 1765\ \text{J}$
c. $w = -507\ \text{J}$
$w_{\text{surr}} = 507\ \text{J}$

3.35
$\Delta T = 0.117\ \text{K}$

3.37
$q = 81{,}338\ \text{J}$
$w = -6203\ \text{J}$
$\Delta U = 74{,}135\ \text{J}$

3.39
$P_2 = 0.947\ \text{atm}$

3.41
a. $T_2 = 171.2\ \text{K}$
b. $T_2 = 170.8\ \text{K}$

3.45

$$C_{P,\tau} = C_{P,L} + \left(\left(\frac{\partial H}{\partial L}\right)_{P,t} - \tau\right)\left(\frac{\partial L}{\partial T}\right)_{P,\tau}$$

3.47
a. $\Delta T \approx -2.60\ \text{K}$
$t_{\text{C}}(\text{final}) = -2.60°\text{C}$
b. $\left(\frac{\partial H_m}{\partial P}\right)_T = -\left(\frac{\partial H_m}{\partial T}\right)_P \left(\frac{\partial T}{\partial P}\right)_H = C_{\bar{P},m}\mu_{\text{JT}}$
$\left(\frac{\partial \bar{H}}{\partial P}\right)_T = -1.28\ \text{J mol}^{-1}\ \text{atm}^{-1}$

3.49
$\Delta H_{\text{m}} = -40{,}802\ \text{J mol}^{-1}$

3.53
a. $\Delta C_P^\circ = 192.401\ \text{J K}^{-1}\ \text{mol}^{-1} = 0.192401\ \text{kJ K}^{-1}\ \text{mol}^{-1}$
$\Delta H^\circ_{348\ \text{K}} = -2210.42\ \text{kJ mol}^{-1}$
b. $\Delta C_P^\circ = -0.00781\ \text{kJ K}^{-1}\ \text{mol}^{-1}$
$\Delta H^\circ_{348\ \text{K}} = -198.24\ \text{kJ mol}^{-1}$

3.55
a. $\Delta_{\text{f}}H^\circ(\text{CH}_4)_{373\ \text{K}} = -76.56\ \text{kJ mol}^{-1}$
$\Delta_{\text{f}}H(\text{CO}_2)_{373\ \text{K}} = -392.98\ \text{kJ mol}^{-1}$
$\Delta_{\text{f}}H^\circ(\text{H}_2\text{O})_{373\ \text{K}} = -283.443\ \text{kJ mol}^{-1}$
b. $\Delta H^\circ_{373\ \text{K}} = -883.306\ \text{kJ mol}^{-1}$
c. $\Delta H^\circ_{373\ \text{K}} = -883.282\ \text{kJ mol}^{-1}$

3.57
a. $\Delta_{\text{f}}U^\circ(\text{CO}_2) = -393.522\ \text{kJ mol}^{-1}$
$\Delta_{\text{f}}U^\circ(\text{CO}) = -111.766\ \text{kJ mol}^{-1}$
b. $\Delta U^\circ = -563.512\ \text{kJ mol}^{-1}$
c. $\Delta H^\circ \approx -565.991\ \text{kJ mol}^{-1}$

3.59
a. $\Delta U^\circ \approx -2796\ \text{kJ mol}^{-1}$
$\Delta H^\circ \approx -2794\ \text{kJ mol}^{-1}$
b. $\Delta H^\circ_{298\ \text{K}} = -2855.68\ \text{kJ mol}^{-1}$
$\Delta H^\circ_{373\ \text{K}} = -2852.74\ \text{kJ mol}^{-1}$
c. $\Delta U^\circ \approx -606\ \text{kJ mol}^{-1}$
$\Delta H^\circ \approx -608\ \text{kJ mol}^{-1}$

3.63
a. Assume that the volume of the liquid water is constant.
$w = 0$
$\Delta U = 0$
$q = 0$
$\Delta H = 180\ \text{J}$
b. Since $q = 0$ in part (a), everything is the same as in part (a).

3.65
a. TRUE
b. FALSE
c. FALSE
d. FALSE
e. TRUE
f. FALSE
g. TRUE
h. FALSE
i. FALSE

Chapter 4

Answers to selected exercises

4.2
$\eta_{\text{c}} = 0.378$

4.3
a. $\eta_{\text{hp}} = 17.6$
b. $\eta_{\text{r}} = 15.4$
c. Cost $= 4.1 \times 10^{-9}$ dollars J^{-1}
d. Cost $= 3.6 \times 10^{-8}$ dollars J^{-1}

4.5
$\Delta S = 13.43\ \text{J K}^{-1}$

4.6
$\Delta S = 124.9\ \text{J K}^{-1}$

4.7
$$\Delta S = na\ \ln\left(\frac{T_2}{T_1}\right) + nb(T_2 - T_1) - \frac{nc}{2}\left(\frac{1}{T_2^2} - \frac{1}{T_1^2}\right)$$

4.8
$\Delta S = 12.26\ \text{J K}^{-1}$

4.9
$dS/dt = 0.00274\ \text{J K}^{-1}\ \text{s}^{-1}$

4.10
$\Delta S = 24.47\ \text{J K}^{-1}$
$\Delta S_{\text{surr}} = 0$
$\Delta S_{\text{univ}} = 24.47\ \text{J K}^{-1}$

4.11
a. $\Delta S_{\text{mix}} = 5.762\ \text{J K}^{-1}$
b. $\Delta S_{\text{mix}} = 8.644\ \text{J K}^{-1}$

4.12
a. The first number is the number showing on the first die, and the second number is the number showing on the second die. For example, 1,2 is different from 2,1.

1,1	2,1	3,1	4,1	5,1	6,1
1,2	2,2	3,2	4,2	5,2	6,2
1,3	2,3	3,3	4,3	5,3	6,3
1,4	2,4	3,4	4,4	5,4	6,4
1,5	2,5	3,5	4,5	5,5	6,5
1,6	2,6	3,6	4,6	5,6	6,6

b. $N = 1296$
c. $N = 21$

4.13
$W = 10^{6.61\times 10^{24}}$

4.15
b. $S(T_1) = \dfrac{aT_1^3}{3} + bT_1$

4.17
$\Delta S_{\text{surr}} = 1898.3\ \text{J K}^{-1}$
$\Delta S_{\text{univ}} = 1725.5\ \text{J K}^{-1}$

4.18
$S_{\text{st}} = 14.90\ \text{J K}^{-1}\ \text{mol}^{-1}$

Answers to selected problems

4.19
a. $\eta = 0.211$
$V_2 = 2.10\ \text{L}$
$V_4 = 0.714\ \text{L}$
b. $w_1 = -1129\ \text{J}$
$w_2 = -249\ \text{J}$
$w_3 = 890\ \text{J}$
$w_4 = 249\ \text{J}$

4.21
$P_4 = 6.09\ \text{atm}$
$P_3 = 1.52\ \text{atm}$
$V_1 = 0.369\ \text{L}$
$V_2 = 1.477\ \text{L}$
$V_3 = 3.013\ \text{L}$
$V_4 = 0.753\ \text{L}$

4.23
b. $w = 1.56\ \text{kWh}$

4.25
$\Delta S_1 = 1.73\ \text{J K}^{-1}$
$\Delta S_3 = -1.73\ \text{J K}^{-1}$
$\Delta S_{\text{cycle}} = 0$

4.27
$q = 0$
$w = -810.6\ \text{J}$
$T_{\text{f}} = 461\ \text{K}$
$\Delta U = -810.6\ \text{J}$
$\Delta S = 8.15\ \text{J}$

4.29
a. $\Delta S = 5.763\ \text{J K}^{-1}$
b. $\Delta S = 3.371\ \text{J K}^{-1}$
c. The value of the increase in volume is immaterial. It is the ratio of the final volume to the initial volume that matters.

4.31
$\Delta S = 2.159 \times 10^{-21}\ \text{J K}^{-1}$

4.35
a. $\Delta S^\circ = -326.607\ \text{J K}^{-1}\ \text{mol}^{-1}$
b. $\Delta S^\circ = -88.839\ \text{J K}^{-1}\ \text{mol}^{-1}$
c. Assume that the $CaCO_3$ is calcite, not aragonite: $\Delta S^\circ = 159.1\ \text{J K}^{-1}\ \text{mol}^{-1}$

4.39
a. $\Delta_{\text{f}} S^\circ(\text{CO}) = 89.340\ \text{J K}^{-1}\ \text{mol}^{-1}$
$\Delta_{\text{f}} S^\circ(\text{CO}_2) = 2.908\ \text{J K}^{-1}\ \text{mol}^{-1}$
b. $\Delta S^\circ = -172.864\ \text{J K}^{-1}\ \text{mol}^{-1}$

4.41
a. $S_{\text{m}}^\circ(\text{solid},\ 231.49\ \text{K}) = 111.04\ \text{J K}^{-1}\ \text{mol}^{-1}$
b. $S_{\text{m}}^\circ(\text{liquid},\ 231.49\ \text{K}) = 146.80\ \text{J K}^{-1}$
c. $S_{\text{m}}^\circ(\text{liquid}),\ 298.15\ \text{K}) = 178.75\ \text{J K}^{-1}\ \text{mol}^{-1}$

4.43
$\Delta S = -145.11\ \text{J K}^{-1}$
$\Delta H = -44.004\ \text{kJ mol}^{-1}$
$$\Delta S_{\text{surr}} = \frac{q_{\text{surr}}}{T_{\text{surr}}} = \frac{44{,}004\ \text{J}}{298.15\ \text{K}} = 147.59\ \text{J K}^{-1}$$

4.45
a. $\Delta H_{\text{comb}} = -1.225 \times 10^5\ \text{kJ}$
b. $h_{\text{max}} = 7.08\ \text{km}$
c. $h_{\text{max}} = 6.03\ \text{km}$

Chapter 5

Answers to selected exercises

5.1

$dA \le -P_{\mathrm{ext}}\, dV + dw_{\mathrm{net}}$ (if T is constant)
$dA \le dw_{\mathrm{net}}$ (if T and V are constant)
$dw_{\mathrm{net(surr)}} \le -dA$ (if T and V are constant)

5.2

a. $\left(\frac{\partial P}{\partial S}\right)_{V,n} = 8124\ \mathrm{K\ m^{-3}}$
b. $\left(\frac{\partial P}{\partial S}\right)_{V,n} = 4062\ \mathrm{K\ m^{-3}}$
c. $\left(\frac{\partial P}{\partial S}\right)_{V,n} = 16248\ \mathrm{K\ m^{-3}}$

5.3

a. $\left(\frac{\partial V}{\partial S}\right)_{P,n} = \frac{nR}{C_V + nR}\left(\frac{T}{P}\right)$
b. $\left(\frac{\partial V}{\partial S}\right)_{P,n} = 0.00118\ \mathrm{K\ Pa^{-1}}$
c. $\left(\frac{\partial V}{\partial S}\right)_{P,n} = 0.00118\ \mathrm{K\ Pa^{-1}}$

5.5

$G^{\circ}_{\mathrm{m}}(\mathrm{atm}) - G^{\circ}_{\mathrm{m}} = 32.62\ \mathrm{J\ mol^{-1}}$

5.6

a. $f = 4.976\ \mathrm{atm} = 504{,}200\ \mathrm{Pa} = 504.2\ \mathrm{kPa}$
b. $f = 4.831\ \mathrm{atm} = 489{,}500\ \mathrm{Pa} = 489.5\ \mathrm{kPa}$

5.7

a. $G_{\mathrm{m}} - G^{\circ}_{\mathrm{m}} = 7.09 \times 10^{-2}\ \mathrm{J\ mol^{-1}}$
b. $G_{\mathrm{m}} - G^{\circ}_{\mathrm{m}} = 6.38\ \mathrm{J\ mol^{-1}}$

5.8

b. $\Delta G_{383.15\ \mathrm{K}} \approx -1090\ \mathrm{J\ mol^{-1}}$
c. $\Delta G_{383.15\ \mathrm{K}} = -1090\ \mathrm{J\ mol^{-1}}$

5.12

a. $\mu_i - \mu_i^{\circ} = -11{,}550\ \mathrm{J\ mol^{-1}} = -11.55\ \mathrm{kJ\ mol^{-1}}$
b. $\mu_i - \mu_i^{\circ} = 0.326\ \mathrm{J\ mol^{-1}} = 0.000326\ \mathrm{kJ\ mol^{-1}}$

5.13

c. $\left(\frac{\partial U}{\partial V}\right)_{T,n} = 309\ \mathrm{J\ m^{-3}} = 309\ \mathrm{Pa}$

5.14

c. $\left(\frac{\partial H}{\partial P}\right)_{T,n} = -9.0 \times 10^{-5}\ \mathrm{J\ Pa^{-1}} = -9.0\ \mathrm{J\ bar^{-1}} = -9.1\ \mathrm{J\ atm^{-1}}$

5.15

a. $C_V = 74.509\ \mathrm{J\ K^{-1}\ mol^{-1}}$
b. $C_{P,\mathrm{m}} - C_{V,\mathrm{m}} = 0$
d. $\gamma = 1.0106$

5.16

$C_V = 0.4418\ \mathrm{J\ K^{-1}\ g^{-1}}$

Answers to selected problems

5.21

a. $U = U_0\left(\frac{V_0}{V}\right)^{2/3}\left(\frac{n}{n_0}\right)^{5/3} \exp\left[\frac{2}{3R}\left(\frac{S}{n} - \frac{S_0}{n_0}\right)\right]$
b. $T = \frac{2U}{3nR}$
c. $P = \frac{2U}{3V} = \frac{nRT}{V}$

5.23

b. $\Delta S_{\mathrm{m}} = 5.688\ \mathrm{J\ K^{-1}\ mol^{-1}}$

5.25

b. $\Delta S = 23.157\ \mathrm{J\ K^{-1}}$
$\Delta S_{\mathrm{ideal}} = 23.053\ \mathrm{J\ K^{-1}}$

5.27

a. $\Delta G = 34.68\ \mathrm{J}$
b. $\Delta G = 37.83\ \mathrm{J}$
c. $\Delta G = 0$
d. $\Delta G = -3.15\ \mathrm{J}$

5.29

a. $\Delta A = -nRT\ \ln\left(\frac{V_2}{V_1}\right)$
b. $\Delta A = 2723\ \mathrm{J}$
c. $\Delta A = 1718\ \mathrm{J}$

5.31

b. $\Delta A_{\mathrm{m}} = -2269\ \mathrm{J\ mol^{-1}}$ (ideal gas: $-2271\ \mathrm{J\ mol^{-1}}$)
c. $\Delta A_{\mathrm{m}} = -2269\ \mathrm{J\ mol^{-1}}$

5.35

a. $\left(\frac{\partial U}{\partial V}\right)_{T,n} = \frac{n^2 a}{V^2}$
b. $\left(\frac{\partial U}{\partial V}\right)_{T,n} = 229\ \mathrm{J\ m^{-3}} = 229\ \mathrm{Pa}$
$P = 1.015 \times 10^5\ \mathrm{Pa}$
c. $\left(\frac{\partial U}{\partial V}\right)_{T,n} = \frac{0.1363\ \mathrm{Pa\ m^6\ mol^{-2}}}{(5.0 \times 10^{-5}\ \mathrm{m^3\ mol^{-1}})^2} = 5.45 \times 10^7\ \mathrm{Pa}$
$P = 8.47 \times 10^7\ \mathrm{Pa}$
d. $\left(\frac{\partial U}{\partial V}\right)_{T,n} = 310\ \mathrm{J\ m^{-3}} = 310\ \mathrm{Pa}$

5.37

b. $v_{\mathrm{s}} = 346\ \mathrm{m\ s^{-1}}$
c. $v_{\mathrm{s}} = 1016\ \mathrm{m\ s^{-1}}$
d. For air, ratio = 0.741
For helium, ratio = 0.809

5.39

c. $\lim_{P \to 0} \mu_{\mathrm{JT}} = 4.3 \times 10^{-6}\ \mathrm{K\ Pa^{-1}} = 0.44\ \mathrm{K\ atm^{-1}}$

5.41

a. $H_m(\text{liquid, 20 atm}) - H_m(\text{liquid, 1 atm}) = 35.3\ \text{J mol}^{-1}$
b. $H_m(\text{solid, 20 atm}) - H_m(\text{solid, 1 atm}) = 35.902\ \text{J mol}^{-1}$
c. At 20.00 atm, $\Delta_{\text{fus}}H_m = 6005\ \text{J mol}^{-1}$

5.43

a. Homogeneous, degree 2
b. Not homogeneous
c. Not homogeneous
d. Not homogeneous
e. Not homogeneous

5.45

a. FALSE
b. FALSE
c. FALSE
d. FALSE
e. FALSE
f. FALSE
g. TRUE
h. TRUE

5.47

	(1) Spontaneous?	(2) ΔG	(3) ΔH	(4) ΔS	(5) ΔH vs. $T\,\Delta S$
a.	Reversible	0	Positive	Positive	Equal
b.	Spontaneous	Negative	Positive	Positive	Smaller
c.	Nonspontaneous	Positive	Positive	Positive	Larger
d.	Spontaneous	Negative	Positive	Positive	Smaller
e.	Reversible	0	Positive	Positive	Equal
f.	Reversible	0	Negative	Negative	Equal
g.	Spontaneous	Negative	Positive	Positive	Smaller

Chapter 6

Answers to selected exercises

6.2

a. $c = 3$
b. $c = 4$
c. $c = 2$
d. $c = 2$
e. $c = 2$
f. $c = 1$
g. $c = 2$

6.4

$P_2 - P_1 = 1.350 \times 10^6\ \text{Pa} = 13.32\ \text{atm}$

6.6

$P_2 = 0.450\ \text{atm} = 342\ \text{torr} = 0.456\ \text{bar}$

6.7

$P_2 = 0.678\ \text{atm} = 515\ \text{torr} = 68.7\ \text{kPa}$

6.8

$P_2' = 125{,}000\ \text{Pa} = 1.24\ \text{atm} = 940\ \text{torr}$

6.11

a. $\gamma \approx 0.142\ \text{J m}^{-2}$ (Any value near this can be expected.)
b. Ratio $\approx 8.5 \times 10^{-9}$

6.12

a. $h = 0.049\ \text{m} = 4.9\ \text{cm}$
b. $h = 0.00025\ \text{m} = 0.25\ \text{mm}$

6.13

$h = -0.00655\ \text{m} = -6.55\ \text{mm}$

6.14

b. $P_2 = 23.753$ Torr

Answers to selected problems

6.17

$G_m^{(g)} - G_m^{(l)} = 0$
$A_m^{(g)} - A_m^{(l)} = -3.101\ \text{kJ mol}^{-1}$
$H_m^{(l)} - H_m^{(s)} = 40.66\ \text{kJ mol}^{-1}$
$U_m^{(l)} - U_m^{(s)} = 37.56\ \text{kJ mol}^{-1}$
$S_m^{(l)} - S_m^{(s)} = 109.0\ \text{J K}^{-1}\ \text{mol}^{-1}$

6.19

a. $f = 1$
b. $f = 1$
c. $f = 4$
d. $f = 3$
e. $f = 2$

6.21

With only one component, the largest possible number of phases is 3, in which case $f = 0$. Four phases of one substance cannot coexist at equilibrium.

6.23

a. $T_2 = 239.5\ \text{K}$; $t_C = -33.6°\text{C}$
b. $\Delta_{\text{vap}}H = 24{,}400\ \text{J mol}^{-1}$

6.25

a. $P = 1.95$ atm
$P(\text{gauge}) = 0.95\ \text{atm} = 13.9$ psig
b. $T_f = 273.145\ \text{K}$
$t_{Cf} = -0.00488°\text{C}$

6.27

$T = 367.9\ \text{K}$
$t_C = 94.7°\text{C}$

6.31

b. With the modified equation, $P_2 = 92.44$ torr
With the original Clausius–Clapeyron equation, $P_2 = 93.91$ torr
From the CRC Handbook, $P_2 = 92.51$ torr.

6.35

a. $\Delta\text{slope} = -21.99\ \text{J K}^{-1}\ \text{mol}^{-1}$
b. $\Delta\text{slope} = 1.63 \times 10^{-6}\ \text{J Pa}^{-1}\ \text{mol}^{-1} = 0.163\ \text{J bar}^{-1}\ \text{mol}^{-1}$
c. $\Delta\text{slope} = -109.0\ \text{J K}^{-1}\ \text{mol}^{-1}$
d. $\Delta\text{slope} = 0.0306\ \text{J Pa}^{-1}\ \text{mol}^{-1} = 3060\ \text{J bar}^{-1}\ \text{mol}^{-1}$

6.39
$h = 0.0490\ \text{m} = 4.90\ \text{cm}$

6.41
$F = 0.0021\ \text{N}$

6.45
$\Gamma_2 = 5.7 \times 10^{-6}\ \text{mol m}^{-2}$ for both concentrations

6.47
- **a.** FALSE
- **b.** TRUE
- **c.** FALSE
- **d.** TRUE
- **e.** FALSE
- **f.** FALSE
- **g.** FALSE
- **h.** TRUE
- **i.** TRUE
- **j.** FALSE
- **k.** TRUE

Chapter 7

Answers to selected exercises

7.1
$V^*_{\text{m1}}(P^*_1 - P) = -5.609\ \text{J mol}^{-1}$
$RT\ \ln\left(\frac{P^*_i x_i}{P^\circ}\right) = -8804\ \text{J mol}^{-1}$

7.6
Any two of *o*-xylene, *m*-xylene, *p*-xylene
Ethylbenzene and toluene
1-Propanol and 2-propanol
Any two of naphthalene, anthracene, and phenanthrene
2-Methylpentane and 3-Methylpentane
3-Pentanone and 2-pentanone
Propanal and propanone

7.8
$x(\text{benzene}) \approx 0.86$; $T(\text{boil}) \approx 357\ \text{K}$.

7.10
$k_1 \approx 985\ \text{torr}$

7.11
b. $x^{(\text{eq})}_{i(\text{H}_2\text{O})} = 0.000022$
$x^{(\text{eq})}_{i(\text{CCl}_4)} = 0.009978$

7.13
$c_2 = 0.0999\ \text{mol L}^{-1}$

7.15
$$k_i^{(\text{ppm})} = k_i \frac{M_1}{M_i}(10^{-6})$$
$$k_i^{(\%)} = k_i \frac{M_1}{M_i}(10^{-2})$$
$$k_i^{(V\%)} = k_i \frac{V^*_{\text{m1}}}{V^*_{\text{mi}}}(10^{-2})$$

7.16
$P = 1.47 \times 10^6\ \text{Pa} = 14.7\ \text{bar} = 14.5\ \text{atm}$

7.18
$a_i^{(\text{I})} = 0.9513$
$\gamma_i^{(\text{I})} = 1.312$

7.19
$a_i^{(\text{I})} = 0.9232$
$\gamma_i^{(\text{I})} = 1.026$

7.22
$I = 0.600\ \text{mol kg}^{-1}$

7.29
$x_{\text{Au}} = 0.88$

7.32
a. $\ln(1 - x_2) = -x_2 - \frac{x_2^2}{2} - \frac{x_2^3}{3} + \cdots$
b. $\frac{x_2^2}{2} = 5 \times 10^{-5}$
$\frac{x_2^3}{3} = 3.33 \times 10^{-7}$
c.

$-x_2$	$\ln(x_1)$	% Difference
-0.100	-0.10536	5.36%
-0.0100	-0.010050	0.50%
-0.00100	-0.00100050	0.05%
-0.000100	-0.0001005	0.005%

7.34
a. $K_{\text{b1}} = 0.513\ \text{K kg mol}^{-1}$
b. $t_{\text{b}} = 100.014°\text{C}$

7.35
a. $P_1 = 0.99947\ \text{atm} = 101{,}272\ \text{Pa}$
b. $\Delta P_{\text{vap}} = P^*_1 M_1 m_2$

7.36
b. $\Pi \approx 6.88 \times 10^4\ \text{Pa} = 0.679\ \text{atm}$

Answers to selected problems

7.39
$\gamma_2^{(\text{m})} = 0.9275$
$\gamma_1^{(\text{c})} = 1.036$

7.43
a. $K_{\text{d}}^{(\text{c})} = 0.012$
b. $V_{\text{thio}} = 0.0045\ \text{L} = 4.5\ \text{mL}$

7.45
$k_2^{(y)} = 2380\ \text{torr}$

7.47
$a = e^{0.907} = 2.48$

7.49
$\gamma = 1.0044$

7.51
Acetone = substance 1
a. $a_1^{(\mathrm{I})} = 0.669$
$\gamma_1^{(\mathrm{I})} = 0.944$
$a_2^{(\mathrm{I})} = 0.1892$
$\gamma_2^{(\mathrm{I})} = 0.650$
b. $\Delta G_{\mathrm{mix}} = -1973$ J
$G^{\mathrm{E}} = -427$ J
c. $a_2^{(\mathrm{II})} = 0.382$
$\gamma_2^{(\mathrm{II})} = 1.31$

7.53
a. $\Delta H^{\circ}_{\mathrm{diff}}(\mathrm{KOH}) = -57.61\ \mathrm{kJ\ mol^{-1}}$
b. $\mu^{\circ(m)}(\mathrm{KOH, aq}) - G^{*}_{\mathrm{m}}(\mathrm{KOH, s}) = -61.43\ \mathrm{kJ\ mol^{-1}}$

7.55
$\alpha = 3.89\ \mathrm{kg^{1/2}\ mol^{-1/2}}$
$\beta = 4.53 \times 10^{9}\ \mathrm{kg^{1/2}\ mol^{-1/2}\ m^{-1}}$

7.69
a. $\Delta T_{\mathrm{b}} = 0.0788$ K
b. $\Delta T_{\mathrm{b}} = 0.0786$ K (0.3% difference from part (a))
c. $\Delta T_{\mathrm{b}} = 0.0789$ K (0.1.% difference from part (a))

7.73
From Eq. (7.6-10), $T_{\mathrm{f}} = 253.4$ K
From Eq. (7.6-7), $T_{\mathrm{f}} = 254.2$ K

7.75
a. $\Pi = 3.63 \times 10^{5}$ Pa = 3.58 atm
$h = 36.3$ m
b. $\Pi = 3.73 \times 10^{5}$ Pa = 3.70 atm
$h = 37.5$ m
c. The result is the same as in part (b).

7.77
a. FALSE
b. FALSE
c. FALSE
d. TRUE
e. TRUE
f. TRUE
g. TRUE
h. TRUE
i. TRUE
j. TRUE

7.79
a. $K_{\mathrm{f}} = 3.14\ \mathrm{K\ kg\ mol^{-1}}$
b. $T_{\mathrm{f}} = 259.9$ K
c. $T_{\mathrm{f}} = 272.85$ K
e. $T_{\mathrm{f}} = 247$ K
Volume ratio at the eutectic =2.94 parts of ethylene glycol to 1 part of water

Chapter 8

Answers to selected exercises

8.1
a. $\Delta G^{\circ} = 20.661\ \mathrm{kJ\ mol^{-1}}$
b. $\Delta H^{\circ} = 71.488\ \mathrm{kJ\ mol^{-1}}$
$\Delta S^{\circ} = 170.473\ \mathrm{J\ K^{-1}\ mol^{-1}}$
c. $\Delta G^{\circ} = 20.661\ \mathrm{kJ\ mol^{-1}}$
d. $\Delta G^{\circ} = 20.665$ kJ mol

8.3
a. $\left(\dfrac{\partial G}{\partial \xi}\right)_{T,P} = 22.118\ \mathrm{kJ\ mol^{-1}}$
b. $\left(\dfrac{\partial G}{\partial \xi}\right)_{T,P} = 13.235\ \mathrm{kJ\ mol^{-1}}$

8.4
a. $P(\mathrm{C_3H_8}) = 7.4 \times 10^{-58}$ Pa
$P(\mathrm{O_2}) = 3.7 \times 10^{-57}$ Pa
b. Volume per molecule = $5.5 \times 10^{36}\ \mathrm{m^3}$

8.5
$\Delta G^{\circ(\mathrm{II})} = -558.518\ \mathrm{kJ\ mol^{-1}}$

8.8
b. $\gamma_{\pm} = (\gamma_+^3 \gamma_-^2)^{1/5}$
$m_{\pm} = (m_+^3 m_-^2)^{1/5} = m(3^3 2^2)^{1/5} = 2.55085$ m

8.9
a. $\Delta G^{\circ} = 79{,}885\ \mathrm{kJ\ mol^{-1}}$
$K = 1.01 \times 10^{-14}$
b. $m(\mathrm{H^+}) = m(\mathrm{OH^-}) = 1.005 \times 10^{-7}\ \mathrm{mol\ kg^{-1}}$

8.10
pH = 1.63

8.12
b. pH = 3.91
c. pH = 3.91

8.16
$K_p(1000.\ \mathrm{K}) = 0.098$

8.17
b. $K = 14.8$
$\Delta G^{\circ} = 8.37\ \mathrm{kJ\ mol^{-1}}$

8.18
$\alpha = 0.115$

8.20
$(\partial G/\partial \xi)_{T,P} = -10.9\ \mathrm{kJ\ mol^{-1}}$

8.21
a. $K = 1.81 \times 10^{4}$
b. $[\mathrm{ATP}] = 0.00993\ \mathrm{mol\ L^{-1}}$

8.22
b. $\Delta G^{\circ\prime} = 19.4\ \mathrm{kJ\ mol^{-1}}$
$K = 48$

Answers to selected problems

8.25
a. $\Delta G^\circ = -141.782\ \mathrm{kJ\ mol^{-1}}$
c. $\Delta G^\circ = -300.125\ \mathrm{kJ\ mol^{-1}}$
e. $\Delta G^\circ = -70.692\ \mathrm{kJ\ mol^{-1}}$

8.29
a. $K = 5.43 \times 10^5$
b. $P(N_2) = 0.01555\ \mathrm{atm}$, $P(H_2) = 0.04665\ \mathrm{atm}$,
$P(NH_3) = 0.9378\ \mathrm{atm}$

8.31
a. $\Delta G^\circ = -162.715\ \mathrm{kJ\ mol^{-1}}$
$K = 3.2 \times 10^{28}$
c. $\Delta G^\circ = 28.644\ \mathrm{kJ\ mol^{-1}}$
$K = 9.59 \times 10^{-6}$
e. $\Delta G^\circ = -68.552\ \mathrm{kJ\ mol^{-1}}$
$K = 1.02 \times 10^{12}$

8.35
a. $\Delta H^\circ = -223.94\ \mathrm{kJ\ mol^{-1}}$
$\Delta S^\circ = -216.537\ \mathrm{J\ K^{-1}\ mol^{-1}}$
$\Delta G^\circ = -159.316\ \mathrm{kJ\ mol^{-1}}$
$\Delta H^\circ - T\,\Delta S^\circ = -159.377\ \mathrm{kJ\ mol^{-1}}$
b. $\Delta H^\circ = -753.99\ \mathrm{kJ\ mol^{-1}}$
$\Delta S^\circ = -156.63\ \mathrm{J\ K^{-1}\ mol^{-1}}$
$\Delta G^\circ = -707.79\ \mathrm{kJ\ mol^{-1}}$
$\Delta H^\circ - T\,\Delta S^\circ = -707.29\ \mathrm{kJ\ mol^{-1}}$

8.37
a. $K = 1.77 \times 10^{-10}$
b. $m(\mathrm{Ag^+}) = 1.34 \times 10^{-5}\ \mathrm{mol\ kg^{-1}}$

8.41
a. $\mathrm{pH} = -\log[(0.791)(0.0837)] = 1.18$
c. $\mathrm{pH} = -\log[(0.946)(2.65 \times 10^{-3})] = 2.60$

8.43
Assuming unit activity coefficients, $\mathrm{pH} = 2.95$
Using the Davies equation, $\mathrm{pH} = 2.96$

8.45
$m(\mathrm{HCO_3^-})/m^\circ = 1.25 \times 10^{-3}$
$m(\mathrm{H_2CO_3})/m^\circ = 2.86 \times 10^{-7}$

8.47
a. 0.0863 mol of NaOH
b. 0.0890 mol of NaOH

8.49
$\mathrm{pH} = 6.72$

8.53
a. $K_{400\ \mathrm{K}} = 43.6$
b. $x_{N_2} = 0.121,\quad x_{H_2} = 0.363,\quad x_{NH_3} = 0.516$

8.55
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. $K_{1000\ \mathrm{K}} = 3.11 \times 10^{-3}$

8.57
a. $K_{750\ \mathrm{K}} = 9.05 \times 10^3$
b. $K_{750\ \mathrm{K}} = 9.7 \times 10^3$

8.62
$K = 262$

8.64
a. FALSE
b. TRUE
c. TRUE
d. TRUE
e. FALSE
f. FALSE
g. FALSE

8.66
a. $\Delta G^\circ = 28.644\ \mathrm{kJ\ mol^{-1}}$ at 298.15 K.
$K_P = 9.6 \times 10^{-6}$ at 298.15 K
$\Delta G^\circ = 3.021\ \mathrm{kJ\ mol^{-1}}$ at 1000 K.
$K_P = 0.695$ at 1000 K
b. $\Delta H^\circ = 41.169\ \mathrm{kJ\ mol^{-1}}$ at 298.15 K
$\Delta H^\circ = 34.783\ \mathrm{kJ\ mol^{-1}}$ at 1000 K.
c. High temperature favors the production of CO.
Pressure makes no difference.
d. $\Delta G^\circ = -5.248\ \mathrm{kJ\ mol^{-1}}$
$K_P = 1.65$ at 1259 K
e. $\Delta G^*_{1259\ \mathrm{K}} = -5988\ \mathrm{J\ mol^{-1}}$
$K_P = 1.77$

Chapter 9

Answers to selected exercises

9.2
b. $E = 1.091\ \mathrm{V}$

9.6
$E = 1.1076\ \mathrm{V}$

9.7
$E = -0.0464\ \mathrm{V}$

9.9
$\mathrm{pH} = 1.100$

9.11
$E^{(\mathrm{II})} - E^{(\mathrm{I})} = 0.325\ \mathrm{V}$

9.12
$K = 7.6 \times 10^{36}$

Answers to selected problems

9.13
$|\nabla c| = 4 \times 10^7$ mol L^{-1} m^{-1}

9.15
a. $E = 0.3527$ V
b. $E = 0.3517$ V

9.17
a. $\mathrm{Pt|Ag|AgCl(s)|HCl(aq)||Pb(NO_3)_2(aq)Pb(s)|Pt}$
c. $E = -0.4195$ V

9.19
$E^\circ = 0.772$ V

9.21
Assuming unit activity coefficients, $E = 0.083$ V
Using activity coefficients from Figure 7.12, $E = 0.092$ V

9.23
$\gamma_\pm = 0.757$

9.25
$E = 1.0424$ V
pH = 12.88

9.29
a. $K = 1.42 \times 10^{-18}$
b. $K = 1.8 \times 10^{-52}$

9.31
a. $K = 3.23 \times 10^8$
b. $m(\mathrm{Ce^{4+}}) = m(\mathrm{Cl^-}) = 0.00929$ mol kg^{-1}
$m(\mathrm{Ce^{3+}}) = 0.01571$ mol kg^{-1}

9.33
$K = 3.57 \times 10^2$

9.35
a. FALSE
b. TRUE
c. TRUE
d. FALSE
e. TRUE
f. FALSE
g. FALSE

9.37
a. $E^\circ = 1.060$ V
b. $w = 2.013 \times 10^6$ kJ
c. $w_{\mathrm{max}} = 559.2$ kWh
d. $w_{\mathrm{max}} = 1416$ kWh

Chapter 10

Answers to selected exercises

10.1
b. $v = 1040$ m s^{-1}
c. $\mathscr{K} = 7.25 \times 10^{-20}$ J

10.2
$\dfrac{p_1}{p_2} = 1.80 \times 10^{-6}$

10.4
a. $\sigma = \sqrt{\dfrac{k_B T}{m}} = \sqrt{\dfrac{RT}{M}}$
b. $\sigma = 278$ m s^{-1}

10.5
a. $k_B T/\sqrt{2}$
b. 2.909×10^{-21} J

10.6
a. Probability $\approx 4 \times 10^{-5}$
b. Probability $\approx 8 \times 10^{-5}$

10.7
a. Fraction = 0.683
b. $v_x' = 583$ m s^{-1}
c. $v_x' = 1068$ m s^{-1}

10.9
b. $v_p = 394$ m s^{-1}
c. $v_p = 1112$ m s^{-1}

10.10
$v_p = 1112$ m s^{-1}
$\langle v \rangle = 1256$ m s^{-1}
$v_{\mathrm{rms}} = 1363$ m s^{-1}

10.11
$\dfrac{\langle v \rangle}{v_p} = \sqrt{\dfrac{8}{2\pi}} = 1.1284$
$\dfrac{v_{\mathrm{rms}}}{v_p} = \sqrt{\dfrac{3}{2}} = 1.2247$

10.12
a. Ratio = 0.103218
b. Ratio = 0.103218
c. Ratio = 0.103218
d. Ratio = 0.109915
e. Ratio = 0.109915
f. Ratio = 0.109915

10.13
$N = 2.15 \times 10^{27}$

10.14
a. $N \approx 2 \times 10^{30}$
b. Amount per second = 1.2×10^3 mol s^{-1}

10.15
b. $\zeta = \dfrac{abk_B T}{mg}\left[1 - e^{-mgc/k_B T}\right]$

10.17

$d = 2.94 \times 10^{-10}$ m $= 294$ pm

10.18

a. $B_2 = \dfrac{2\pi N_{\mathrm{Av}} d^3}{3}$

10.19

a. $L = 3.44 \times 10^{-9}$ m
b. $\lambda = 1.94 \times 10^{-7}$ m
c. $\lambda / L = 56.5$

10.20

a. $z_{1(2)} = 1.34 \times 10^{9}\ \mathrm{s}^{-1}$
$z_{2(1)} = 5.34 \times 10^{9}\ \mathrm{s}^{-1}$
$z_{1(1)} = 5.72 \times 10^{9}\ \mathrm{s}^{-1}$
$z_{2(2)} = 1.25 \times 10^{9}\ \mathrm{s}^{-1}$
b. $Z_{12} = 2.63 \times 10^{34}\ \mathrm{s}^{-1}\ \mathrm{m}^{-3}$
$Z_{11} = 5.63 \times 10^{34}\ \mathrm{s}^{-1}\ \mathrm{m}^{-3}$
$Z_{22} = 3.08 \times 10^{33}\ \mathrm{s}^{-1}\ \mathrm{m}^{-3}$
c. Total rate of collisions $= 2.10 \times 10^{33}\ \mathrm{s}^{-1}$

10.21

Number ≈ 9.2

Answers to selected problems

10.23

$\langle \sin(x) \rangle = 0$

$(\sin(x))_{\mathrm{rms}} = \dfrac{1}{\sqrt{2}}$

10.25

Fraction with speed $> c \approx 10^{-2.11 \times 10^{11}}$

10.27

Fraction $= 0.317$

10.29

a. Fraction $= 1.000 - 0.199 = 0.801$
b. Fraction $= 0.801$

10.33

b. $\sigma_v = 187.4\ \mathrm{m\ s}^{-1}$

10.35

$\langle v \rangle = 5.72 \times 10^{-10}\ \mathrm{m\ s}^{-1}$

10.39

$m \approx 2.0 \times 10^{4}$ kg $= 4.4 \times 10^{4}$ pounds

10.41

Mass lost $= 3.24 \times 10^{-5}$ kg $= 32.4$ mg

10.43

a. $\mathcal{N}_{\mathrm{O}_2} = 6.5 \times 10^{11}\ \mathrm{m}^{-3}$
$\mathcal{N}_{\mathrm{N}_2} = 2.6 \times 10^{12}\ \mathrm{m}^{-3}$
b. Total number per second $= 3.8 \times 10^{10}\ \mathrm{s}^{-1}$

10.45

$t = 4.39$ h

10.47

a. Probability $= 0.0003698$
b. Probability $= 0.0003771$
c. Probability $= 0.0007541$

10.49

$P = 0.0692$ atm
Percent $\mathrm{N}_2 = 85.3\%$
Percent $\mathrm{O}_2 = 14.7\%$

10.51

$P - P_0 = 0.014$ atm

10.53

$$V_{\mathrm{excl}} = N_1 \frac{2\pi}{3} d_1^3 + N_2 \frac{4\pi}{3} d_{12}^3$$

10.55

a. Ratio $= 6.5 \times 10^{-4}$
b. Ratio $= 4.0 \times 10^{-4}$

10.57

$a = 1.05 \times 10^{10}\ \mathrm{m}^{-1}$
$b = 2.72 \times 10^{-19}$ J
$c = 1.03 \times 10^{-77}\ \mathrm{J\ m}^{-6}$

10.59

$$B_2 = \frac{2\pi N_{\mathrm{Av}}}{3} c^3 - \frac{2\pi n_{\mathrm{Av}}}{3} (c^3 - d^3) e^{-u_0/k_{\mathrm{B}}T}$$

10.61

a. $\dfrac{PV_{\mathrm{m}}}{RT} = 1 + 4y + 10y^2 + 18y^3 + \cdots$
$B_2 = \dfrac{2N_{\mathrm{Av}} \pi d^3}{3}$

10.63

a. $z_{\mathrm{CO(O_2)}} = 1.80 \times 10^{9}\ \mathrm{s}^{-1}$
b. $z_{\mathrm{O_2(CO)}} = 3.60 \times 10^{9}\ \mathrm{s}^{-1}$
c. Time $= 3.35 \times 10^{14}$ s $= 1.06 \times 10^{7}$ years

10.67

a. $\rho = 3100\ \mathrm{kg\ m}^{-3}$
b. No. of nearest neighbors ≈ 10.6

10.69

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 $\approx 10^{-1.7 \times 10^{8}}$ ($\approx$ 0 to 64 digits)
c. $z_{2(2)} = 2.8 \times 10^{-5}\ \mathrm{s}^{-1}$
d. $Z_{22} = 1.4 \times 10^{4}\ \mathrm{m}^{-3}\ \mathrm{s}^{-1}$
e. $z_{2(1)} = 1.8 \times 10^{17}\ \mathrm{s}^{-1}$

10.71

a. $\mathcal{N}_{\mathrm{pairs}} \approx 4.3 \times 10^{22}\ \mathrm{m}^{-3}$
b. $Z_{\mathrm{p1}} \approx 3.2 \times 10^{32}\ \mathrm{m}^{-3}\ \mathrm{s}^{-1}$

10.73

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 11

Answers to selected exercises

11.1

$$\nabla c_2 = -\mathbf{k}\, ab\, \sin(bz)e^{-t/\tau}$$

$$\frac{\partial c_2}{\partial t} = -\frac{a}{\tau}\cos(bz)e^{-t/\tau}$$

11.2

$J_z = -1.57 \times 10^{-7}\ \mathrm{mol\ m^{-2}\ s^{-1}} = -1.57 \times 10^{-11}\ \mathrm{mol\ cm^{-2}\ s^{-1}}$

11.7

Torque $= 0.0079$ N m

11.8

$$\frac{dV}{dt} \approx 32\ \mathrm{L\ min^{-1}}$$

11.9

$\mathscr{R} = 1.2 \times 10^{-3}$

11.10

$\mathscr{R} = 1.02$

11.11

At 77.7 K, $d = 4.61 \times 10^{-10}\ \mathrm{m} = 461\ \mathrm{pm} = 4.61\ \text{Å}$
At 273.2 K, $d = 346$ pm
At 353.2 K, $d = 333$ pm

11.13

$$\frac{\eta}{\mathcal{N} m D} = \frac{5}{6}$$

$$\frac{c_V \eta}{\kappa m} = \frac{2}{5}$$

$$\frac{D c_V \mathcal{N}}{\kappa} = \frac{12}{25}$$

11.14

a. $V_\mathrm{m} = 75\ \mathrm{L\ mol^{-1}}$
b. $V_\mathrm{m} = 51\ \mathrm{L\ mol^{-1}}$

11.15

$D(313\ \mathrm{K}) = 1.7 \times 10^{-9}\ \mathrm{m^2\ s^{-1}}$

11.19

$$t_+ = \frac{c_+ z_+ u_+}{c_+ z_+ u_+ + c_- |z_-| u_-}$$

$$t_- = \frac{c_- |z_-| u_-}{c_+ z_+ u_+ + c_- |z_-| u_-}$$

11.20

a. For H^+, $r_{i(\mathrm{eff})} = 2.63 \times 10^{-11}$; m $= 26.3$ pm $= 0.263$ Å
For OH^-, $r_{i,(\mathrm{eff})} = 4.66 \times 10^{-11}$ m $= 46.6$ pm $= 0.466$ Å
b. For Li^+, $r_{i(\mathrm{eff})} = 238$ pm $= 2.38$ Å

11.21

a. $\Lambda = 3.907 \times 10^{-2}\ \mathrm{m^2\ ohm^{-1}\ mol^{-1}} = 390.7\ \mathrm{cm^2\ ohm^{-1}\ mol^{-1}}$

Answers to selected problems

11.23

b. $\dfrac{1}{b_2} = D_2 a_2^2$
c. $b_2 = 1.00 \times 10^7$ s

11.25

$t = 2.5 \times 10^{-6}\ \mathrm{s} = 2.5\ \mu\mathrm{s}$

11.27

a. $u(0.002\ \mathrm{m}) = 0.0382\ \mathrm{m\ s^{-1}}$
b. $P_2 - P_1 = 7.29\ \mathrm{N\ m^{-2}} = 7.29$ Pa
c. $\dfrac{dV}{dt} = 1.79 \times 10^{-6}\ \mathrm{m^3\ s^{-1}} = 1.79 \times 10^{-3}\ \mathrm{L\ s^{-1}} = 1.79\ \mathrm{mL\ s^{-1}}$
d. $\mathscr{R} = 114$

11.31

$t(H_2SO_4) = 2970$ s

11.33

a. $(P_2 - P_1) = 350$ Pa
b. $\mathscr{R} = 2.3 \times 10^4$

11.37

a. $D = 1.01 \times 10^{-5}\ \mathrm{m^2\ s^{-1}}$
b. $D = 2.65 \times 10^{-5}\ \mathrm{m^2\ s^{-1}}$

11.41

$\mathscr{D}_{12} = 3.60 \times 10^{-5}\ \mathrm{m^2\ s^{-1}}$

11.43

At 100°C, $d = 4.18 \times 10^{-10}\ \mathrm{m} = 418$ pm
At 200°C, $d = 3.88 \times 10^{-10}\ \mathrm{m} = 388$ pm

11.45

$E_{a\eta} = 1.02 \times 10^4\ \mathrm{J\ mol^{-1}} = 10.2\ \mathrm{kJ\ mol^{-1}}$

11.47

$M_2 = 17.4\ \mathrm{kg\ mol^{-1}} = 17{,}400\ \mathrm{g\ mol^{-1}}$

11.49

a. $|\mathbf{F}| = 8.37 \times 10^{19}$ N
b. $m = 8.54 \times 10^{18}$ kg $= 1.88 \times 10^{19}$ lb

11.51

$r_{\mathrm{K^+(eff)}} = 1.25 \times 10^{-10}$ m $= 125$ pm
$r_{\mathrm{K^+(eff)}} = 1.21 \times 10^{-10}$ m $= 121$ pm

11.53

a. $t(\mathrm{Na^+}) = 0.437$
$t(\mathrm{Cl^-}) = 0.444$
$t(\mathrm{Ac^-}) = 0.119$
b. $\kappa = 0.01720$ ohm^{-1} m^{-1}
c. $R = 5820$ ohm

11.59

a. TRUE
b. FALSE
c. TRUE
d. FALSE
e. FALSE
f. TRUE
g. FALSE
h. TRUE

Chapter 12

Answers to selected exercises

12.2

a. $t_{1/2} = 135$ s
$\tau = 195$ s

12.3

$k = 9.8 \times 10^{-10}$ y^{-1}
$t = 2.4 \times 10^{9}$ y

12.5

a. $[\mathrm{A}] = 0.026$ mol L^{-1}
b. $[\mathrm{A}] = 0.034$ mol L^{-1}

12.6

a. $t_{1/2} = 150$ min
b. $t_{1/2} = 380$ min
c. $t_{1/2} = 75.8$ min

12.7

First order, $t = \dfrac{4\ \ln(2)}{k} = 4t_{1/2}$

Second order, $t = \dfrac{15}{k[\mathrm{A}]_0} = 15t_{1/2}$

12.9

a. $[\mathrm{A}]_t = 0.925$ mol L^{-1}
b. $t = \dfrac{1.000\ \text{mol L}^{-1}}{0.0150\ \text{mol L}^{-1}\ \text{s}^{-1}} = 66.7$ s
c. $t_{1/2} = \dfrac{[\mathrm{A}]_0}{2k_\mathrm{f}}$
$t_{1/2} = 33.3$ s

12.11

a. $t_{1/2} = \dfrac{1}{kb[\mathrm{A}]_0}$
b. $t_{1/2} = 0.77$ s
c. $t_{1/2} = 0.015$ s

12.17

$K_\mathrm{eq} = 0.528$
$[\mathrm{B}]_\mathrm{eq} = 0.0518$ mol L^{-1}
$[\mathrm{A}]_\mathrm{eq} = 0.0982$ mol L^{-1}
$t_{1/2} = 0.0139$ min
$\tau = 0.0200$ min
At $t = 0.100$ min, $[\mathrm{A}] = 0.0986$ mol L^{-1}, $[\mathrm{B}] = 0.0514$ mol L^{-1}

Answers to selected problems

12.23

a. Rate $= 1.42 \times 10^{-4}$ mol L^{-1} s^{-1}
b. $\dfrac{d[\mathrm{NO}]}{dt} = -1.42 \times 10^{-4}$ mol L^{-1} s^{-1}
$\dfrac{d[\mathrm{NOCl}]}{dt} = 1.42 \times 10^{-4}$ mol L^{-1} s^{-1}
$\dfrac{d[\mathrm{Cl_2}]}{dt} = -7.1 \times 10^{-5}$ mol L^{-1} s^{-1}

12.25

First order, $k = 6.25 \times 10^{-4}$ s^{-1}

12.27

a. $[\mathrm{A}] = 0.0443$ mol L^{-1}
b. $[\mathrm{A}] = 0.0357$ mol L^{-1}

12.29

$k_\mathrm{app} = 1.23 \times 10^{-4}$s^{-1}

12.31

a. $t_{1/2} = 1.19 \times 10^{5}$ s
b. $t = 3.6 \times 10^{5}$ s
c. $t = 2.3 \times 10^{6}$ s

12.37

a. The reaction is pseudo first order; $k_\mathrm{f} = 4.24 \times 10^{-4}$ s^{-1}
b. $P = 10.64$

12.39

$[\mathrm{A}] = 0.110$ mol L^{-1}
$[\mathrm{B}] = 0.890$ mol L^{-1}

12.49

a. Order with respect to NO $= 2.1 \approx 2$
Order with respect to $\mathrm{H_2} = 1.05 \approx 1$
$k = 1.7 \times 10^{-6}$ kPa^{-2} s^{-1} (average of four values)
b. Initial rate $= 1.7$ kPa s^{-1}
c. $P(\mathrm{NO}) = P(\mathrm{H_2}) = 98$ kPa

d. $t_{1/2} = \dfrac{\ln(2)}{0.068\ \text{s}^{-1}} = 10.\ \text{s}$
e. $t_{1/2} = 590.\ \text{s}$

Chapter 13

Answers to selected exercises

13.2
b. $f = 1.11 \times 10^{-11}$

13.4
For $z_2z_3 = 2$, $f = 0.174$
For $z_2z_3 = 1$, $f = 0.450$
For $z_2z_3 = 0$, $f = 1$
For $z_2z_3 = -1$, $f = 1.88$
For $z_2z_3 = -2$, $f = 3.03$

13.5
a. $E_a = 51{,}200\ \text{J mol}^{-1} = 51.2\ \text{kJ mol}^{-1}$
b. $E_a = 78{,}000\ \text{J mol}^{-1} = 78.0\ \text{kJ mol}^{-1}$

13.8
$\varphi = 7.0 \times 10^{-3}$

13.9
$E_a = 10{,}200\ \text{J mol}^{-1} = 10.2\ \text{kJ mol}^{-1}$

13.11
a. $\text{Rate} = \dfrac{d[\text{N}_2]}{dt} = k_f[\text{NO}_2]^2[\text{H}_2]$
b. $\text{Rate} = k_2K_1\dfrac{[\text{NO}]^2[\text{H}_2]^2}{[\text{N}_2]}$

13.16
b. One possibility is
(1) $\text{HNO}_3 \rightleftharpoons \text{HO} + \text{NO}_2$
(2) $\text{HO} + \text{HNO}_3 \rightarrow \text{H}_2\text{O} + \text{NO}_3$
(3) $\text{NO}_3 + \text{NO}_2 \rightarrow \text{O}_2 + \text{NO}_2 + \text{NO}$
(4) $2\text{HO} + \text{NO} \rightarrow \text{H}_2\text{O} + \text{NO}_2$

13.17
$$k_{\text{app}} = \frac{2A_1A_2e^{-(E_{a1}+E_{a2})/RT}}{A_{1'}e^{-E'_{a1}/RT} + 2A_2e^{-E_{a2}/RT}}$$

13.19
$\nu_{\text{min}} = 4.86 \times 10^{14}\ \text{s}^{-1}$
$\lambda_{\text{max}} = 6.17 \times 10^{-7}\ \text{m} = 617\ \text{nm}$

13.20
a. $\text{Rate} = -\dfrac{d[\text{H}_2]}{dt} = k_2K_1[\text{I}_2][\text{H}_2]$
b. $\text{Rate} = -\dfrac{d[\text{H}_2]}{dt} = \dfrac{k_2k_1[\text{I}_2][\text{H}_2]}{k'_1 + k_2[\text{H}_2]}$

13.24
$$\text{Rate} = \frac{k_2K_1^{1/2}[\text{A}]^{1/2}}{1 + K_1^{1/2}[\text{A}]^{1/2}}$$

13.28
$K_m = 16.3\ \mu\text{mol L}^{-1}$

Answers to selected problems

13.29
$k = 6.8 \times 10^9\ \text{L mol}^{-1}\ \text{s}^{-1}$

13.31
$d_{23} = 5.6 \times 10^{-10}\ \text{m}$

13.33
a. $k = 1.1 \times 10^3\ \text{L mol}^{-1}\ \text{s}^{-1}$
b. Fraction $= 1.3 \times 10^{-11}$

13.35
a. $E_a = 1.94 \times 10^5\ \text{J mol}^{-1} = 194\ \text{kJ mol}^{-1}$
$A = 2.38 \times 10^{12}\ \text{L mol}^{-1}\ \text{s}^{-1}$
b. $k(773\ \text{K}) = 0.185\ \text{L mol}^{-1}\ \text{s}^{-1}$
c. $t_{1/2} = 686\ \text{s}$

13.37
a. $E_a = 2.13 \times 10^5\ \text{J mol}^{-1} = 213\ \text{kJ mol}^{-1}$
$A = 3.46 \times 10^9\ \text{L}^{-1}\ \text{mol s}^{-1}$
b. $\varphi = 0.0077$

13.43
One possibility is
(1) $\text{ICl} + \text{H}_2 \rightarrow \text{HI} + \text{HCl}$ (slow, rate-limiting)
(2) $\text{HI} + \text{ICl} \rightarrow \text{HCl} + \text{I}_2$ (fast)

13.51
a. $\text{Rate} = k_3\theta_A = \dfrac{k_3K_1[\text{A}]}{1 + K_1[\text{A}] + K_2[\text{C}]}$
b. $\text{Rate} = \dfrac{k_3K_1[\text{A}]}{1 + K_2[\text{C}]}\left(\text{or } \dfrac{k_3K_1[\text{A}]}{K_2[\text{C}]} \text{ if } K_2[\text{C}] \text{ is large enough}\right)$

13.55
a. $\ln\left(\dfrac{[\text{B}][\text{A}]_0}{[\text{A}][\text{B}]_0}\right) = ([\text{A}]_0 + [\text{B}]_0)kt$
b. $[\text{A}] = 0.4995$

13.57
d. $K = \dfrac{[\text{P}]}{[\text{R}]} = \dfrac{k_1k_2}{k'_1k'_2}$

13.59
a. $E_a(\text{reverse}) = 178\ \text{kJ mol}^{-1}$
b. $K(373.15\ \text{K}) = 314$
c. $k' = 2.78 \times 10^{-12}\ \text{L mol}^{-1}\ \text{s}^{-1}$

13.61
b. $E_a = -6.0 \times 10^3\ \text{J mol}^{-1} = -6.0\ \text{kJ mol}^{-1}$

13.63
a. TRUE
b. FALSE
c. FALSE
d. TRUE
e. TRUE

f. TRUE
g. FALSE
h. FALSE
i. FALSE
j. TRUE

Chapter 14

Answers to selected exercises

14.1

c. Number of nodes = $n - 1$ (excluding the nodes at the ends of the string)

14.4

To quadruple the speed, ρ would have to be made smaller by a factor of 1/16.
To double the speed, T would have to be increased by a factor of 4.

14.6

$\lambda = 1.28$ m

14.9

$T = 4450$ K

14.11

$\sigma = 5.671 \times 10^{-8}$ J m^{-2} s^{-1} K^{-4}

14.12

a. $\lambda_{\text{threshold}} = 2.5 \times 10^{-7}$ m = 250 nm
b. $v_{\max} = 6.91 \times 10^{5}$ m s^{-1}

14.13

$|\mathbf{F}| = 53.4$ N

14.16

c. $\lambda = 4.86272 \times 10^{-7}$ m = 486.272 nm
$\nu = 6.165119 \times 10^{14}$ s^{-1} = 6.165119×10^{14} Hz

14.17

$v = 3.38 \times 10^{6}$ m s^{-1}

14.20

If the length of the box is doubled, the energy decreases by a factor of 1/4.
If the mass of the particle is doubled, the energy decreases by a factor of 1/2.

14.23

$\nu = 4.546 \times 10^{14}$ s^{-1}
$\lambda = 6.594 \times 10^{-7}$ m = 0.6594 μm = 659.4 nm

14.24

For the $n = 2$ state, $\nu = 3.637 \times 10^{14}$ s^{-1}
For the $n = 3$ state, $\nu = 8.183 \times 10^{14}$ s^{-1}

14.26

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

14.27

$B = D + F,\ C = i(D - F)$

14.29

$$\frac{dx}{dt} = -\frac{E}{\hbar\kappa}$$

14.32

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$$

14.34

a. $\nu_{\text{wave function}}(1) = \dfrac{3}{2}\dfrac{1}{2\pi}\sqrt{\dfrac{k}{m}}$
b. $\nu_{\text{wave function}}(2) = \dfrac{5}{2}\dfrac{1}{2\pi}\sqrt{\dfrac{k}{m}}$
c. For the $v = 1$ state, $\nu_{\text{wave function}} = \frac{3}{2}\nu_{\text{oscillator}} = \frac{3}{2}\nu_{\text{photon}}$
For the $v = 2$ state, $\nu_{\text{wave function}} = \frac{5}{2}\nu_{\text{oscillator}} = \frac{5}{2}\nu_{\text{photon}}$
d. $\nu_{\text{wave function}}(2) - \nu_{\text{wave function}}(1) = h\nu_{\text{oscillator}} = h\nu_{\text{photon}}$

14.35

$z_t = 1.23 \times 10^{-11}$ m

Answers to selected problems

14.37

$\nu = 4.282 \times 10^{13}$ s^{-1}

14.39

a. $\nu_{\text{a}} = 264$ Hz
$\nu_{\text{b}} = 428$ Hz
$\nu_{\text{c}} = 792$ Hz
$\nu_{\text{d}} = 1056$ Hz
b. $\lambda = 1.28$ m

14.43

c(in water) = 2.25×10^{8} m s^{-1}
$\varepsilon = 1.57 \times 10^{-11}$ N^{-1} C^{2} m^{-2}

14.45

$\lambda_{\max} = 1.06$ mm

14.47

a. For $n = 4$, $v = 5.47 \times 10^{5}$ m s^{-1}
For $n = 400$, $v = 5.47 \times 10^{3}$ m s^{-1}
b. For $n = 4$, $v/c = 1.82 \times 10^{-3}$
For $n = 400$, $v/c = 1.82 \times 10^{-5}$

14.49

For $n_2 = 3$, $\lambda = 656.46$ nm (in the red)
For $n_2 = 4$, $\lambda = 486.27$ nm (in the green-blue)
For $n_2 = 5$, $\lambda = 434.17$ nm (in the blue-violet)
For $n_2 = 6$, $\lambda = 410.29$ nm (in the violet)

14.51

a. $a(\text{positronium}) = 1.0584 \times 10^{-10}$ m
b. $E_1(\text{positronium}) = -6.80$ eV
c. $r = 0.529 \times 10^{-10}$ m

14.53

$\lambda = 2.307 \times 10^{-11}$ m

14.57

a. $E_1 = 1.247 \times 10^{-19}$ J
$E_2 = 4.989 \times 10^{-19}$ J
$E_3 = 1.1226 \times 10^{-18}$ J
b. $\nu = 9.41 \times 10^{14}\ \mathrm{s}^{-1}$
$\lambda = 3.19 \times 10^{-7}$ m $= 319$ nm

14.59

$E = \mathscr{K} = 131$ J
Number of nodes $= 3.4 \times 10^{35}$
$\lambda = 5.4 \times 10^{-35}$ m

14.67

a. $\mu = 1.653 \times 10^{-27}$ kg
b. $k = 411.8\ \mathrm{kg\ s^{-2}} = 411.8\ \mathrm{N\ m^{-1}}$

14.69

a. $k = 4.9 \times 10^{4}\ \mathrm{N\ m^{-1}}$
b. $z = 0.070$ m $= 7.0$ cm
c. $\mathscr{V} = 120$ J
d. $\nu = 7.0\ \mathrm{s}^{-1}$
$\tau = 0.14$ s
e. $v = 3.1\ \mathrm{m\ s^{-1}}$
f. $E(\text{quantum}) = 4.6 \times 10^{-33}$ J
g. $n = 2.6 \times 10^{34}$
h. $\lambda = 4.3 \times 10^{4}$ km

14.71

a. $a_0 = 2.34 \times 10^{-138}$ m
b. $n = 2.53 \times 10^{74}$
c. $E_n = -2.66 \times 10^{33}$ J
$\mathscr{V} = -5.31 \times 10^{33}$ J
$\mathscr{K} = 2.66 \times 10^{33}$ J
d. $\dfrac{m_1}{\mu} = 1.000003$

Chapter 15

Answers to selected exercises

15.1

$$\left[x^2, \frac{d}{dx}\right] = -2x$$

15.2

a. $(\hat{\mathscr{K}} + \hat{\mathscr{V}})^3 = \hat{\mathscr{K}}^3 + \hat{\mathscr{K}}^2\hat{\mathscr{V}} + \hat{\mathscr{K}}\hat{\mathscr{V}}\hat{\mathscr{K}} + \hat{\mathscr{K}}\hat{\mathscr{V}}^2 + \hat{\mathscr{V}}\hat{\mathscr{K}}^2 + \hat{\mathscr{V}}\hat{\mathscr{K}}\hat{\mathscr{V}} + \hat{\mathscr{V}}^2\hat{\mathscr{K}} + \hat{\mathscr{V}}^3$
b. $(\hat{A} + \hat{B})^3 = \hat{A}^3 + 3\hat{A}^2\hat{B} + 3\hat{A}\hat{B}^2 + \hat{B}^3$

15.4

$$\left[x, i\frac{d}{dx}\right] = -i$$

15.7

a. $\hat{L}_x = \dfrac{\hbar}{i}\left(y\dfrac{\partial}{\partial z} - z\dfrac{\partial}{\partial y}\right)$
b. $\hat{L}_y = \dfrac{\hbar}{i}\left(z\dfrac{\partial}{\partial x} - x\dfrac{\partial}{\partial z}\right)$
c. $\hat{L}_z^2 = -\hbar^2\left(x^2\dfrac{\partial^2}{\partial y^2} - xy\dfrac{\partial^2}{\partial y\,\partial x} - x\dfrac{\partial}{\partial x} - xy\dfrac{\partial^2}{\partial x\,\partial y} - y\dfrac{\partial}{\partial y} + y^2\dfrac{\partial^2}{\partial x^2}\right)$

15.8

a. $[\hat{p}_x, \hat{p}_y] = 0$

15.12

$\langle x \rangle = a/2$

15.13

Probability $\approx 8.000 \times 10^{-6}$

15.14

Probability $= 0.1955$

15.16

a. (Probability) $= 0.5225$
b. (Probability) $= 0.4666$

15.17

Ratio $= 0.36788$

15.22

$\Delta t \geq 5 \times 10^{-14}$ s

15.23

b. $\langle E \rangle = \dfrac{3}{2}h\nu$
$\sigma_E^2 = 0$

15.24

$$\langle E \rangle = 3\frac{h^2}{8ma^2} = 3E_1$$

$$\sigma_E = \sqrt{2}\frac{h^2}{8ma^2} = \sqrt{2}E_1$$

15.25

$p_1 = 1/3$
$p_2 = 2/3$

Answers to selected problems

15.27

a. Not linear, not hermitian
b. Linear, hermitian
c. Linear, hermitian

15.29

$$\left[\frac{1}{x}+\frac{d}{dx}\right]^2=\frac{2}{x}\frac{d}{dx}+\frac{d^2}{dx^2}$$

15.33

b. Eigenvalue $= a$

15.35

a. The eigenvalue p is equal to $b\hbar$ where b can take on any real value.
b. The function is not an eigenfunction.
c. The wave function of Eq. (14.5-21) is an eigenfunction only if $D = 0$ or $F = 0$.

15.41

a. For $n = 1$, $\langle p_x^2\rangle = \dfrac{h^2}{4a^2}$

For $n = 2$, $\langle p_x^2\rangle = \dfrac{h^2}{a^2}$

For $n = 3$, $\langle p_x^2\rangle = \dfrac{9h^2}{4a^2}$

b. $\langle p_x^2\rangle = \dfrac{h^2n^2}{4a^2}$

c. $\lim\limits_{n-\infty}\langle p_x^2\rangle \to \infty$

15.43

a. $\Delta p_x = \Delta p_y = \Delta p_z \approx 5.27 \times 10^{-26}$ kg m s^{-1}
b. $\Delta E \approx 5.41 \times 10^{-20}$ J

15.45

a. $\sigma_x\sigma_p = \sqrt{\dfrac{1}{2a}\hbar}\sqrt{\dfrac{a}{2}} = \dfrac{\hbar}{2} = \dfrac{h}{4\pi}$

b. For the $v = 1$ state, the uncertainty product will be larger than for the $v = 0$ state.

c. $\sigma_x\sigma_p = \dfrac{3h}{4\pi}$

15.47

a. $\langle E\rangle = \frac{3}{2}h\nu$

b. $\sigma_E = \sqrt{\dfrac{2}{3}}h\nu$

c. E_0, E_1, and E_2 occur. Each value will occur 1/3 of the time.

15.49

The wave function prior to the measurements is $\psi = c_1\psi_1 + c_2\psi_2 + c_3\psi_3 + c_4\psi_4$ where $|c_1|^2 = 0.25$, $|c_2|^2 = 0.375$, $|c_3|^2 = 0.125$, $|c_4|^2 = 0.25$.

15.51

a. $\sigma_x = a\left(\dfrac{1}{12} - \dfrac{1}{2n^2\pi^2}\right)^{1/2}$

b. $\lim\limits_{n\to\infty} \sigma_x = \dfrac{a}{\sqrt{12}} = 0.28868a$

c. $\sigma_p = \dfrac{hn}{2a}$

d. $\sigma_x\sigma_p = \dfrac{h}{2}\left(\dfrac{n^2}{12} - \dfrac{1}{2\pi^2}\right)^{1/2}$

e. $\sigma_x = 5.28$ m
f. $\sigma_p = 6.16$ kg m s^{-1}
g. $\sigma_x\sigma_p = 32.5$ J s

Chapter 16

Answers to selected exercises

16.2

a. $\dfrac{\mu}{m_e} = 0.99946$

b. Distance from the nucleus to the center of mass $= 5.44 \times 10^{-14}$ m
Distance from the electron to center of mass $= 9.995 \times 10^{-11}$ m

16.7

Eigenvalue = 0

16.11

The percentage error in both quantities is 0.054%

16.12

n	l	m	m_s	n	l	m	m_s
4	0	0	1/2	4	2	−2	1/2
4	0	0	−1/2	4	2	−2	−1/2
4	1	1	1/2	4	3	3	1/2
4	1	1	−1/2	4	3	3	−1/2
4	1	0	1/2	4	3	2	1/2
4	1	0	−1/2	4	3	2	−1/2
4	1	−1	1/2	4	3	1	1/2
4	1	−1	−1/2	4	3	1	−1/2
4	2	2	1/2	4	3	0	1/2
4	2	2	−1/2	4	3	0	−1/2
4	2	1	1/2	4	3	−1	1/2
4	2	1	−1/2	4	3	−1	−1/2
4	2	0	1/2	4	3	−2	1/2
4	2	0	−1/2	4	3	−2	−1/2
4	2	−1	1/2	4	3	−3	1/2
4	2	−1	−1/2	4	3	−3	−1/2

16.14

$\langle 1/r\rangle = 1.89 \times 10^{10}$ m^{-1}
$\langle \mathcal{V}\rangle = -4.36 \times 10^{-18}$ J

16.15

a. $\langle r\rangle = \dfrac{3a}{2Z}$

b. $\langle r^2\rangle = \dfrac{3a^2}{Z^2}$

c. $r_{\mathrm{mp}} = \dfrac{a}{Z}$

16.20

Wave function	M_L	M_S	M_J	Term
$(\psi_s\psi_{p1} + \psi_{p1}\psi_s)(\alpha\beta - \beta\alpha)$	1	0	1	${}^1\mathrm{P}_1$
$(\psi_s\psi_{p1} - \psi_{p1}\psi_s)\alpha\alpha$	1	1	2	${}^3\mathrm{P}_2$
$(\psi_s\psi_{p1} - \psi_{p1}\psi_s)(\alpha\beta + \beta\alpha)$	1	0	1	${}^3\mathrm{P}_2$
$(\psi_s\psi_{p1} - \psi_{p1}\psi_s)\beta\beta$	1	−1	0	${}^3\mathrm{P}_0$
$(\psi_s\psi_{p0} + \psi_{p0}\psi_s)(\alpha\beta - \beta\alpha)$	0	0	0	${}^1\mathrm{P}_1$
$(\psi_s\psi_{p0} - \psi_{p0}\psi_s)\alpha\alpha$	0	1	1	${}^3\mathrm{p}_1$
$(\psi_s\psi_{p0} - \psi_{p0}\psi_s)(\alpha\beta + \beta\alpha)$	0	0	0	${}^3\mathrm{P}_1$
$(\psi_s\psi_{p0} - \psi_{p0}\psi_s)\beta\beta$	0	−1	−1	${}^3\mathrm{P}_1$
$(\psi_s\psi_{p-1} + \psi_{p-1}\psi_s)(\alpha\beta - \beta\alpha)$	−1	0	−1	${}^1\mathrm{P}_1$
$(\psi_s\psi_{p-1} - \psi_{p-1}\psi_s)\alpha\alpha$	−1	1	0	${}^3\mathrm{P}_2$
$(\psi_s\psi_{p-1} - \psi_{p-1}\psi_s)(\alpha\beta + \beta\alpha)$	−1	0	−1	${}^3\mathrm{P}_2$
$(\psi_s\psi_{p-1} - \psi_{p-1}\psi_s)\beta\beta$	−1	−1	−2	${}^3\mathrm{P}_2$

16.25

b. one ^{4}S term and two ^{2}S terms.
c. $E^{(0)} = -166.6$ eV

Answers to selected problems

16.29

Eigenvalue $= 0$

16.31

a. Difference of 0.027%
b. Difference of 0.027%
c. Difference of 0.004%

16.33

$35.26° = 0.61548$ radian
$65.91° = 1.1503$ radian
$90.00° = 1.5708$ radian
$114.94° = 1.9913$ radian
$144.74° = 2.5261$ radian

16.35

$$\langle r\rangle_{2s} = \frac{6a}{Z}$$

$$\langle r\rangle_{2p} = \frac{5a}{Z}$$

16.37

For $b = a$: probability $= 0.3233 = 32.33\%$
For $b = 2a$: probability $= 0.7619 = 76.19\%$
For $b = 3a$: probability $= 0.9380 = 93.80\%$

16.39

$\langle p_x\rangle = 0$
$\langle p_x^2\rangle = 1.32228 \times 10\ \mathrm{kg^2\ m^2\ s^{-2}}$

16.43

b. f_r vanishes at $r = 0$ and at $r \to \infty$.
c. $r = 12a = 6.35 \times 10^{-10}$ m

16.51

^{3}F, ^{1}F, ^{3}D, ^{1}D, ^{3}P, and ^{1}P.
The ^{3}F term probably has the lowest energy.

16.53

^{2}P

16.55

a. The only term is ^{1}S.
b. The terms are ^{3}S and ^{1}S.
c. The terms are ^{5}S, ^{3}S, ^{3}S, ^{3}S, ^{1}S, ^{1}S, and ^{1}S.

16.57

a. 5
b. 4
c. 0
d. 0

16.59

a. TRUE
b. FALSE
c. FALSE
d. TRUE
e. TRUE
f. FALSE
g. FALSE
h. FALSE

Chapter 17

Answers to selected exercises

17.6

a. $\langle r\rangle_{1s} = 2.95 \times 10^{-11}$ m $= 29.5$ pm
b. $\langle r\rangle_{2s} = 1.79 \times 10^{-10}$ m $= 179$ pm

17.7

a. S: $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^4$
b. Ta: $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^{10}(4p)^6(5s)^2(4d)^{10}(5p)^6(6s)^2(5d)^3$
c. Hg: $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^{10}(4p)^6(5s)^2(4d)^{10}(5p)^6(6s)^2(4f)^{14}(5d)^{10}$, same as $[\mathrm{Xe}](6s)^2(4f)^{14}(5d)^{10}$

17.8

a. B: ${}^2\mathrm{P}_{1/2}$
b. C: ${}^3\mathrm{P}_0$
c. O: ${}^3\mathrm{P}_2$
e. F: ${}^2\mathrm{P}_{3/2}$

Answers to selected problems

17.11

a. $W = \dfrac{5h^2}{4\pi^2 ma^2} = 0.12665\dfrac{h^2}{ma^2}$

b. $W = \dfrac{6h^2}{4\pi^2 ma^2} = 0.15198\dfrac{h^2}{ma^2}$

17.15

a. $Z_{\text{eff}} = 1.344$

b. Total ionization energy = 78.98 eV ≈ 79.0 eV

17.17

a. $E \approx E_1^{(0)} + E_1^{(1)} = \dfrac{h^2}{8ma^2} + \dfrac{ba}{2}$

b. $E = 6.02 \times 10^{-20}\ \text{J} + 2.73 \times 10^{-21}\ \text{J} = 6.29 \times 10^{-20}\ \text{J}$

17.19

$$E = E^{(0)} + \frac{3c}{4a^2} = \frac{\hbar}{2}\sqrt{\frac{k}{m}} + \frac{3c\hbar^2}{4km}$$

17.25

a. Fe: $(1s)^2(2s)^2(2p)^6(3s)^2(3p)^6(4s)^2(3d)^6$

b. Rn: $[\text{Xe}](6s)^2(4f)^{14}(5d)^{10}(6p)^6$

c. Tc: $[\text{Kr}](5s)^2(4d)^5$

d. Rb: $[\text{Kr}](5s)^1$

17.27

a. P: ^2D, ^2P, and ^4S

b. Ca: ^1S

c. Cu: ^2S

d. Cl: ^2P

17.29

$Z_{\text{eff}} = 1.837$

17.31

H: 1 He: 0

Li: 1 Be: 0 B: 1 C: 2 N: 3 O: 2 F: 1 Ne: 0

Na: 1 Mg: 0 Al: 1 Si: 2 P: 3 S: 2 Cl: 1 Ar: 0

Chapter 18

Answers to selected exercises

18.1

a. $\hat{i}(1, 2, 3) = (-1, -2, -3)$

b. $\hat{\sigma}_{\text{h}}(4, -2, -2) = (4, -2, 2)$

c. $\hat{\sigma}_{\text{v}yz}(7, -6, 3) = (-7, -6, 3)$

18.2

a. $\hat{C}_{2x}(1, 2, 3) = (1, -2, -3)$

b. $\hat{C}_{3y}(1, 1, 1) = (0.37, 1, -1.37)$

18.3

a. $\hat{i}(r, \theta, \phi) = (r,\ 180° - \theta,\ 180° + \phi)$

$\hat{\sigma}_{\text{h}}(\text{r}, \theta, \phi) = (r,\ 180° - \theta,\ \phi)$

18.9

$$C_{\text{VB}} = C_{\text{CI}}\left[\left(\frac{1}{2+2S}\right) - c_u\left(\frac{1}{2-2S}\right)\right]$$

$$C_{\text{I}} = C_{\text{CI}}\left[\left(\frac{1}{2+2S}\right) + c_u\left(\frac{1}{2-2S}\right)\right]$$

18.14

a. $^3\Pi_{\text{g}}$ and $^1\Pi_{\text{g}}$

b. $^3\Pi_{\text{g}}$

c. Bond order = 1

18.16

a. $\psi_{3\sigma} \approx -0.99\psi_{2sp(2)\text{Li}} + 0.1236\psi_{1s\text{H}}$

b. $\psi_{4\sigma} \approx -1.34\psi_{2sp(1)\text{Li}} + 1.24\psi_{1s\text{H}}$

18.20

$C_{\text{C}} = 0.575$

$C_{\text{O}} = 0.818$

18.22

$c_{\text{VB}} = 0.41,\quad c_{\text{I}} = 0.77$

% Ionic = 78%

18.23

a. 1.7

b. 1.1

c. 0.6

18.24

a. Polar covalent

b. Polar covalent

c. Polar covalent

d. Primarily ionic

f. Purely covalent

18.25

$z' = -3.593$

$y' = 0.232$

18.26

E, C_3, C_3^2, and three σ_{v} operations

18.37

$$\Psi_{\text{I}} = C_{\text{I}}[\psi_{2sp^32}(7)\psi_{2sp^32}(8) + \psi_{2sp^33}(9)\psi_{2sp^33}(10)]\,[\alpha(1)\beta(2) - \beta(1)\alpha(2)]$$

18.42

Resonance energy of benzene = 3(137.15 kJ mol^{-1}) − 206.0 kJ mol^{-1} = 205 kJ mol^{-1}

18.43

$\beta = -5.5 \times 10^{-19}$ J, which is equivalent to −330 kJ mol^{-1}

18.45

$1/\lambda = 2.23 \times 10^6\ \text{m}^{-1} = 2.23 \times 10^4\ \text{cm}^{-1}$

18.46

	$\hat{E}$	$\hat{C}_2$	$\hat{\sigma}_x$	$\hat{\sigma}_y$
O1s	1	1	1	1
O2s	1	1	1	1
O2$_{px}$	1	−1	1	−1
O2$_{py}$	1	−1	−1	1
O2$_{pz}$	1	1	1	1
a$_1$	1	1	1	1
b$_2$	1	−1	−1	1

Answers to selected problems

18.49
$\hat{i}\hat{\sigma}_h(x, y, z) = \hat{C}_{2z}(x, y, z)$

18.51
$\psi_{2py}(r, \theta, \phi)$

18.59
a. $^1\Pi$ and $^3\Pi$
b. $^1\Sigma$ and $^3\Sigma$

18.61
Li_2 $^1\Sigma_g^+$
Be_2 $^1\Sigma_g^+$
B_2 $^3\Sigma_g^-$
C_2 $^1\Sigma_g^+$
N_2 $^1\Sigma_g^+$
O_2 $^3\Sigma_g^-$
F_2 $^1\Sigma_g^+$
N_2 $^1\Sigma_g^+$

18.63
a. Bond order 3/2 1 unpaired electron
b. Bond order 5/2 1 unpaired electron
c. Bond order 3/2 1 unpaired electron

18.75
41.3% ionic: $c_I = 0.643$

18.77
a. 0.63
b. 0.6

18.79
$\hat{E}$, $\hat{C}_2$, and $2\hat{\sigma}_v$ operators. The group is C_{2v}.

18.83
a. 1,4-Dichlorobenzene D_{2h}
b. 1,2-Dichlorobenzene C_{2v}
c. Tetrachloroethene D_{2h}

18.87
$HClO_4$ is polar.

18.97
For benzene, $\beta = 5.5 \times 10^{-19}$ J = 3.4 eV
For 1,3-butadiene, $\beta = 7.4 \times 10^{-19}$ J = 4.6 eV

18.99
$\lambda = 7.89 \times 10^{-8}$ m

18.103
$Q_{Cl} = -2.90 \times 10^{-20}$ C $= -0.181e$
$Q_H = 9.7 \times 10^{-21}$ C $= 0.060e$

18.109
f. NH_3 belongs to C_{3v} and BH_3 belongs to D_{3h}.

Chapter 19

Answers to selected exercises

19.1
$\Delta E = 7.55 \times 10^{-41}$ J $= 4.71 \times 10^{-22}$ eV
Ratio of energies $= 5.67 \times 10^{-23}$

19.2
a. $n = 9.07 \times 10^9$
b. $\Delta E = 4.57 \times 10^{-31}$ J

$$\frac{\Delta E}{E} = 7.36 \times 10^{-11}$$

19.3
a. $E_0 = 0$

$$E_1 = \frac{h^2}{8\pi\mu r_e^2}(1)(2) = 1.206 \times 10^{-22}\ \text{J}$$

b. $\nu = 1.820 \times 10^{11}$ s^{-1} $= 1.820 \times 10^{11}$ Hz
$\lambda = 1.647 \times 10^{-3}$ m = 1.647 mm

19.5
For translation, $E_{211} - E_{111} = 1.42 \times 10^{-40}$ J $= 8.86 \times 10^{-22}$ eV
For rotation, $E_2 - E_0 = 2.90 \times 10^{-23}$ j $= 1.81 \times 10^{-4}$ eV
For vibration, $E_1 - E_0 = 1.12 \times 10^{-20}$ J = 0.070 eV

19.6
a. $F_r = 2aD_e[1 - e^{-a(r-r_e)}]e^{-a(r-r_e)}$

19.7
a. $\lambda = 4.6576 \times 10^{-4}$ cm $= 4.6576\ \mu$m
$\nu = 6.4365 \times 10^{13}$ s^{-1}
b. $\lambda = 4.6576 \times 10^{-4}$ cm $= 4.6576\ \mu$m
$\nu = 6.4365 \times 10^{13}$ s^{-1}
c. $\lambda = 4.6005 \times 10^{-4}$ cm $= 4.6005\ \mu$m
$\nu = 6.5164 \times 10^{13}$ s^{-1}

19.10
J must be even.

19.12
a. $\sigma = 3$
b. $\sigma = 2$
c. $\sigma = 12$
d. $\sigma = 2$
e. $\sigma = 1$
f. $\sigma = 24$

19.14
$J_{mp} = 2$

19.15
Ratio = 0.539

19.16

$$\frac{N(2,1)}{N(0,0)} = 1.34 \times 10^{-4}$$

19.17
Ratio $= 1.0 \times 10^{-36}$

Answers to selected problems

19.19
$n_x = 2.66 \times 10^{11}$

19.21
a. $\frac{1}{\lambda} = 243.40\ \text{cm}^{-1}$
$\lambda = 4.108 \times 10^{-3}\ \text{cm} = 41.08\ \mu\text{m}$
b. $\frac{1}{\lambda} = 182.60\ \text{cm}^{-1}$
$\lambda = 5.4765 \times 10^{-3}\ \text{cm} = 54.765\ \mu\text{m}$

19.23
$\nu(\text{HD}) = 1.14287 \times 10^{14}\ \text{s}^{-1}$
$\nu(\text{D}_2) = 9.3332 \times 10^{13}\ \text{s}^{-1}$

19.25
$D_e/hc \approx 42320\ \text{cm}^{-1}$

19.27
a. $\lambda = 0.29777$ cm
$\nu = 1.00679 \times 10^{11}\ \text{s}^{-1}$
b. $\lambda = 0.14888$ cm
$\nu = 2.0136 \times 10^{11}\ \text{s}^{-1}$

19.31
a. Oblate symmetric top
b. Prolate symmetric top
c. Asymmetric top
d. Linear
e. Asymmetric top
f. Asymmetric top

19.33
a. 30 **b.** 18 **c.** 18
d. 12 **e.** 7 **f.** 12

19.37
a. $I_z = 4.92 \times 10^{-45}\ \text{kg m}^2 = I_C$
$I_y = I_x = 2.96 \times 10^{-45}\ \text{kg m}^2 = I_A = I_B$

19.39
Number of normal modes = 17

19.41
a. 15 **b.** 7 **c.** 6
d. 48 **e.** 6 **f.** 24

19.43
a. Ratio $= 4.83 \times 10^{-7}$
b. Ratio $= 5.14 \times 10^{-7}$
c. Ratio $= 3.01 \times 10^{-5}$
d. Ratio $= 3.14 \times 10^{-5}$

19.45
For ortho hydrogen, $J_{\text{mp}} = 1$
For para hydrogen, $J_{\text{mp}} = 0$

19.49
a. FALSE
b. TRUE
c. FALSE
d. FALSE
e. TRUE
f. FALSE
g. TRUE
h. FALSE
i. TRUE
j. TRUE
k. FALSE

Chapter 20

Answers to selected exercises

20.1
a. $E_{\text{photon}} = 2.0 \times 10^{-23}$ J
$E_{\text{einstein}} = 12\ \text{J mol}^{-1}$
b. $E_{\text{photon}} = 2.0 \times 10^{-15}$ J
$E_{\text{einstein}} = 1.2 \times 10^{9}\ \text{J mol}^{-1}$

20.2
$\frac{N_2}{N_1} = 3.2 \times 10^{-173}$

20.3
$a = 1.23 \times 10^{-4}\ \text{L mol}^{-1}\ \text{cm}^{-1}$

20.4
For $2 \rightarrow 1$, $\lambda = 121.568$ nm, in the ultraviolet
For $3 \rightarrow 2$, $\lambda = 656.467$ nm, in the visible (red)
For $4 \rightarrow 3$, $\lambda = 1875.62$ nm, in the infrared

20.6
For H^{35}Cl, $21.17\ \text{cm}^{-1}$
For H^{37}Cl, $21.13\ \text{cm}^{-1}$

20.7
a. $J_{\text{mp}} = 3$
b. $J_{\text{mp}} = 35$

20.10
For the third overtone, $1/\lambda = 8413.4\ \text{cm}^{-1}$
For the fourth overtone, $1/\lambda = 10450.3\ \text{cm}^{-1}$

20.11
c. For $J = 0$, $\frac{1}{\lambda_R} = 4263.6\ \text{cm}^{-1}$
For $J = 1$, $\frac{1}{\lambda_R} = 4267.3\ \text{cm}^{-1}$

For $J = 2$, $\dfrac{1}{\lambda_R} = 4271.0\ \text{cm}^{-1}$

20.12
$\lambda = 1.544 \times 10^{-7}\ \text{m} = 154.4\ \text{nm}$

20.13
No

20.14
$E_{\text{photon}} = 6.62 \times 10^{-19}\ \text{J}$
$E_{\text{einstein}} = 399\ \text{kJ mol}^{-1}$

20.15
b. For 11-*cis* retinal, $\lambda = 7.02 \times 10^{-7}\ \text{m} = 702\ \text{nm}$
For rhodopsin, $\lambda = 8.31 \times 10^{-7}\ \text{m} = 831\ \text{nm}$

20.16

ν_1	Raman active	ν_2	Raman active
ν_3	Raman active	ν_4	Raman active
ν_5	Raman active	ν_6	Raman active
ν_7	IR active	ν_8	Raman active
ν_9	IR active	ν_{10}	IR active
ν_{11}	IR active	ν_{12}	IR active

20.17

$$\Delta\tilde{\nu} = \Delta\left(\frac{1}{\lambda}\right) = 1556.2\ \text{cm}^{-1}$$

$\lambda = 2.641 \times 10^{-5}\ \text{cm} = 264.1\ \text{nm}$

20.19
a. $\nu = 1.40 \times 10^{10}\ \text{s}^{-1}$
$\lambda = 2.14 \times 10^{-2}\ \text{m}$

20.20
b. $\Delta E = 1.41 \times 10^{-26}\ \text{J}$

20.22
$B_z = 18.677\ \text{T} = 186{,}770\ \text{gauss}$

20.24
a.
$$\begin{aligned} c(\omega) &= A\left(\frac{D}{2}\right)^{1/2} e^{i\omega t_0} e^{-D\omega^2/4} \\ &= A\left(\frac{D}{2}\right)^{1/2} e^{-D\omega^2/4}[\cos(\omega t_0) + i\ \sin(\omega t_0)] \end{aligned}$$

Answers to selected problems

20.25
$a = 9.34 \times 10^{3}\ \text{L mol}^{-1}\ \text{cm}^{-1}$

20.29
a. $\lambda = 1.3122 \times 10^{-4}\ \text{cm} = 1312.2\ \text{nm}$
b. $\lambda = 9.7201 \times 10^{-4}\ \text{cm} = 972.01\ \text{nm}$
c. $\lambda = 8.6787 \times 10^{-4}\ \text{cm} = 867.87\ \text{nm}$
d. $\lambda = 8.2014 \times 10^{-1}\ \text{cm} = 820.14\ \text{nm}$

20.31
$\lambda = 1.10 \times 10^{-8}\ \text{m} = 11.0\ \text{nm}$
$a = \text{box size} = 3.33 \times 10^{-10}\ \text{m} = 333\ \text{pm}$

20.35
$1/\lambda = 22.027\ \text{cm}^{-1},\ 44.054\ \text{cm}^{-1},\ 66.081\ \text{cm}^{-1}$, etc.
$J_{\text{mp}} = 2$

20.37
(a) CH_3Cl and (c) NH_3

20.41
712.1 cm^{-1}: bend
2089.0 cm^{-1}: symmetric stretch
3312.0 cm^{-1}: asymmetric stretch
1412.0 cm^{-1}: first overtone of the bend
2116.7 cm^{-1}: second overtone of the bend
2800.3 cm^{-1}: combination band: bend and symmetric stretch
4004.5 cm^{-1}: combination band: bend and asymmetric stretch
5394 cm^{-1}: combination band: symmetric stretch and asymmetric stretch
6521.7 cm^{-1}: first overtone of the asymmetric stretch

20.43
Overtones near 1178 cm^{-1}, 2570 cm^{-1}, and 4447 cm^{-1}
Bend–symmetric stretch combination band near 1874 cm^{-1}
Bend–asymmetric stretch combination band near 2228 cm^{-1}
Symmetric stretch–asymmetric stretch combination band near 3508 cm^{-1}

20.47
a. $\nu = 7.97 \times 10^{14}\ \text{s}^{-1}$
$\lambda = 3.76 \times 10^{-7}\ \text{m} = 376\ \text{nm}$
b. $\nu = 7.24 \times 10^{14}\ \text{s}^{-1}$
$\lambda = 4.14 \times 10^{-7}\ \text{m} = 414\ \text{nm}$

20.49
$R_e = 7.57 \times 10^{-11}\ \text{m} = 75.7\ \text{pm} = 0.757\ \text{Å}$

20.51
BF_3 and CO_2

20.53
All but CCl_4

20.57
Three lines with approximately equal intensities

20.59
Population ratio = 0.99853

20.65
$\nu_{\text{Larmor}} = 6.000 \times 10^{7}\ \text{s}^{-1}$

20.67

$$I(t) = \sqrt{\frac{2}{\pi}}\frac{a}{a^2 + t^2}$$

20.71
a. $1/\lambda = 2143.2\ \text{cm}^{-1}$
b. $1/\lambda = 4259.9\ \text{cm}^{-1}$

c. $1/\lambda = 3.844\ \text{cm}^{-1}$
d. $1/\lambda = 7.688\ \text{cm}^{-1}$

Chapter 21

Answers to selected exercises

21.4.

c. $T = \dfrac{h\nu}{k_B \ln(2)} = (6.9238 \times 10^{-11}\ \text{K s})\nu$

21.5

a. 3.09% error
b. 0.00030% error

21.7

For $N = 10$: 0.05516% error
For $N = 60$: 0.00074% error
For $N = 1 \times 10^9$: no difference to 9 significant digits

21.10

$\mathscr{z}_{tr} = 1.937 \times 10^{29}$

21.11

Term = $\mathscr{T} = 0.61609$
$\Delta\mathscr{T} = 1.705 \times 10^{-11}$

21.12

$$U_{tr} = \frac{3}{2}Nk_BT$$

$$p_i = \frac{1}{\mathscr{z}}e^{-3N\varepsilon_i/2U}$$

$$\mathscr{z} = \sum_i e^{-3N\varepsilon_i/2U}$$

21.13

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 $\rightarrow 1$ as $T \rightarrow \infty$
b. Ratio $= 2.451$ at 298.15 K
Ratio $= 2.824$ at 1000 K
Ratio $\rightarrow 3$ as $T \rightarrow \infty$
c. $J_{mp} = 3$

21.14

$T = -5.95 \times 10^4$ K

21.18

a. $\mathscr{z}_{rot} = 1.703$
b. $\mathscr{z}_{rot} = 1.88403$
c. $\mathscr{z}_{rot} = 424.807$
From the formula, $\mathscr{z}_{rot} = 424.7$.

21.19

For H_2, $\mathscr{z}_{vib} = 1.0000000006$
For I_2, $\mathscr{z}_{vib} = 1.5508$

21.20

$\mathscr{z}_{vib} = 0.2778$

21.21

a. $\mathscr{z} = 1.5052 \times 10^{33}$
b. $\mathscr{z} = 1.4900 \times 10^{33}$

21.22

$\mathscr{z}_{rot} = 36.42$

21.24

$\mathscr{z}_{vib} = 1.095$

21.25

$3 \times \mathscr{z}_{rot}(\text{ortho}) + \mathscr{z}_{rot}(\text{para}) = 3(1.87559) + 1.88403 = 7.5108$
$4 \times \mathscr{z}_{rot}(\text{integral approx.}) = 4(1.703) = 6.812$

21.26

a. $d\ \ln(x)/dx = 1$
b. $d\ \ln(x)/dx = 1.00 \times 10^{-5}$
c. $d\ \ln(x)/dx = 1.00 \times 10^{-10^5}$

21.31

b. $U_{vib} = \dfrac{Nh\nu}{2} + \dfrac{Nh\nu}{e^{h\nu/k_BT} - 1}$

21.32

a. $\mathscr{z}_{vib} = 0.005327$
$U_{vib} = 12979\ \text{J mol}^{-1}$
b. With the zero of vibrational energy taken at the zero-point energy:
$\mathscr{z}_{vib} = 2.1713$
$U_{vib} = 3005\ \text{J mol}^{-1}$
With the zero of vibrational energy taken at the minimum of the vibrational potential energy:
$\mathscr{z}_{vib} = 1.595$
$U_{vib} = 4288\ \text{J mol}^{-1}$

21.33

$\mathscr{z}_{elec} = 3.1219$
$U_{m,elec} = 515.1\ \text{J mol}^{-1}$

21.34

b. $C_{V,m} = 25.466\ \text{J K}^{-1}\ \text{mol}^{-1}$

21.35

$\mu_{tr} = -6.978 \times 10^{-20}$ J
$\mu_{rot} = -2.491 \times 10^{-20}$ J
$\mu_{vib} = -2.86 \times 10^{-22}$ J
$\mu_{elec} \approx 0$

21.36

$K \approx 4.24$

21.39

b. $A \approx 2.4 \times 10^8\ \text{m}^3\ \text{mol}^{-1}\ \text{s}^{-1} = 2.4 \times 10^{11}\ \text{L mol}^{-1}\ \text{s}^{-1}$

21.50

a. $S_m = -1304\ \text{J K}^{-1}\ \text{mol}^{-1}$
b. $S_m = 146.532\ \text{J K}^{-1}\ \text{mol}^{-1}$

Answers to selected problems

21.53

b. The average distribution is:

$f_0 = \frac{4}{10} = 0.4$

$p_1 = \frac{3}{10} = 0.3$

$p_2 = \frac{2}{10} = 0.2$

$p_3 = \frac{1}{10} = 0.1$

c. The most probable distribution is

$p_0 = \frac{1}{3} = 0.3333$

$p_1 = \frac{1}{3} = 0.3333$

$p_2 = \frac{1}{3} = 0.3333$

$p_3 = 0$

d. The Boltzmann distribution is exactly as in Table 21.2.

21.55

b. Average distribution:

$$p_0 = \frac{657}{4056} = 0.16198$$

$$p_1 = \frac{1005}{4056} = 0.24778$$

$$p_2 = \frac{1755}{4056} = 0.43269$$

$$p_3 = \frac{630}{4056} = 0.15533$$

$$p_4 = \frac{9}{4056} = 0.00222$$

c. Boltzmann distribution

$$p_J = \frac{1}{\mathscr{z}_{\text{rot}}}(2J+1)e^{-yJ(J+1)}$$

where $y = hb/k_BT = 0.0491776$ and $\mathscr{z}_{\text{rot}} = 20.671$

21.57

a. The difference is 2.02%.

b. The difference is 0.00200%.

21.59

$\mathscr{V} = -1.69 \times 10^{-4}\ \text{J mol}^{-1}$

21.61

$x = 1, \quad y = 1$

21.63

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. In the limit as $T \to \infty$, the ratio$\to 1$.

21.65

a. Ratio $= 2.639$ at 298.15 K

b. Ratio $= 2.887$ at 1000 K

c. In the limit as $T \to \infty$, the ratio $\to 3$.

21.67

$J_{\text{mp}} \approx 9$

21.69

For $V = 0.00100\ \text{m}^3$, $\mathscr{z} = 2.44 \times 10^{29}$

For $V = 1.00\ \text{m}^3$, $\mathscr{z} = 2.44 \times 10^{32}$

21.71

For helium, $\mathscr{z} = 1.911 \times 10^{29}$

For krypton, $\mathscr{z} = 1.815 \times 10^{31}$

21.75

a. $\mathscr{z}_{\text{rot}} = 1.880$

b. $\mathscr{z}_{\text{rot}} = 424.8$

21.79

Distance from the N nucleus to the center of mass $=$ 0.1282×10^{-10} m

$I_A = 2.450 \times 10^{-47}\ \text{kg m}^2$

$I_B = I_C = 3.464 \times 10^{-47}\ \text{kg m}^2$

The symmetry number is 3.

$\mathscr{z}_{\text{rot}} = 140.0$

21.83

For argon, $S_{\text{m}}^{\circ} = 154.85\ \text{J K}^{-1}\ \text{mol}^{-1}$

For helium, $S_{\text{m}}^{\circ} = 126.16\ \text{J K}^{-1}\ \text{mol}^{-1}$

21.85

$H_{\text{m}}^{\circ} = 10.393\ \text{kJ mol}^{-1}$

From Table A.8, $H_{\text{m}}^{\circ} = 10.393\ \text{kJ mol}^{-1}$

21.87

$S_{\text{m}}^{\circ} = 197.60\ \text{J K}^{-1}\ \text{mol}^{-1}$

21.89

$S_{\text{m}}^{\circ} = 196.3\ \text{J K}^{-1}\ \text{mol}^{-1}$

21.93

$K = 0.462$

21.95

a. $K_P \approx 6$

b. $K_P \approx 2$

21.99

$\Delta S^{\ddagger\circ} = -100\ \text{J K}^{-1}\ \text{mol}^{-1}$

21.103

$\mathscr{Z} \approx 10^{4.48 \times 10^{24}}$

21.105

$z = 3.074 \times 10^{32}$

21.109

5% agreement at $T = 3960$ K

1% agreement at $T = 8985$ K

Chapter 22

Answers to selected exercises

22.1

b. sp^3 hybrids

22.2

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

22.3

b. Packing fraction $= 0.680175$

22.5

b. $\nu = 2.75 \times 10^{13}\ \mathrm{s^{-1}} = 2.75 \times 10^{13}\ \mathrm{Hz}$
c. $U - N\mathcal{V}_0 = 398\ \mathrm{J\ mol^{-1}}$ at 298.15 K
$U - N\mathcal{V}_0 = 2530\ \mathrm{J\ mol^{-1}}$ at 500. K
d. $G - N\mathcal{V}_0 = 7350\ \mathrm{J\ mol^{-1}}$ at 298.15 K
$= 11{,}580\ \mathrm{J\ mol^{-1}}$ at 500. K

22.6

b. $C_V = 3Nk_B\left(\frac{\Theta_E}{T}\right)^2 \frac{e^{\Theta_E/T}}{(e^{\Theta_E/T}-1)^2}$
At 298.15 K, $C_V = 5.983\ \mathrm{J\ K\ mol^{-1}}$
At 500. K, $C_V = 14.39\ \mathrm{J\ K\ mol^{-1}}$
At 1320 K, $C_V = 22.96\ \mathrm{J\ K\ mol^{-1}}$

22.10

$\nu_{\mathrm{av}} = \frac{3}{4}\nu_D$
$\nu_{\mathrm{av}} = 2.95 \times 10^{13}\ \mathrm{s^{-1}}$
$\nu_E = 2.75 \times 10^{13}\ \mathrm{s^{-1}}$

22.13

a. $A = 2.7236 \times 10^{-38}\ \mathrm{J\ m^2}$
b. $\varepsilon_{F0} = 5.26 \times 10^{-19}\ \mathrm{J} = 3.28\ \mathrm{eV}$

22.14

a. $C_{\mathrm{m,elec}} = 0.016\ \mathrm{J\ K^{-1}\ mol^{-1}}$
b. Ratio $= 0.0013$
c. Ratio $= 0.077$

22.17

a. $v = 1.98 \times 10^3\ \mathrm{m\ s^{-1}}$
b. $T = 158\ \mathrm{K}$

22.22

$$X_x = \frac{(c_0k't)^{x-1}}{(1+c_0k't)^x}$$

22.25

$$\left(\frac{\partial T}{\partial L}\right)_S = \left(\frac{\partial f}{\partial S}\right)_L$$

$$\left(\frac{\partial T}{\partial f}\right)_S = -\left(\frac{\partial L}{\partial S}\right)_f$$

$$\left(\frac{\partial S}{\partial f}\right)_T = \left(\frac{\partial L}{\partial T}\right)_f$$

22.26

a. $q = -w = -\frac{nRT}{2}\left(\alpha'^2 + \frac{2}{\alpha'} - 3\right)$
b. $q = -0.00083\ \mathrm{J}$
$w = 0.00083\ \mathrm{J}$

Answers to selected problems

22.29

Molecular: neon, krypton
Ionic: cesium nitrate
Covalent: diamond
Metallic: copper, sodium

22.33

Unit cell dimension $= 269\ \mathrm{pm}$

22.35

Primitive cubic, one basis per unit cell
$a = 4.123 \times 10^{-10}\ \mathrm{m}$

22.39

a. $d_{110} = 2.023 \times 10^{-10}\ \mathrm{m}$
b. $\theta = 22.439° = 0.3916$ radian

22.41

$k = 44\ \mathrm{N\ m^{-1}}$

22.43

a. $\nu = 2.75 \times 10^{12}\ \mathrm{s^{-1}}$

22.49

a. $\varepsilon_{F0} = 4.11 \times 10^{-19}\ \mathrm{J} = 2.57\ \mathrm{eV}$

22.51

a. Ratio $= 2.2 \times 10^{-20}$

22.53

Number ≈ 4.4

22.55

$P = 2.93 \times 10^8\ \mathrm{Pa} = 2.89 \times 10^3\ \mathrm{atm}$

22.57

$\bar{M}_n = 20{,}000$ amu
$\bar{M}_w = 25{,}000$ amu

22.59

b. $p = 0.987$
c. $\bar{M}_n = 1.0 \times 10^4$ amu
d. $\bar{X}_n = 76$

22.63

a. $r_{\mathrm{rms}} = 3 \times 10^{-9}\ \mathrm{m}$
Ratio $= 0.1$

b. $r_{\mathrm{rms}} = 3 \times 10^{-8}$ m
Ratio = 0.01

22.69
$\bar{M}_v = 2.46 \times 10^4$ amu

22.71
a. FALSE
b. TRUE
c. TRUE
d. FALSE
e. TRUE
f. TRUE
g. FALSE
h. FALSE
i. TRUE

Chapter 23

Answers to selected exercises

23.1
$k = 2.7 \times 10^{-35}$ s^{-1}
$t^{1/2} = 2.6 \times 10^{34}$ s $\approx 8 \times 10^{26}$ years

23.3
a. $E_a = 14{,}200$ J mol^{-1}
b. $\Delta S^{\ddagger\circ} = -13$ J K^{-1} mol^{-1}

23.5
$d = 1.8 \times 10^{-11}$ m

23.7
Debye length $= 2.15 \times 10^{-9}$ m = 2150 pm = 21.5 Å

23.9
b. $\eta_{\mathrm{conc}} = -3.6 \times 10^{-6}$ V

Answers to selected problems

23.15
a. $\Delta E_a = 272$ kJ mol^{-1}
b. $\dfrac{k(310\text{ K})}{k(300\text{ K})} = 34$

23.17
$E_a = 15.8$ kJ mol^{-1}

23.19
a. $a = 6.45 \times 10^{-14}$ s

23.21
$a(\mathrm{Cl}^-) = 153$

23.23
$a = 1.08$ V
$b = 0.090$ V

23.27
a. TRUE
b. FALSE
c. TRUE
d. TRUE
e. TRUE
f. FALSE
g. FALSE
h. TRUE
i. TRUE

Additional Reading

General References

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Quantum Mechanics, Atomic Structure, and Molecular Structure

P. W. Atkins, *Molecular Quantum Mechanics*, 3d ed., Oxford University Press, Oxford and New York, 1997. This book is written at the senior/first year graduate level, and although it focuses on molecular quantum mechanics, it also introduces the fundamental theory.

C. J. Ballhausen and H. B. Gray, *Molecular Orbital Theory*, W. A. Benjamin, New York, 1964. This paperback book contains notes from series of lectures on molecular orbital theory for advanced undergraduates and first-year graduate students, as well as a collection of reprints of articles on the subject.

Hans A. Bethe and Edwin E. Salpeter, *Quantum Mechanics of One- and Two-Electron Atoms*, Plenum Press, New York, 1977. This is a book by two well-respected physicists, and gives a complete and careful treatment.

R. L. Carter, *Molecular Symmetry and Group Theory*, Wiley, New York, 1998.

F. A. Cotton, *Chemical Applications of Group Theory*, Wiley, New York, 1990. This is one of the most authoritative textbooks on chemical group theory, and has appeared in various printings since 1963.

J. C. Davis, Jr., *Advanced Physical Chemistry*, Ronald Press, New York, 1965. This is one of very few existing textbooks for a general physical chemistry course following the standard one-year undergraduate course. It contains a clear and fairly detailed discussion of nonrelativistic quantum mechanics.

M. W. Hanna, *Quantum Mechanics in Chemistry*, 3d ed., Benjamin/Cummings, Menlo Park, CA, 1981. This is a fairly small book, available in paperback, which is designed as a supplementary text for an undergraduate course in physical chemistry, or as a text for part of a course. It is quite clear and gives somewhat more detail than most physical chemistry textbooks.

W. E. Hatfield and W. E. Parker, *Symmetry in Chemical Bonding and Structure*, Charles E. Merrill, Columbus, OH, 1974. This textbook is an introduction to the subject for senior undergraduates and beginning graduate students.

J. E. House, *Fundamentals of Quantum Mechanics*, Academic Press, San Diego, 1998.

M. Jammer, *The Conceptual Development of Quantum Mechanics*, McGraw-Hill, New York, 1966. This is a book for physicists, and presents the foundations of quantum mechanics in historical context.

M. Jammer, *The Philosophy of Quantum Mechanics*, Wiley, New York, 1974. This book is what its title suggests, and includes discussion of some controversial aspects, including paradoxes that arise in certain interpretations of the postulates.

S. F. A. Kettle, *Symmetry and Structure: Readable Group Theory for Chemists*, Wiley, New York, 1995.

I. N. Levine, *Quantum Chemistry*, 4th ed., Prentice-Hall, Englewood Cliffs, NJ, 1991. This is a widely used text for a one-semester quantum chemistry course at the senior/first year graduate level. It is clear and authoritative.

J. P. Lowe, *Quantum Chemistry*, 2d ed., Academic Press, San Diego, 1993. This is a book for a course in quantum chemistry at the senior/first year graduate level, and presents basic concepts, although it is oriented mostly toward molecular orbital theory.

F. Mandl, *Quantum Mechanics*, Butterworths, London, 1957. This book is a theoretically inclined book for physics students at the graduate level, and presents the basic concepts in a careful and rather complete way. Many concepts are unfortunately buried in a welter of detail.

D. A. McQuarrie, *Quantum Chemistry*, University Science Books, Mill Valley, CA, 1983. This book is a text for a standard course in quantum mechanics at the senior/first year graduate level.

R. McWeeny, *Symmetry—An Introduction to Group Theory and Its Applications*, Macmillan, New York, 1963. This is a standard introduction to the use of group theory, but it appears to be out of print at present.

G. L. Miessler and D. A. Tarr, *Inorganic Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1991. This is a textbook for a senior-level inorganic chemistry course, and contains a clearly written introduction to group theory and its application to chemical bonding and spectroscopy.

Michael A. Morrison, Thomas F. Estle, and Neal F. Lane, *Quantum States of Atoms, Molecules, and Solids*, Prentice-Hall, Englewood Cliffs, NJ, 1976.

F. L. Pilar, *Elementary Quantum Chemistry*, McGraw-Hill, New York, 1968. This is a book for a one-year course in quantum chemistry at the first-year graduate level, and contains some things not readily found elsewhere in books written for chemists. Most undergraduates will feel that the word "elementary" does not belong in the title.

John A. Pople and David L. Beveridge, *Approximate Molecular Orbital Theory*, McGraw-Hill, New York, 1970. This is a small book that is designed to aid senior and first-year graduate students in learning Hartree–Fock and semiempirical molecular orbital methods.

Donald J. Royer, *Bonding Theory*, McGraw-Hill, New York, 1968. This is a small book designed for advanced undergraduates. It has a clear discussion of Hückel molecular orbitals.

J. Simons and J. Nichols, *Quantum Mechanics in Chemistry*, Oxford University Press, Oxford and New York, 1997. This is a comprehensive text at the senior/first year graduate level with a large number of exercises and problems with solutions.

Boris S. Tsukerblat, *Group Theory in Chemistry and Spectroscopy*, Academic Press, San Diego, 1994. This book is intended as a practical guide to group theory by chemists involved with spectroscopy and molecular structure. It does not emphasize formal mathematics and presents material by way of examples as much as possible.

Spectroscopy

R. J. Abraham and P. Loftus, *Proton and Carbon-13 NMR Spectroscopy*, Heyden, London, 1978. This book is an integrated approach to the two principal types of NMR spectroscopy, carbon-13 and proton NMR.

Robert G. Bacher and Samuel Goudsmit, *Atomic Energy States*, McGraw-Hill, New York, 1932. This book is a compilation of numerical energy level values.

Gordon M. Barrow, *Introduction to Molecular Spectroscopy*, McGraw-Hill, New York, 1962. This is a general introductory text at the senior undergraduate/first year graduate level.

Alan Carrington and Andrew D. McLachlan, *Introduction to Magnetic Resonance*, Harper and Row, New York, 1967. This book is a clear and authoritative treatment of both ESR and NMR spectroscopy.

D. B. Chase and J. F. Rabolt, eds., *Fourier Transform Raman Spectroscopy*, Academic Press, San Diego, 1994. This is a collection of chapters written by various experts in the field, covering the theory and techniques of Raman spectroscopy carried out in Fourier transform instruments.

Norman B. Colthup, Lawrence H. Daly, and Stephen W. Wiberley, *Introduction to Infrared and Raman Spectroscopy*, 2d ed., Academic Press, New York, 1975. This book includes considerable information about instrumentation in addition to spectroscopic theory, and is probably well suited for use by analytical chemists.

Wolfgang Demtroder, *Laser Spectroscopy—Basic Concepts and Instrumentation*, Springer-Verlag, Berlin, 1981. This contains a modern account of various types of spectroscopy using lasers as sources of incident radiation. Fourier transform spectroscopy is included, as is multiphoton spectroscopy.

Russell S. Drago, *Physical Methods in Chemistry*, W. B. Saunders, Philadelphia, 1977. The bulk of this book is devoted to spectroscopy of various sorts, but it also includes chapters on molecular orbital theory, group theory, and X-ray crystallography.

Thomas C. Farrar and Edwin D. Becker, *Pulse and Fourier Transform NMR*, Academic Press, New York, 1971. This is a brief book on the subject that includes information about instrumentation as well as theory.

John R. Ferraro and Kazuo Nakamoto, *Introductory Raman Spectroscopy*, Academic Press, San Diego, 1994. This book is an authoritative general introduction to Raman spectroscopy. It includes a thorough discussion of the application of group theory to selection rules.

Gerhard Herzberg, *Molecular Spectra and Molecular Structure*

Vol. I, *Spectra of Diatomic Molecules*, 2d ed., D. Van Nostrand, Princeton, New Jersey, 1950.

Vol. II, *Infrared and Raman Spectra of Polyatomic Molecules*, Van Nostrand Reinhold, New York, 1945.

Vol. III, *Electronic Spectra and Electronic Structure of Polyatomic Molecules*, Van Nostrand Reinhold, New York, 1966.

Vol. IV, *Constants of Diatomic Molecules*, by K. P. Huber and G. Herzberg, Van Nostrand Reinhold, New York, 1979.

This set of books is the most authoritative information source for molecular spectroscopy, both in theory and in critically evaluated experimental data on molecular structure.

William G. Laidlaw, *Introduction to Quantum Concepts in Spectroscopy*, McGraw-Hill, New York, 1970. This is a book at the level of undergraduate physical chemistry that interprets spectroscopy in terms of qualitative quantum-mechanical concepts.

Ira N. Levine, *Molecular Spectroscopy*, Wiley, New York, 1975. This is a text for a graduate-level course in molecular spectroscopy, and is clearly written and authoritative.

J. A. Pople, W. G. Schneider, and H. J. Bernstein, *High-Resolution Nuclear Magnetic Resonance*, McGraw-Hill, New York, 1959. This book presents an authoritative account of NMR theory as of the date of its publication, and is still very useful.

Nicholas J. Turro, *Modern Molecular Photochemistry*, Benjamin/Cummings, Menlo Park, CA, 1978. This is an authoritative account of photochemistry written from the perspective of physical organic chemistry.

Harvey Elliott White, *Introduction to Atomic Spectra*, McGraw-Hill, New York, 1934. This book is now primarily useful only as a source of data on atomic energy levels.

Statistical Mechanics

D. Chandler, *Introduction to Modern Statistical Mechanics*, Oxford University Press, New York, 1987. This small book is a text for a one-quarter or one-semester course in statistical mechanics for chemists at the senior/first year graduate level. It is written by one of the prominent practitioners of statistical mechanics, and emphasizes modern applications.

N. Davidson, *Statistical Mechanics*, McGraw-Hill, New York, 1962. This book presents a complete and clear exposition of the principles of statistical mechanics for chemists at the first-year graduate level.

E. A. Desloge, *Statistical Physics*, Holt, Rinehart, and Winston, New York, 1966. This is a textbook for a senior/first year graduate course in statistical mechanics and kinetic theory for physics students. It is clearly written and useful.

H. L. Friedman, *A Course in Statistical Mechanics*, Prentice-Hall, Englewood Cliffs, NJ, 1985. This book is a text for a one-semester course in statistical mechanics for chemists at the graduate level. It is mathematically oriented, and emphasizes the liquid state.

T. Hill, *Statistical Thermodynamics*, Addison-Wesley, Reading, MA, 1960. This book is a clear and useful introduction to equilibrium statistical mechanics for chemistry students at the first-year graduate level.

A. I. Khinchin, *Mathematical Foundations of Statistical Mechanics*, Dover, New York, 1949. This book is a highly mathematical treatment of some theoretical aspects of classical statistical mechanics. Chapter 3 treats the ergodic hypothesis.

C. Kittel and H. Kroemer, *Thermal Physics*, 2d ed., W. H. Freeman, San Francisco, 1980. This book is a text for an undergraduate physics course in thermodynamics and statistical mechanics. It is clear and useful.

D. A McQuarrie, *Statistical Mechanics*, Harper and Row, New York, 1976. This book is a complete and carefully written account of statistical mechanics for first-year graduate students in physical chemistry.

L. E. Reichl, *Statistical Physics*, University of Texas Press, Austin, 1980. This book is a rigorous text for a graduate course in statistical mechanics for physicists.

Norman O. Smith, *Elementary Statistical Thermodynamics: A Problems Approach*, Plenum Press, New York, 1982. This book is a very clearly written work on equilibrium statistical mechanics at approximately the level of an undergraduate physical chemistry course.

Structure of Solid and Liquid Phases

H. R. Allcock and F. W. Lampe, *Contemporary Polymer Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1981. This is a complete, clearly written and useful textbook for a course in polymer chemistry.

J. S. Blakemore, *Solid-State Physics*, 2d ed., W. B. Saunders, Philadelphia, 1974. This book is one of the standard textbooks for an undergraduate course in solid state physics, and is quite clear and readable.

C. A. Croxton, *Liquid State Physics—A Statistical Mechanical Introduction*, Cambridge University Press, Cambridge, 1974. This is a reference book in the statistical mechanical theory of liquids at an advanced graduate level.

P. A. Egelstaff, *An Introduction to the Liquid State*, Academic Press, New York, 1967. This book is an introduction to the theory of the liquid state at the level of beginning graduate students in physics. Although it grew out of a course, it is more a reference book than a textbook.

P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, 1953. This book is a classic textbook in polymer chemistry, and is still very useful.

N. B. Hannay, *Solid-State Chemistry*, Prentice-Hall, Englewood Cliffs, NJ, 1967. This is a paperback book that is intended for advanced undergraduates. It includes chemical reactions as well as structure, and is nicely written and very informative.

J. P. Hansen and I. R. McDonald, *Theory of Simple Liquids*, Academic Press, New York, 1976. This is a reference book, not a textbook. It is at a rather advanced level, and is quite complete for its time.

C. Kittel, *Introduction to Solid State Physics*, 6th ed., Wiley, New York, 1986. This is one of the best-known textbooks of solid state physics at the undergraduate level.

W. Moore, *Seven Solid States*, W. A. Benjamin, New York, 1967. This is a small paperback book, written at a fairly elementary undergraduate level, in which the principles of solid state chemistry and physics are illustrated by study of seven example solids.

R. B. Seymour and C. E. Carraher, Jr., *Polymer Chemistry—An Introduction*, Marcel Dekker, New York, 1981. This book is a nonmathematical survey of polymer chemistry.

D. Tabor, *Gases, Liquids and Solids*, 2d ed., Cambridge University Press, Cambridge, UK, 1979. This is a fairly small paperback book. It is a clear and valuable reference, and derives approximate formulas for nearly all properties of gases, liquids, and solids from simple model systems.

C. Tanford, *Physical Chemistry of Macromolecules*, Wiley, New York, 1961. This book is written by a prominent biophysical chemist, but gives good coverage of synthetic polymers as well as of biological macromolecules.

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